Assessment Techniques of Heavy Metal Bioavailability in Soil - A critical Review.

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The concept of metal bioavailability, rather than total metal in soils, is increasingly becoming important for a thorough understanding of risk assessment and remediation. This is because bioavailable metals generally represented by the labile or soluble metal components existing as either free ions or soluble complexed ions are likely to be accessible to receptor organismsrather than heavy metals tightly bound on soil surface. Consequently, many researchers have investigated the bioavailability of metals in both soil and solution phases together with the key soil properties influencing bioavailability. In order to study bioavailability changes various techniques have been developed including chemical based extraction (weak salt solution extraction, chelate extraction, etc.) and speciation of metals using devices such as ion selective electrode (ISE) and diffusive gradient in the thin film (DGT). Changes in soil metal bioavailability typically occur through adsorption/desorption reactions of metal ions exchanged between soil solution and soil binding sites in response to changes in environment factors such as soil pH, organic matter (OM), dissolved organic carbon (DOC), low-molecular weight organic acids (LMWOAs), and index cations. Increasesin soil pH result in decreases in metal bioavailability through adsorption of metal ions on deprotonated binding sites. Organic matter may also decrease metal bioavailability by providing more negatively charged binding sites, and metal bioavailability can also be decreases as concentrations of DOC and LMWOAs increase as these both form strong chelate complexeswith metal ions in soil solution. The interaction of metal ions with these soil properties also varies depending on the soil and metal type.

Key words: Metal bioavailability, Dissolved organic carbon (DOC), Low-molecular weight organic carbon (LMWOAs), Soil, Speciation.

Introduction

Contamination of soils by metal(loids)s through both anthropogenic and geogenic activities is a widespread and serious problem confronting society, scientists and regulators worldwide. Consequently, many researchers have investigated contaminated areas to assess the potential risk to a variety of receptors including plants, animals, and humans, from exposure to these hazardous substances. Recent studies ofrisk assessment and remediation have focussed more on the bioavailability of heavy metals in soils, instead of total metal concentrations,and there has been a significant movementby regulators toward a bioavailability based

rationale as an indicator of risk. For example, in some European countries, operationally defined extractions using weak salt solutions were adopted to estimate the bioavailability of heavy metals in soils as one of the actions to improve risk assessment (PrüeB, 1997). In addition, Hamon and McLaughlin proposed 'bioavailable contaminant stripping (BCS) as a time and cost effective strategy for application of phytoremediation technology (Hamon and McLaughlin,1999). Conventionally, phytoextraction would take a long time to meet remedial targets based on total metal concentrations, but with BCS, remediation time can be substantially shortened by targeting the extraction of only the most labile, bioavailable metal pools.

Recognition that bioavailability is the underlying basis for risk assessment has led to much research worldwide in the development of different methods to examine the

bioavailable fraction of contaminants in either the solid or solution phases. However, there was no universal accepted technique for assessing bioavailability even though different techniques were demonstrated as being significant indicators for bioavailable metal pools. Fundamentally, exact determination of heavy metal bioavailability is difficult due to diversity of soil nature and continuous transformation of metal ions in plant root-soil solution-soil interface. For this reason, each technique produces a discrepancy in assessing bioavailability of heavy metals in different soils.

In this paper, some of the more commonly used methods for estimating heavy metal bioavailability are assessed and importance of the soluble metal ions as a bioavailable pool together with environmental parameters influencing on heavy metal bioavailability was discussed.

Analytical techniques for the assessment of bioavailability

Ion exchange extractions   Among the different metal species present in soils, water soluble and exchangeable ions are all considered readily available for plant uptake. These exchangeable forms can be extracted from the negatively charged exchange sites on clays or organic particles by competitivereplacement with salt solutions (Beckett, 1989). From this simple theory emerged a range of ion exchange methods which used weak salt solutions to predict bioavailable metal fractions. To date there is no universally accepted extraction procedure for assessing phytoavailable metals. For instance ammonium chloride (1M NH_4Cl) is the common extractant in Canada (Krishnamurti et al., 1995), ammonium nitrate (1M NH_4NO_3) in Europe (DIN, 1995) and sodium chloride (1M NaCl) in Switzerland. Elsewhere, $CaCl_2$ and $NaNO_3$ were also broadly implicated (McLaughlin et al., 1999; Nolan et al., 2005). Separately the investigators have shown strong positive correlations between extractable metals and plant metal contents (Beckett, 1989; Gray et al., 1999; Krishnamurti et al., 1995; Symeonides and McRae, 1977; Whitten and Ritchie, 1991). For this reason, metals extracted using these methods have often been defined as the phytoavailable fraction.

The effectiveness of the various proposed extraction agents varies with the metal under investigation. Among these extracting agents, $CaCl_2$ may be the only genuinely useful substitute for determining phytoavailable Cd since $CaCl_2$ extractable Cd was the only extractant to show any

significant relationship with Cd in plant tissue (McLaughlin et al., 1999; Nolan et al., 2005). $NaNO_3$ extractsexchangeable metals mainly because its ionic strength is similar to that of soil solutions and it does not affect the equilibrium between the soil solution and the solid phase (Gupta and Aten, 1993). Calciumis the dominant cation of soils and would reflect the differences in binding strength of solubility between different soils, hence although easily exchangeable metals can be extracted with $NaNO_3$ and $CaCl_2$, Sodium nitrate exertsa weak competition for the adsorption sites of organic matter and oxide surfaces because Na has less binding strength than Ca (Novozamsky et al., 1993).

A recent study of Cd availability of soils for durum wheat plants showed that 1M NH_4Cl extractable soil Cd was the best Cd bioaccumulation indicator among the methods examined (Krishnamurti et al., 1995). However, Cl^- in NH_4Cl could contribute to increased Cd desorption through formation of Cd-Cl ion pairs (Bingham et al., 1984; McLaughlin et al., 1999). Ligand complexation is typically a stronger reaction than cation exchange and consequently greater complexation promotes mobility. For this reason, extraction with 1M NH_4NO_3 is preferred when Cd is one of the metals of interestfor investigation and the1 M NH_4NO_3extraction is normally used in Europe as a standard method for assessing phytoavailable metal pools (DIN, 1995).

Chelate Extractions   These extraction techniques use the ability of chelates to form strong complexes with metal ions in soils to predict phytoavailability. The chelates commonly used are synthetic chelates such as EDTA and DTPA. In the extracting solution chelates can complex with labile metal ions to indirectly increase metal dissolution from the soil into the soil solution.

EDTA has been generally used as a strong chelating reagent and DTPA was also used in a number of studies to examine heavy metal availability of soils to plants (Bermond et al.,1998; Jackson and Alloway, 1991; Street et al., 1978). These studies indicated that chelate extractable metals could give a satisfactory estimation of phytoavailability. However, these methods were not always accurate for predicting phytoavailability because these chelate based methods are highly dependent on soil type (Feng et al., 2005).

DTPA showed good relationship only in neutral and near alkaline soils for Cu, Zn, and Cd, while EDTA showed good relationships only in acidic soils with Cu

and Zn as this technique was originally developed only for acidic soils (Hammer and Keller, 2002). When DTPA is applied to acidic soils, the buffering capacity of the soil solution may be increased (O'Connor, 1988), and considerable amountsof heavy metals occluded by Fe/Mn oxides and carbonate could be released, which would overestimate phytoavailability since normal plant mechanisms would not access these metal pools (Hammer and Keller, 2002).

Rhizosphere Extractions   A rhizosphere based extraction using a solution containing 10 mM of several organic acids, which are normally present in the vicinity of plant roots, including acetic, lactic, citric, malic, and formic at the molar ratio of 4:2:1:1:1 has recently been developed by Feng et al. (Feng et al., 2005). This method successfully estimated the phytoavailable metals in soil showing a strong relationship between the heavy metal concentration in above ground plant tissue and extractable metals (Chen et al., 2004; Feng et al., 2005; Gramss et al., 2003). Linear relationships for extractable metal and plant tissue metals concentrations were obtained with correlation coefficients ranging from 0.70 to 0.80 (Chen et al., 2004). In addition, correlations between the root contents and the rhizosphere extractable contents for Cr, Cu, Zn, and Cd were higher in the rhizosphere than in the bulk soil (Chen et al., 2004). However, this method failed to accurately assess the bioavailability of Ni and Pb (Feng et al., 2005). Pitchel et al. (1997) showed that soil Pb is generally unavailable to plants and observed no correlation with plant accumulation probably because Pb predominantly exists as an immobilized form in soil (Blaylock et al., 1997).

Isotopic dilution techniques   Two different terminologies, L-values and E-values, are commonly associated with this technique, which represent the biologically labile pool (L-value) and the chemically labile pool (E-value). L-values can be determined biologically through plant cultivation in radioisotope spiked soils (Hamon et al., 1997). A metal radioisotope is thoroughly mixed with the soil to distribute it homogeneously within the different fractions of the isotopically exchangeable (labile) metal pools (Tiller, 1979; Tiller et al., 1972). At equilibrium heavy metals in plant tissue growing in a radioisotope dosed soil will have the same isotopic ratio as the labile metal reservoir in the soil. Thus, assay of the specific activity in the plant

enables calculation of the radio-labile metal content of the soil.

The E-value is a chemical estimate of the radio-labile metal pool. This is determined by spiking a soil suspension with an appropriate isotope and measuring the specific activity of the separated solution phase following equilibration (Nakhone and Young, 1993). As such the E-values are a measure of bioaccessibility and can have a significant range depending on both soil and metal type. Nakhone and Young (1993) determined E-values for Cd ranging from 6 to 102% of the total Cd released by concentrated HNO_3 digestion in contaminated soils.

The isotopic dilution technique allows the determination of the amount of metal solubilised from the non-labile to labile fraction by plant root operation. In soil spiked with a metallic radioisotope, preferential uptake of non-labile (unlabelled) metal by the plant would result in a decrease in the expected specific activity of the isotope in the plant and cause L-values to be higher than E-values (Grinsted et al., 1982). Thus differences between the L- and E-values should provide quantitative estimates of the solubilization of non-labile metals within the rhizosphere (Hutchinson et al., 2000). Smolders et al.(1999) measured E- and L-values for wheat grown in ten Belgian soils with a total Cd concentration in the range 0.33-6.5 mg kg^{-1}. L-values consistently exceeded the corresponding E-values by factors of between 1.05 and 1.4, suggesting that rhizosphere conditions caused solubilization of the non-labile soil metal fraction. However, in the Hutchinson's study, there was virtually no evidence that T. caerulescens was able to solubilize non-labile Cd from soils contaminated by sewage sludge or metal rich mine spoil with the observation that the ratio of E- to L-values was very close to one (Hutchinson et al., 2000).

Diffusive gradients in thin films (DGT)   Zhang et al. (2001) first introduced the concept of an effective concentration, C_E, to describe the available pool of heavy metals to plants. This C_E included both the soil solution concentration and an additional term, expressed as a concentration, which represents metal supplied from the solid phase as the plant consumed the soluble fraction. Effective concentration was measured using the technique of diffusive gradients in thin films (DGT). In order to examine the validation of this technique, Zhang et al. (2001) grew pepperwort (*Lepidium heterophyllum* Benth.) in 29 soil samples covering a wide range of total

Cu concentrations and found that plant Cu concentrations were linearly correlated with C_E, while there were no linear relationship between plant Cu concentration and other Cu availability test including free Cu^{2+} activity, EDTA extraction, and soil solution concentration (Zhang et al., 2001). Theseresults indicated that overall the dominant supply processes to pepperwort plants in those soils were solution pools, coupled with diffusion and labile metal release from the solid phase induced by fast biological uptake. In contrast, in the study by Nolan et al. (2005), DGT was unsuccessful in predicting the phytoavailable Cu pool, but was effective in estimating plant Zn, Cd, and Pb accumulation in wheat from contaminated soils (Nolan et al., 2005).

Sequential extractions Solid phase speciation of heavy metals in soils is generally related to the physicochemical form in which the metal exists in the solid phase and may include free and complexed ions in interstitial solution; exchangeable ions; metals associated withsoil organic fractions; occluded or co-precipitated with metal oxides, carbonates or phosphates and other secondary mineral ions in the crystal lattices of primary minerals (Zhu and Alva, 1993).

Sequential extraction methods have been extensively employed to study these metal distributions in soils. So far, the 5 step sequential extraction procedure of Tessier et al. (1979) has been used extensively by environmental researchers for the solid phase speciation of metal in soil and this procedure has also been modified and adapted by many researchers for their own research needs (Tessier et al., 1979).

Krishnamurti et al. (1995) proposed a modified 9 step sequential extraction speciation scheme, which divided the species into: exchangeable; specifically adsorbed; bound to metal organic complexes; easily reducible metal oxides; organics; amorphous mineral colloids;crystalline Fe oxides; and residual. Krishnamurti and Naidu (2000) studied phytoavailable Cd and its distribution in soil with a 9 step sequential extraction. The average relative abundance of Cd bound to the different particulate forms in the soils was in the order: residual (0.777 mg kg^{-1}) > specifically adsorbed/carbonated-bound (0.066 mg kg^{-1}) > organic-bound (0.033 mg kg^{-1}) > metal-fulvic acid-complex-bound (0.031 mg kg^{-1}) > easily reducible metal oxide-bound (0.019 mg kg^{-1}) > crystalline Fe oxide-bound (0.001 mg kg^{-1}) $\geq$ amorphous mineral colloid-bound (0.001 mg kg^{-1}).

The exchangeable Cd (r^2=0.753) and the fulvic acid fraction of the organic-complex-bound Cd (r^2=0.824) correlated with the Cd accumulation in plants (Krishnamurti and Naidu, 2000). This result is in good agreement with other research which indicated that the Cd associated with the simple organic C molecules in the fulvic acid fraction of the metal-organic complexes is apparently more mobile and easily available to the plant than the Cd associated with the high molecular weight humic acid fraction (Cabrera et al., 1988; Krishnamurti and Huang, 1999).

Wang et al. (2002) used a 5 step sequential extraction to show that all elements (Cd, Cu, Pb, Zn) that accumulated in wheat root were correlated well with the concentration of heavy elements in fraction B1 (water soluble, exchangeable, carbonate bound), while no significant correlation was found between the root accumulation and the concentration in fraction B2 (Fe/Mn oxide bound) and B3 (OM and sulphide bound).

Despite some successful results using sequential extraction method to estimate the metal distribution and to assess bioavailability, sequential extraction has been widely criticized. The main drawbacks of sequential extraction techniques are that 1) no information on "true speciation"of elements in the soils is obtained because no individual species are determined, 2) the extractants are non-selective and extract a range of different species simultaneously and 3) redistribution of trace elements among geochemical phases during extraction processes can occur (Howard and Brink, 1999; Shan and Chen, 1993) since the extraction itself alters the chemical equilibrium. For this reason there has been an increasing emphasis on the application extended X-ray adsorption fine structure (EXAFS) to directly assess the solid phase speciation of metals (Manceau et al., 1996).

Dissolved metal ions in soil solution

The soil solution has been defined by Adams (Adams, 1974) as "the aqueous component of a soil at field-moisture content" and by the SSSA (SSSA, 1997) as "the aqueous liquid phase of the soil and its solutions."Information on soil solution composition including the concentration of dissolved metal ions is vital for understanding the bioavailability of metals in soils given that a portion of the solution phase ions are representative of the accessible metal pool to biota. Soil solution composition varies significantly with both soil type and

changes in the soil environment (Harter and Naidu, 2001).

In order to investigate soluble metal composition and factorswhich affect this composition, metal distribution analysis between solid and aqueous phases is conducted using solid-solution partitioning coefficients (K_d) defined simply as the ratio of metal in a soil to the metal in the solution as is shown in the equation (1) (Krishnamurti and Naidu, 2003; Sauvé et al., 2000a Sauvé et al., 2000b)

$$(Kd) = \frac{\text{metal concentration in soil}}{\text{metal concentration in solution}} \quad (1)$$

where metal concentration in soil is in mg kg^{-1} and dissolved metal concentration in the soil solution is in mg L^{-1}, and hence the unit for K_d is L kg^{-1}. From this equation, it is clear that the solid phase metal concentration is directly proportional to K_d while the solution phase metal concentrations areinversely proportional to K_d. The K_d value allows the potential ability of soil for metal retention to be evaluated, which may in turn be related to bioavailable soil metal pools.

K_d was generally used for estimating the bioavailability of metal ions in soils through step wise linear regression using solution chemical factors including pH, CEC, iron/aluminium oxide, and OM/DOM which influencing the metal distribution. Buchter et al. (1989) examined the influence and extent of soil solution chemical factors on partitioning coefficients and found that;

a) pH is the most important soil property that affects K_d
b) CEC influences K_d for cationic species;
c) the amounts of amorphous iron oxides, aluminium oxides, and amorphous material in soils influence both cation and anion retention parameters;
d) except for Cu and Hg, transition metals (Co and Ni) and group IIB cations (Zn and Cd) have similar K_d values for a given soil;
e) significant relationships between soil properties and K_d exist even in a group of soils with greatly different characteristics (Buchter et al., 1989).

While the significant influence of soil pH on K_d was shown in other studies (Nolan et al., 2003; Sauvé et al., 2000b) there was some discrepancy with the influence of soil organic carbon (SOC) on K_d. Inclusion of SOC as a parameter considerably improved the linear regression of K_d coupled with soil pH in Nolan's study (Nolan et al., 2003), while it did not significantly improve the degree of relationship in Sauvé's study (Sauvé et al., 2000b). In

addition, different heavy metals have different solubilities. For example increasing Pb concentrations in solution will promote adsorption onto the soil surface and increase the apparent K_d. Conversely, higher concentrations of Zn will decrease the apparent K_d, reflecting higher solubility in the soil-solution interface as it moves toward saturation (Nolan et al., 2003; Sauvé et al. 2000a). Metal mobility in 14 agricultural soils and 12 contaminated soils was in the order of Cd > Cu > Zn > Pb (Nolan et al., 2003).

Solution-phase speciation　In the soil solution, dissolved heavy metals exist as different species including free ions and complexed compounds with organic or inorganic ligands. These species are highly influenced by plant roots and microorganisms exposed to the soil solution (Hinsinger, 2001; Nolan et al., 2005). An understanding of dissolved metal species and its relationship to metal uptake by plants is critical to further the development of applicable phytoextraction techniques. Free metal ions are widely considered to be the most important metal contributing to plant uptake (Christensen and Christensen, 1999; Weng et al., 2002)as noted by the free ion activity model (FIAM) which states that the free metal activity or concentration controls or is an index of the metal availability to plants and aquatic organisms (Campbell, 1995). While increasing metal solubility generally enhances metal uptake by plants, the extent to which free metal ions and complexed metals in soil solution contribute to metal uptake by plants is still to be fully understood. For this reason, solution phase speciation has been emphasized by many researchers (Sauvé et al., 1996; Sauvé et al., 1998).

Recognizing the importance of free metal ions in solution in terms of bioavailability and toxicity made it possible to develop diverse methods for practical measurement of free metal ions in solution. The results from these experimental techniques were often compared with the metal speciation predictionsobtained using chemical speciation programs such as GEOCHEM (Weggler et al., 2004) and MINTEQA2 (Christensen and Christensen, 1999),which were developed to predict metal species using an iterative procedure where stability constants and soil solution parameters are included as input. Pore water pH, DOC, organic acids, and total soluble cations and anions are mainly used as input parameters to estimate free metal ions in soil solution but speciation accuracy depends on the appropriateness of

the models and the associated stability constants. The accuracy of the computed estimate of free metal ions depends on the stability constants used (Turner, 1995)

Donnan membrane technique (DMT)   The Donnan Membrane Technique (DMT) was developed using a cation exchange membrane to separate the cationic free and monovalent species from the other complex species. This technique is based on the use of a 'donor solution' that contains the 'free' metal ions and their complexes, and an 'acceptor solution'separated by a semi-permeable, negatively charged, cation exchange membrane (Temminghoff et al., 2000). The initial composition of the acceptor solution can be selected. Cations will be transported through the membrane until so-called 'Donnan equilibrium' is reached (Fitch and Helmke, 1989; Salam and Helmke, 1998).

This technique has several advantages (Temminghoff et al., 2000)

a) it is free from interference from neutral and anionic species as these do not traverse the cation exchange resin;

b) it does not alter the equilibrium composition of the sample solution,

c) all the free cation ions can be measurable simultaneously, and

d) it is relatively sensitive.

Temminghoff et al. (2000) enlarged the cell size for DMT in order to apply pH electrodes and ICP-MS measurement to the sub-samples from the acceptor solution and validated the modified DMT using artificially contaminated solution.

Measured percentages of free metal ions obtained with DMT in artificial solutions composed of known concentrationsof metal ions and ligands showed good agreement with calculated free metal ions percentages predicted by GEOCHEM with coefficients of variation of 0.96, 0.97, 0.96, and 0.93 for Zn, Cd, Cu, and Pb, respectively (Nolan et al., 2003). This indicated that DMT should be applicable for the determination of free metal ions in soil solution.

When DMT was used for metal speciation in soil solution the concentration of free metal ions in the soil solution was calculated based on the theory of donnan membrane equilibrium, which implies that the charge-corrected ratios of the cation activities in the solutions on the both sides of the membrane are equal when

equilibrium is reached:

$$\frac{[M^{2+}]_A}{[M^{2+}]_D} = \frac{[K^{2+}]_A}{[K^{2+}]_D}$$

where the subscripts D and A indicate the donor or acceptor solution (Weng et al., 2003). In Donnan membrane analysis with natural soil solution samples, potassium can be used as the reference cation, since K is naturally present in soil and it forms very weak complexes with most ligands in the soil solution (Weng et al., 2001a). Weng et al. (2001a) compared measured free Cu^{2+} in soil solution by DMT with corrected free Cu^{2+} in donor solution with K concentration in both acceptor and donor solution. The measured concentration of free Cu^{2+} in the acceptor varied considerably with the salt concentration in the acceptor, whereas that calculated in the donor was fairly constant, as it should be. With the natural soil solution samples, the percentages of free Zn^{2+} and Cd^{2+} in pore water measured by DMT showed good agreement with calculated values by GEOCHEM and WHAM VI (Nolan et al., 2003). The coefficients of variation were 0.66 and 0.40 between measured and calculated value by GEOCHEM and 0.71 and 0.52 between measured and calculated values by WHAM for Zn and Cd, respectively (Nolan et al., 2003).

Free metal ions in soil solution   The degree of metal dissociation into free metal ions in soil solution varies considerably depending on the nature of metal species. Weng et al. (2001a) found that in the soil solution, the free Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+} comprise 4-73 %, 44-91 %, 21-75 %, and 47-99 % of the respective totals of dissolved metal. In the study by Sauvé et al. (2000b), free Cu^{2+} comprised a very small part of the total dissolved Cu with only 1-20 % of the total dissolved Cu (isolated with 1:1 soil:water ratio) in soil solution, while free Cd^{2+} was 20-40 % of the total dissolved Cd (Sauvé et al., 2000b). Weng et al. (2001a) introduced soil column DMT (SC-DMT) to measure the free metal ions in soil solution. With this technique, they suggested that the metal adsorption on the cation exchangeablemembrane can be compensated by the subsequent dissociation of metal ions from solid phase resulting in a reduced error. In the study by Cances et al. (2003), Cd speciation was dominated by free Cd^{2+} which rangedfrom 70 to 100 % of the total Cd in pH range of 4.5 to 5.9. Pb^{2+} represented 11 to 97 % of the total Pb and decreased as DOC increased. While Cu^{2+} represented 5 to 50% of the total Cu.

Over all theseresults showed that dissolved Cu and Pb are largely in the form of organo-metal complexes, whereas Cd and Zn substantially exist as the free cation form (McBride et al., 1997). Salam and Helmke (1998) also found that Cd^{2+} was more dependent on soil pH than Cu^{2+} using the slope of linear regression equation between free metals ions and soil pH. The free metal ion concentrations were also correlated to the soil/soil solution ratio of the extracting solution for Cd and Zn and showed the higher the soil/soil solution ratio then the higher was the concentration of free metal ions in the acceptor side when using DMT (Cances et al.,2003). This implied that the soil/soil solution ratio should be considered during free metal ion determination

Heavy metal pools for uptake by plant   There is increasing evidence that labile metal complexes (e.g., metal chloride or sulphate complexes, but also metal ions bound to organic ligands) influence metal uptake or toxicity rather than just the free metal ions in soil solution (Smolders and McLaughlin, 1996; Zhang et al., 2001). In addition it was noted that free metal ions do not necessitate a correlation between free ion activity and bioaccumulation, given that numerous other important processes affect plant uptake and toxicity (McLaughlin et al., 1998; Nolan et al., 2003). Therefore, to predict the bioavailability of metals to plants, free metal ion activities in conjunction with the resupply kinetics from the solid phase must be considered and it is necessary to understand both solution- and solid-phase supply processes in soils through speciation (Nolan et al., 2005).

Influence of Environmental factors on bioavailability

pH   The pH dependent behaviour of heavy metal sorption is widely recognized and generally attributed to the increased affinity of soils for heavy metals due to pH dependent surface charge density on soil colloids (Naidu et al., 1994; Tiller et al., 1979). Increasing soil pH leads to a marked increase in the net surface negative charge density of soils through deprotonation and this is coupled with greater metal sorption (Alloway, 1990; Boekhold et al., 1993; Naidu and Harter, 1998). Boekhold et al. (1993) reported a doubling of Cd sorption for each 0.5 increase in pH between pH 3.8 and 4.9. In addition, all metals exhibit a sorption edge whereby sorption increases rapidly over a relatively narrow pH range (Harter and

Naidu, 2001). The rapid increase in sorption is usually assumed to be the result of both variations in the surface charge and shifts in solution ionic species. Further, increase of pH leads to a shift in the binding of metal from non-specific ion exchange binding to a more specific binding and this effect is quite significant for Cd, Zn, and Ni and not significant for Cu.

However, the degree of pH's influence on metal solubility is likely to be considerably affected by DOC above a certain pH level. Sauvé et al. (1998) have shown complex interactions between pH, DOC, and Pb in solution. They reported, as expected, an increase in Pb solubility with decreasing pH below pH 6.5. However, above pH 6.5, DOC increased with pH and they attributed this to the observed increase in dissolved Pb through DOC-Pb complex formation. It was therefore, suggested that the Pb would be more soluble in soil above neutral pH values. Similar results were shown in other studies, where the proportions of soluble Cd and Zn increased strongly as pH decreased below 6.5 and 5.3, respectively and the Cu and Pb solubilities increased strongly as pH decreased below 4.5 and 3.5 respectively (Hornburg and Brümmer, 1993). Above these pH values, solubility was mainly controlled by organic and inorganic metal complexes. The result from the McBride and Blasiak's study can also be explained via this mechanism (McBride and Blasiak, 1979). They found increases in total dissolved metal ions in soil solution while metal ion activity decreased as pH increased above neutrality, as a result of complexation with DOC at high pH. This is also consistent with Fotovat et al. (1998) who found that in soils with alkaline pH values Cu and Pb existed in association with dissolved organics.

Soil pH is also one of the strongest factors controlling solution phase metal speciation. Sauvé et al. (2000b), showed free Cd^{2+} and Cu^{2+} activities were highly linearly correlated with soil pH. The activities of both free metal ions decreased with increasing pH from 4 to 7 and the increase in pH caused a decrease of free metal ions through increasing complexation with organic and inorganic ligands. In addition, there was a highly significant relation between free Pb^{2+}, pH and total soil Pb ($P<0.001$) (Sauvé et al., 1997).

Organic matter (OM)   Soil organic matter (OM) is one of the most important components for the retention of trace metal ions and the presence of soil OM can decrease metal solubility. Organic matter contains a variety of negatively

charged functional groups (-OH⁻, -S⁻, and -COO⁻) which have the potential to enhance cation adsorption and consequently result in decreased metal solubility (Almas et al., 2000; Naidu et al., 1997; Qin et al., 2004). Amendment with organic matter increases the overall cation exchange capacity (CEC) of soils (He and Singh,1993) and increased CEC is negatively correlated with heavy metal solubility .

Organic matter can also potentially enhance desorption of metals from the solid phase and increase metal concentrations in the solution phase. Several investigations have revealed that DOC as a part of OM in the soil solution is able to increase dissolution of heavy metals through formation of metal-DOC complexes (Almas et al., 2000; Christensen and Christensen, 1999). Conversely, in some instances, dissolution of heavy metals can be decreased through soil adsorption of metal-DOC complexes (Harter and Naidu, 2001). Almas et al. (2000) treated two types of soil with organic matter and investigate dissolved Cd and Zn contents in the soil solution. The addition of organic matter increased the concentrations of dissolved Cd and Zn considerably in both soils. Since the concentration of DOC was also significantly increased in the organic matter treated soils, the correlation between DOC and dissolved Cd and Zn was highly significant (r^2=0.99).

Dissolved organic carbon (DOC)   Dissolved organic mater (DOM) which is often difficult to characterize or speciate is one of the main components which complexes with dissolved heavy metals in aquatic systems. It has been shown that DOM can strongly bind heavy metals such as Cu, Pb, Cd, Zn and Ni (Christensen and Christensen, 1999; Sauvé et al., 1997; Temminghoff et al., 1997; Xue et al., 2001). Weng et al. (2000b) demonstrated that DOM has higher affinity to heavy metal ions than that of the clay using a NICA-Donnan model. Therefore, the effect of DOM in an aquatic system must also be considered when researchers are concerned with the solubilization, transport of heavy metals, and risk assessment of sites contaminated with heavy metals. Some researches used dissolved organic carbon (DOC) instead of DOM for their studies, which is normally calculated as half of the dissolved organic matter because humic and fulvic acids contain on average 50 % carbon (Weng et al., 2002).

Composition of DOC   Dissolved organic carbon (DOC) in soil solutions can be operationally defined as the fraction of organic compounds that can pass a 0.45 μm membrane filter (Herbert and Bertsch, 1995). Soil solution DOC consists of a range of low-molecular-weight organics, including fulvic and humic acids comprising less than 10 % of total DOC in most soil solutions, and other low molecular weight organic acids (Fox and Comerford, 1990; Hees et al., 1996; Thurman, 1985). Amino acids and carbohydrates are also found in soil solutions, but fulvic acids are by far the most abundant fraction of DOC in soil solutions (Thurman, 1985).

DOC influence on dissolved metal ions   Several relationships have been observed between DOC and dissolved metal ions in soil solution. Copperand Zn showed a strong dependence on DOC in alkaline sodic soils with an almost linear relationship between DOC and Cu and curvilinear relationship between DOC and Zn (Fotovat and Naidu, 1998).

DOC influence on soil solution speciation is different from the influence ofDOC on metal solubility. Weng et al. (2002) showed DOC effects on metal complexation by comparing speciation results simulated by NICA-Donnan model with that measured by DMT with 4 different types of soils. Although metal binding to DOC does not contribute significantly to the control of metal activity in soil, it can affect the solubility of metals to a considerable extent. Some measurements have shown that complexation with DOC can increase the concentration of dissolved metal by more than 2 orders of magnitude. In addition, the effect of DOC on metal concentration in soil solution is more significant at higher pH and many factors that lead to an increase in the DOC concentration will enhance the solubility and mobility of metals.

In anion stripping voltametric (ASV) studies measuring labile Cd and Zn in soil solution, the influence of DOC varied between labile Cd and Zn (Almas et al., 2000). For Cd the ASV-labile fraction increased with increasing soluble Cd as the DOC increased suggesting that Cd was present as labile complexes with DOC. In contrast the ASV-labile Zn decreased with increasing DOC even though the concentrations of soluble Zn increased, indicating DOC formed more stable complexes with Zn than with Cd. At the naturally low Cd and Zn levels in soil solution, they measured much stronger affinities of Cd and Zn for soluble organics (Almas et al., 2000).

As described in the above section, the degree of DOC

influence on metal solubility is highly dependant on the pH. In the pH range 3 to 6.5, there was no effect of DOC on Pb solubility but from pH 6.5 to 8 increasing pH promoted the formation and dissolution of DOC-Pb complexes resulting in increased Pb solubility and a higher DOC content (Sauvé et al., 1998).

Partitioning of OM by pH and Ca   Since DOC influences metal solubility and speciation in soil solution, factors that lead to the changes in DOC solubility should influence bioavailability (Sauvé et al., 2000a; Weng et al., 2002). Generally soil pH and Ca^{2+} concentrations have been considered two parameters directly influencing DOC distribution between soil and soil solution phases.

An increase in pH induces increases in the negative charge of organic matter and other solid particles having pH dependent binding sites, and a decrease in Ca^{2+} concentration predominantly creates a more negative electrostatic potential (Oste et al., 2002). Both mechanisms lead to increased repulsion between organic matter molecules resulting in increases in soluble organic matter. The influence of pH on OM solubility was previously well illustrated (You et al., 1999). A sudden increase in pH does not only increase metal binding to the soil, but may potentially also increase the concentration of DOC in the soil solution. High calcium concentrations will promote the coagulation of dissolved organic matter and subsequently reduce DOC solubility. Therefore this causes a decrease in the total soluble concentrations of bound metals (Fotovat and Naidu, 1998; Romkens and Dolfing, 1998). Shen (1999) studied the effect of NaCl and CaCl₂ on DOC solubility in a soil suspension and found a strong increase in DOC if the soil was suspended in 0.01 M NaCl, but found hardly any increase in DOM in 0.003 M CaCl₂. In addition, Romkens and Dolfing (1998) added Ca to a soil suspension and observed a decrease in DOC implying coagulation of DOC by Ca ions.

Low molecular weight organic acids (LMWOAs) Low-molecular weight organic acids (LMWOAs) are carbon, oxygen and hydrogen, containing compounds which are found in all organisms and are characterized by the possession of one or more carboxyl groups (Jones, 1998). Depending on the dissociation properties and number of these carboxylic groups, LMWOAs can carry varying negative charge, thereby allowing the complexation of metal cations in solution and the displacement of anions from the soil matrix (Jones, 1998). For this reason, they have been implicated in many soil processes including the solubilization and uptake of nutrients by plants and micro-organisms (e.g., P and Fe), the detoxification of metals by plants (e.g., Al), microbial proliferation in the rhizosphere, and the dissolution of soil minerals leading to pedogenesis (e.g., podzolisation) (Marschner, 1995).

Composition of LMWOAs in soil solution   Low-molecular-weight (LMW) carboxylic acids in soils and soil solutions comprise well-defined and identifiable aliphatic and aromatic carboxylic acids with an arbitrary maximum molecular weight at approximately 300 g mol^{-1} (Fox, 1995). The aliphatic LMW carboxylic acids found in soil solutions comprise mono-, di- and tri-carboxylic acids including compounds containing unsaturated carbons and hydroxyl groups. Most aromatic LMW carboxylic acids found in soil solutions are substituted benzoic and cinnamic acids with hydroxyl and methoxyl groups as the most common substituents. The LMW carboxylic acids function as ligands increasing the total amount of dissolved cations such as aluminium and iron in soil solutions by complexation of metal cations (Drever and Stillings,1977; Hue et al., 1986; Pohlman and McColl, 1988).

Concentration of LMWOAs in soil solution   A concentration range of 1 to 4 mM organic acids was reported in soil solution (Stevenson 1994) and in other studies, the reported concentrations of aliphatic LMW carboxylic acids ranged from less than 1 μM to 2 mM. In most cases, the monocarboxylic acids (formic, acetic and propionic acids) are present in the highest concentrations, exceeding l mM in a fewcases (Hees et al., 1999; Strobel et al., 1999). Generally, soil solution concentrations of aliphatic di- and tri-carboxylic acids are below 50 μM (Hue et al., 1986) and seem to be correlated with DOC (Hees et al.,2000; Strobel et al., 1999). Carbon in aliphatic LMW carboxylic acids constitutes less than 6 % of total DOC in most soil solutions (Hees et al., 1999; Strobel et al., 1999), but a few reports of up to 10 % have been observed (Fox and Comerford, 1990; Hees et al., 1996) and the fraction of the LMWOAs from forest soils of DOC was normally in the range 0.5-5 % (Hees et al., 2000).

Function of LMWOAs   Low-molecular-weight organic acids are of particular importance due to their

metal chelation/complexing properties for mobilization of heavy metals such as Cd and for their ability to participate in mineral dissolution and weathering reactions through detachment of surface complexes into the solution.(Furrer and Stumm, 1986; °·uti°· and Stumm, 1984), including reductive dissolution of iron oxides caused by organic ligands such as oxalic acid (Suter et al., 1991; Wehrli et al., 1989).

The efficiency of LMWOAs as weathering agents of primary minerals has been shown in a number of studies (Lundstrom and Öhman,1990; Manley and Evans, 1986), and their importance for the weathering of soils has been emphasized (Blaser, 1994). Naturally occurring organic acids have been shown to enhance the weathering rate of natural soils about three times at pH 5 (Lundstrom and Öhman, 1990).

Metal complexing ability of LMWOAs is attributed to the carboxyl (-COOH), carbonyl (=CO), phenolic hydroxyl (-OH), methoxyl (-OCH$_3$), amino (-NH$_2$), imino (=NH), and sulfhydryl (-SH) functional groups. The complexation and subsequent increase of heavy metal solubility can occur at the soil-solution interface by the following equation (Unger and Allen, 1988):

$$S_f Me\ (soil) + H^+ + L\ (solution) \leftrightarrow S_f H\ (soil) + Me\ L\ (solution)$$
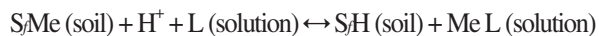
Where S$_f$ represents the different soil components responsible for the fixation of the trace metal and Me and L are respectively the metal ion and soluble organic acid ligand. This shows that the complexation of metals by LMWOAs play an important role in controlling metal solubility (Reuter and Purdue, 1977).

Krishnamurti et al. (1997) demonstrated that various LMWOAs were able to influence the rate of Cd released from different soils and increase the solubility of Cd in bulk soils through the formation of soluble Cd-LMWOAs complexes. In several other studies, this solubility increase mechanism by LMWOAs was also demonstrated (Collins et al., 2003; Schwab et al., 2005). Collins et al. (2003) reported that sodium citrate and tartrate increased the solution concentration of Cd by forming non-sorbing soluble complexes with Cd. In addition, Pb adsorption onto soils decreased with increasing citrate concentrations because formation of surface complexes of Pb-citrate enhanced the dissolution of Pb into the soil solution (Schwab et al., 2005).

If the concentration of LMWOAs in soil solution is relatively low, they would be mostly sorbed by soil organic matter and soil clay minerals and this would lead to the reduction of Cd and Cu desorption because Cd^{2+} and Cu^{2+} in soil solution would be bound by organic ligands sorbed to the soil (Huang and Bethelin, 1995). Benjamin and Leckie (1981) also suggested that citrate adsorbed onto a soil oxide surface may serve as a complexing agent at the surface and increase metal adsorptionby coordination of carboxylic and hydroxy groups to metal cations. The desorption behaviour of heavy metals depends on the organic acid type. When the concentration of total organic acids in an extracting solution was > 2 mmol L^{-1}, the Cd desorption ratio was clearly much higher in the presence of citrate than in tartrate for each spiked soil and naturally contaminated soils (Gao et al., 2003). This implied that desorption behaviour of Cd was correlated with organic acid types and concentration, although soil properties were different.

Cie°·li°·ski etal. (1998) reported that carboxylic acids, particularly bi- and tri- carboxylic acids such as citric and malic acids, can bind divalent cations strongly and form more stable complexes when compared to amino acids.

Index cations   Many studies have reported that the presence of certain index cations can result in increased heavy metal soil solution concentrations through both direct competition for adsorption sites (Fotovat and Naidu, 1998) and indirect affects on the diffuse double-layer. For example the concentration of soluble Zn increased with increasing index cation concentration in acidic soils. Metal desorption processes are also dependant on the type of index cations. Of the cations Ca had the most pronounced effect on Zn solubility in acidic soils (20 folds increase), while Na had the lease effect (Fotovat and Naidu, 1998). Dissolved Cd concentrations observed in soil solution was at least 2-4 times more in the presence of Ca than that in the presence of Na (Naidu et al., 1994). The effect of index cationon solubility was attributed to

a) increased competition between metal ions and Ca^{2+} for sorbing sites,

b) the effect of the divalent cation on the pH of the soil suspension (0.1-0.2 units lower in the presence of Ca^{2+}, and

c) greater specificity of the divalent Ca^{2+} ion and its effect on the thickness of the double layer (Naidu et al. 1994).

Lagerwerff and Brower (1972) observed that the sorption of Cd was dependent on the cation species and decreased

in the order Na > K > Ca > Al.

Other factors   Mn, Fe, and Al oxides are the reactive components of soils. Heavy metals can be strongly adsorbed on to these metal oxides (Huang and Bethelin, 1995; McKenzie, 1980). According to simulations using a NICA-Donnan model, Pb adsorption onto iron hydroxides is very important; therefore, the charge and the site density of clay and SOM has little influence on the predicted Pb^{2+} activities (Weng et al., 2001b). Iron oxides also have a high capacity to adsorb Pb and concomitantly maintain a low Pb^{2+} activity in solution (Sauvé et al., 2000b). The presence of Fe, Al, and Mn oxides in the highly weathered soils of the tropics is well established, and they are able to sorb Cd selectively (Christensen and Huang, 1999).

Conclusion

Recent studies of risk assessment and remediation have focussed more on the bioavailability of heavy metals in soils instead of total metal concentrations and there has been a significant move by regulators toward a bioavailability based rationale as an indicator of risk. This movement enables and requires researchers to develop various techniques to examine bioavailability. A wide variety of techniques are currently available for assessing heavy metal bioavailability. Of these chemical and chelate based extractions are most popular but are not genuining useful to a wide range of metals and/or pH extremes. Emerging techniques that are gaining some popularity include metal speciation techniques in soil solution such as DMT but this technique is only suitable for soil solution speciation so that further advanced investigation is necessary to account for the soil replenishing ability.

Research conducted using these developed technique indicated that the metal interactions in the soils vary considerably depending on the nature of soil type. The solubility of heavy metals was influenced by the nature and composition of the soil solution when soil heavy metal concentrations were elevated. In particular, soil pH, OM, DOC, LMWOAs, and index cations are common environment factors governing metal availability in soils and hence risk-based environment assessment and remediation should consider all of these environment factors together when determining contaminant bioavailability.

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토양 중 중금속 생물유효도 평가방법 - 총설

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오늘날 중금속으로 오염된 토양의 위해도 평가 및 오염토양 복원을 위한 기술의 적용에 있어서 점차 중금속의 생물유효도(bioavailability)가 총함량보다 중요하게 생각되고 있다. 그 결과 많은 연구자들은 토양과 토양수 내의 생물에 유효한 중금속의 함량을 조사함과 더불어 이 유효도에 영향을 미치는 주요 토양환경인자를 연구하고 있다. 따라서 본 총설은 일반적으로 유효도 평가에 이용되는 기존의 여러 방법들을 비교평가하고 중금속 유효도의 중요성을 이에 영향을 미치는 토양 인자와 함께기술하였다. 현재까지 다양한 유효도 측정 방법이 개발되어 많은 연구에 적용되고 있는데, 이에는 화학적 침출 방법 (chemical based extraction)과 이온 선택성 전극 (ion selective electrode, ISE) 및 확산구배막(diffusive gradient in the thin film, DGT)을 이용한 중금속 화학종 분리방법 등을 들 수 있다. 그러나 이와 같이 개발된 다양한 기술이 유효도 측정에 있어서 괄목할 만한 성과를 내고 있음에도 아직 국제적으로 인증되고 있는 기술이 있는 것은 아니다. 게다가 토양 중 중금속의 유효도는 토양의 종류 및 특성 그리고 측정 대상인 중금속의 종류에 따라 매우 다양한 양상을 보여준다. 토양 중 중금속의 유효도 변화는 주로 토양과 토양수 사이에서 일어나는 이온교환 반응을 통한 중금속 흡착(adsorption)과 탈착(desorption)에 의하여 일어나며 이 반응은 토양 pH, 유기물, 토양수 중 유기탄소(dissolved organic carbon, DOC), 유기산(low-molecular weight organic acids, LMWOAs) 및 주요 양이온과 같은 토양환경인자의 변화에 영향을 받는다. 예를들어 토양 pH의 증가는 탈수소화(deprotonation) 작용을 통해서 토양표면의 중금속 흡착능력을 높여 결과적으로 유효도를 감소시킨다. 토양중 유기물은 중금속 유효도를 감소시킴과 동시에 유기탄소 및 유기산의 원천으로서 유효도를 증가시키기도 한다. 즉, 유기물은 주로 음으로 하전된 표면을 가지고 있어 중금속을 고상으로 흡착시켜 유효도를 감소시킨다. 반면에 유기물에서 녹아 나온 토양수중 유기탄소 및 유기산은 강한 킬레이트(chelate)로서 토양표면으로부터 중금속을 떨어져 나오게 하여 유효한 중금속 함량을 높여준다. 이와 같은 중금속 이온과 토양인자 사이의 상호반응은 토양의 종류 및 중금속의 종류에 따라 매우 다양하다.