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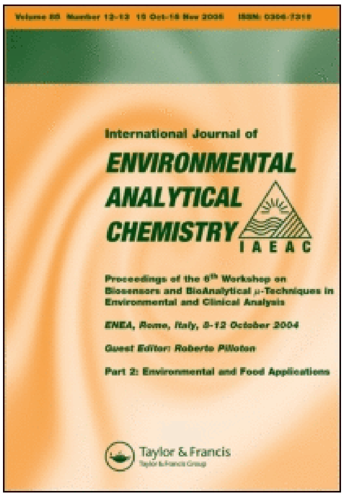

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Marc Verloo[a]; Mia Eeckhout[a]
[a] Laboratory for Analytical Chemistry and Agrochemistry, Gent, Belgium

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METAL SPECIES TRANSFORMATIONS IN SOILS: AN ANALYTICAL APPROACH

MARC VERLOO and MIA EECKHOUT

Laboratory for Analytical Chemistry and Agrochemistry, Rijksuniversiteit, Coupure Links 653, B 9000 Gent, Belgium

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The determination of metal species in solutions is important to evaluate their biological activity in natural ecosystems. The practical possibilities of different analytical techniques to determine and speciate metals in soil systems are discussed. Separative techniques such as ion exchange chromatography and gelpermeation chromatography allow a species estimation based on charge characteristics or molecular size of water soluble metal compounds. Electrochemical techniques such as potentiometry with ion-selective electrodes and polarography provide more detailed information about complex formation and stability.

KEY WORDS: Heavy metal, metal speciation, charge separation, size fractionation, complexation capacity.

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INTRODUCTION

The reactivity of metals in soils has often been assessed by assuming the existence of different species or binding forms in the soil. To estimate these fractions, different extracting solutions have been used. A comprehensive review has been given by Brummer.[1] Thus attempts have been made to distinguish between

- water-soluble: (soil solution–saturation extract–water extract)
- exchangeable: (KNO_3, $Ca(NO_3)_2$, NH_4Cl, $CaCl_2$, $MgCl_2$)
- organically bound: (destruction by H_2O_2 or NaOCl) (NaOH, $Na_4P_2O_7$, $K_4P_2O_7$, Na_2EDTA-extraction)
- occluded in iron and manganese oxides: ($NH_2OH+HCl$, DCB..)
- definite compounds—carbonates: (NaOAc pH 5, Na_2EDTA pH 4.5)
  —phosphates-sulfides: (strong acids)
- and structurally bound elements in silicate or residual forms: (HF-$HClO_4$ digestion)

Various reagents proposed for extraction of each individual fraction are given between brackets.

Sequential extraction procedures as proposed by Tessier[2] and Forstner[3] allow the fractionation of native and polluting heavy metals in the soil. The methods suggested are based on the assumption that the above mentioned binding forms really exist as such in the soil system. In fact, distinct fractions are not present as such and forms are interrelated. Fractionation is mainly a systematical tool born in the mind of the scientist, allowing a better understanding of the metal behaviour in the soil. Indeed it has been shown that contrary to the determination of the total content of any heavy metal in the soil, chemical fractionation may give more useful information with respect to the bioavailability (Verloo and Willaert[4]). Verloo *et al.*[5] also showed that the chemical form of the metals in the water-soluble fraction of the soil is mainly responsible for their wanted or unwanted biological effects.

Successful computer programs such as GEOCHEM (Sposito and Bingham[6]) have been developed for modelling the distribution of metal species in soil solutions. Analytical procedures however are necessary to control the validity of the computer predictions.

CHEMICAL FORMS OF HEAVY METALS IN THE SOIL SOLUTION

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The concentration of heavy metals in the solution phase is of major importance for all ecological considerations because plant uptake as well as transport of metals in the profile depend on it. The chemical form of the elements in solution mainly determines their chemical activity and eventual biological effects. Any metal M can be found in the soil solution either as $M^{n+}{}_{aq}$, the ion in solution, or as a complex compound $[M^{n+}L^{m-}]_{aq}{}^{+,-,0,\pm}$. In this formula, L is either an organic or inorganic ligand and the net charge of the complex can be positive, negative, neutral or amphoteric.

The equilibrium reaction,

$$M_{aq}{}^{n+} + L^{m-} \leftrightarrows [M^{n+}L^{m-}]_{aq}{}^{+,-,0,\pm}$$

is influenced by the soil properties and the concentrations of M and L in the solid phase and the soil solution. Increasing the ion concentration in the soil system may change the metal solubility and speciation. This could be caused by the input of heavy metals and organic or inorganic anions due to pollution, the use of sewage sludge, and the use of mineral or organic fertilizers or waste compounds. The charge characteristics of the soluble species will strongly affect their distribution in the soil system and their biological effects. Cationic metals or ion-pairs are readily adsorbed by soil colloids and are thus involved in a dynamic exchange equilibrium; however, complex or chelate forming organic or inorganic anions may disturb the thermodynamic exchange pattern, especially in contaminated soils.

The influence of the soil parameters pH and cation exchange capacity on the concentration of soluble Zn in the saturation extract of 9 soils with different physico-chemical characteristics and a total Zn content of 300 mg/kg added as sulphate is shown in Figures 1 and 2. The linear relation between the water-soluble Zn content in the soil and the concentration in the leaves of spinach grown on these soils is characterized by a determination coefficient $r^2 = 0.98$ (Verloo *et al.*[5]).

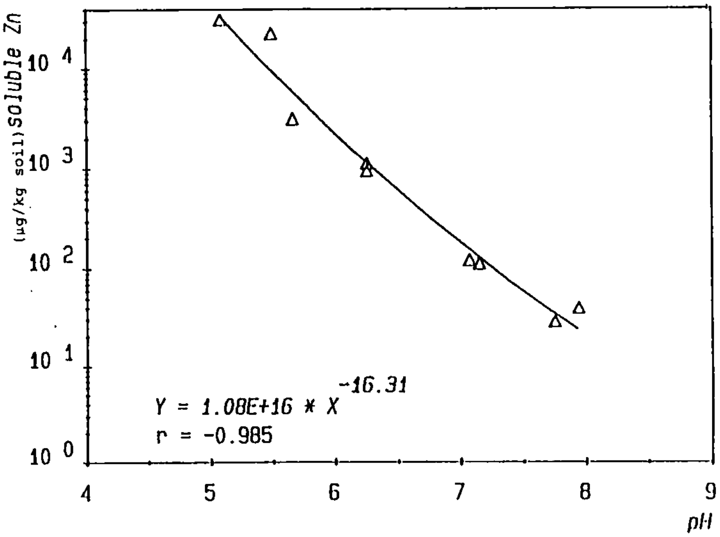

Figure 1 Influence of the pH on the concentration of soluble Zn in the saturation extract of 9 soils with a total Zn content of 300 mg/kg soil added as $ZnSO_4$.

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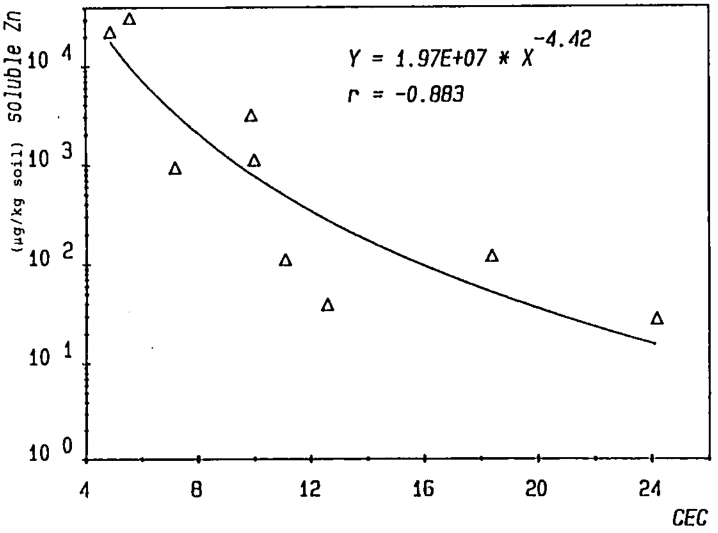

Figure 2 Influence of the CEC (meq/100 g) on the concentration of soluble Zn in the saturation extract of 9 soils with a total Zn content of 300 mg/kg soil added as $ZnSO_4$.

Table 1 Influence of the addition of slurried pig manure on the concentration and speciation of Cd in the saturation extract of a soil treated with Cd and/or pig manure

Soil treatment	*Soluble Cd* $\mu g/L$	M^+ %	M^- %	M^0 %	$M^\pm$ %
Blank	28.7	53	–	18	29
3 mg/kg Cd	58.7	72	18	10	–
Pig manure	51	90	–	–	10
3 mg/kg Cd + pig manure	224	98	–	–	2

METHODS FOR METAL SPECIATION IN THE SOIL SOLUTION

Using current analytical techniques, separation and identification of metal species in the soil solution may be possible.

Ion Exchange Chromatography

The charge characteristics of metal ions, complexes, or ion-pairs are important with respect to the chemical activity of the species. Ion exchange chromatography allows a separation of the metal species according to their net charge. The exchange resins are able to bind cations or anions from the (soil) solution. If a metal ion is complexed, the exchange surface competes with the dissolved organic or inorganic complexing agents for the free metal ions. The final result will depend on the type and specificity of the ion exchanger used. A method developed by Camerlynck and Kiekens[7] used an anion- and a cation-exchange resin and a combination of both, thus distinguishing between positive (M^+), negative (M^-), neutral (M^0) and amphoteric ($M^\pm$) metal species in the solution. Using this method it is possible to follow the transformation of soluble metal species added to soils. The distribution of Cu added to different soils either as $CuSO_4$, Cu-ethylene diamine tetraacetic acid (CuEDTA) or Cu-tetraethylenepentamine (CuTETREN) has been studied by Willaert *et al.*[8] The effect of slurried pig manure on the mobilization of Cd in the soil could easily be evaluated using this technique (see Table 1). It can be observed that application of pig manure results in a strong increase of the water-soluble Cd-fraction, the main form of Cd remaining positively charged.

Gel Chromatography

As ion complexation also affects the ionic size, gel permeation may be a valuable tool to distinguish between free (small) and complexed (large) ions. With this technique, the species are eluted in order of decreasing molecular size. Determination of the metal concentrations and co-eluting components in the different eluate fractions gives useful information with respect to the different species present. The following experiment illustrates the possibilities of this technique.

To estimate whether in a pig slurry solution the chloride ions or the organic

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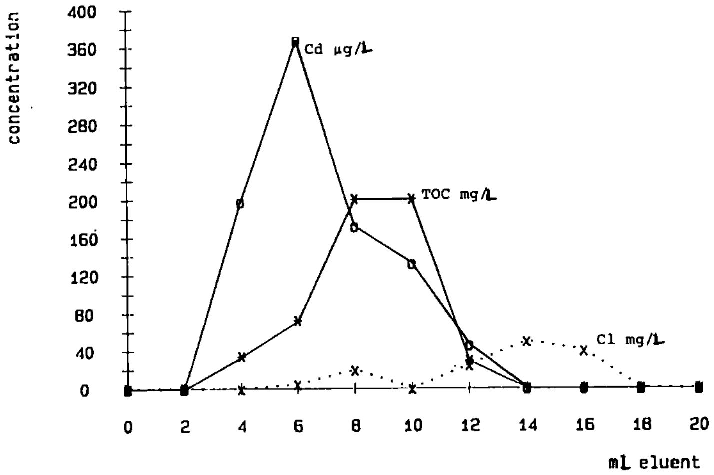

Figure 3 Concentration of TOC, Cd and Cl in the elution fractions of a pig manure solution containing 1 mg/L Cd.

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component were the main complexing agents for Cd^{++}, 1 mg Cd^{++} was added to 1 L pig slurry previously filtered on a 0.45 μm membrane filter. After equilibration the mixture was separated on a G-10 Sephadex column (total bed volume 20 mL) using distilled water as the eluting solution. The effluent was collected in 2 mL fractions and analysed for Cd, Cl^-, and total organic carbon (TOC). The results are summarized in Figure 3 showing that under these experimental conditions the complexation between Cd and organic manure compounds prevails.

Potentiometry with Ion-selective Electrodes

Effects of ionic strength and anion concentration in the soil solution on the solubility and chemical activity may be estimated using ion-selective electrodes. Although these types of electrodes are not directly reliable for the accurate determination of concentrations, they maybe useful tools to monitor a complex formation as they detect changes in chemical ion activity (Bresnahan *et al.*[9]).

Figure 4 shows the influence of increasing concentrations of ClO_4^-, NO_3^-, SO_4^{--}, and Cl^- ions on the activity of a 1 mg/L Cd^{++} solution as measured by the potential decrease of a Cd-selective electrode. The major effects for Cl^- and SO_4^{--} are clearly illustrated. Thus chlorides added to the soil as a fertilizer salt (KCl) or in any other way may alter the heavy metal behaviour in soils.

The same potentiometric technique was used to study the influence of Cl^- on the solubility of Cd^{++} in a soil to which 10 mg/kg Cd^{2+} has been added. The results are shown in Table 2. The addition of Cl^- increases the total Cd concentration in the equilibrium solution; however, the free Cd^{++} concentration decreases due to the formation of CdCl ion-pairs.

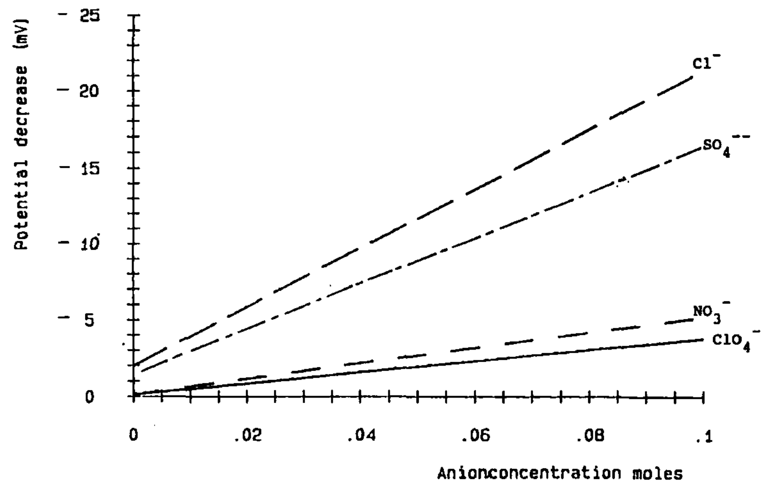

Figure 4 Influence of the anion concentration on the Cd-activity of a 1 mg/L Cd solution as measured with an ion-selective Cd-electrode.

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Table 2 Influence of increasing Cl⁻ concentrations on the solubility of Cd in soil

Cl^- meq/L	Cd_{sol} µg/L	Cd_{free} µg/L	(CdCl) µg/L
0	74	74	0
1	78	73	5
5	89	72	17
10	100	59	41
20	114	34	80

Polarographic Methods

Anodic stripping voltammetry (ASV) has been a widely used analytical method allowing speciation in solutions. In marine systems, this technique has been used to investigate cadmium, copper, lead, and zinc species (Valenta[10]). The metal is initially electrochemically reduced from its oxidized state in the solution to form an elemental amalgam with mercury. This step serves to preconcentrate the metal from the solution into the mercury electrode. The amalgamated metal is then quantified by measuring the current that flows when the metal is oxidized back into the solution. The signal depends on the kinetic characteristics of the metal species in solution; if a portion of a metal is bound to ligands that have slow dissociation kinetics, that fraction will show either no or a lower detectability. ASV is also a useful technique in the speciation study of the soil solution. In the solutions separated by gel chromatography (see Figure 3) it could easily be demonstrated by ASV that Cd had formed a non-labile organo-metal complex

Table 3 Peak height variation for the addition of humic acid to 100 μg/L Cu^{2+} solution as recorded by A.S.V.

Humic acid (*μg/10 mL*)	*Cu^{2+}* *peak height* (*mm*)
0	32
20	27
40	23
60	17
80	13
100	10
120	7
140	4

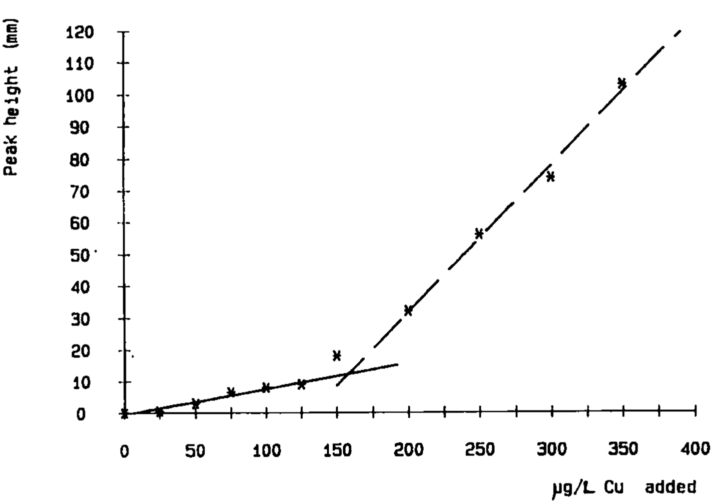

Figure 5 Determination of the complexation capacity of a humic acid solution for Cu as measured with ASV.

with soluble components of the pig slurry. The existence and amount of organometal complexes in a soil solution can simply be estimated by doing a metal analysis using atomic absorption, giving the total amount of soluble metal and subtracting the metal amount as determined by ASV.

Table 3 shows the effect of the addition of a soil humic acid (HA) solution on the free Cu^{++} ASV signal. Polarographic techniques will also allow the estimation of the complexing capacity of natural compounds. The determination of the complexing capacity of a soil HA solution according to a method descibed by Valenta[10] is shown in Figure 5. Initially the oxidation current shows a fast drop as Cu is chelated. The moment all Cu is bound, the slope of the curve changes. The intersection point of the two straight lines indicates the saturation of the bonding sites of the humic acid corresponding to the complexing capacity of the ligand.

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CONCLUSIONS

Although fractionation of heavy metals in polluted soils based on the sequential extraction of solid compounds is able to give useful information with respect to the chemistry of metals in soils, the key for solving the chemical and biological behaviour problem of a soil pollutant has to be found in the soluble fraction.

Several analytical techniques are available to get more information about the different metal forms that appear in the soil solution. Some techniques permit a separation of metal-forms with different characteristics such as charge, size or complex stability. Complementary experimental results, in combination with computer modelling should give the opportunity to estimate the different metal forms with a good accuracy.

References

1. G. W. Brummer, *The Importance of Chemical Speciation in Environmental Processes* (Dahlem Konferenzen, Springer-Verlag, 1986) pp. 169–192.
2. A. Tessier, P. G. C. Campbell and M. Bisson, *Anal. Chem.* **51,** 844 (1969).
3. U. Forstner, W. Calmono, K. Conradt, H. Jaksch, C. Schimkus and J. Schoer, *Heavy Metals in the Environment* (Int. Conf. Amsterdam, 1981) pp. 698–704.
4. M. Verloo and G. Willaert, *Environmental Contamination* (Int. Conf. Amsterdam, 1986) pp. 59–161.
5. M. Verloo, G. Willaert, M. Eeckhout and F. De Spiegeleer, *Heavy Metals in the Environment* (Int. Conf. New Orleans, 1987) vol 1 pp. 253–256.
6. G. Sposito and F. T. Bingham, *J. Plant. Nutr.* **3,** 35 (1981).
7. R. Camerlynck and L. Kiekens, *Plant and Soil* **69,** 331 (1982).
8. G. Willaert, M. Verloo and A. Cottenie, *Metal Cycling in the Environment* (D. Rondia, ed., Presses Universitaires de Liège, 1985) pp. 229–244.
9. W. Bresnahan, C. Grant and J. Weber, *Anal. Chem.* **50,** 1675–1679 (1978).
10. P. Valenta, *Trace Metal Speciation in Surface Water and its Ecological Implication* (G. Leppard, ed., Plenum Press, New York, 1983) pp. 49–67.

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