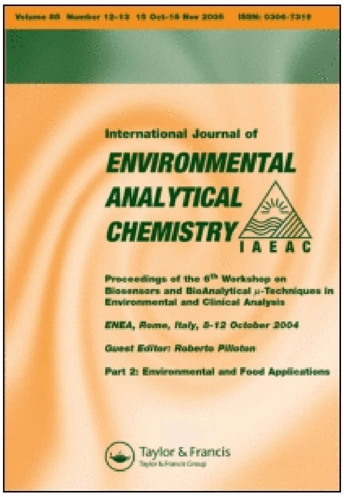

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CHEMICAL ASPECTS OF HEAVY METAL SOLUBILITY WITH REFERENCE TO SEWAGE SLUDGE AMENDED SOILS

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The long term benefits of applications of sewage sludges to land as an alternative source for plant nutrients are frequently limited by potentially toxic contents of heavy metals. While upper limits for metal contents in amended soils have been defined in both North America and Europe, there has been little attention paid to the fate of the metals if soil management practices are changed and the solubility and hence the mobility of the metals increased. This study investigated the role of changes in pH and additions of chloride ions to the content of soluble Cd, Co, Cr, Cu, Pb, Ni, V and Zn in soils to which sewage sludge had been applied. The contents of soluble metals ranged from less than 1 μmol L^{-1} for V to 500 μmol L^{-1} for Zn. For all the metals, contents were greater in the presence of Cl^- ions and increased markedly as the pH decreased below about pH 5. Contents of V, Cr, Cu and Pb increased at pH's above 7. As all metal contents were undersaturated with respect to hydroxide or carbonate precipitates, the changes in their contents were probably related to desorption from variable charge sites on mineral and/or humic surfaces.

KEY WORDS: Soils, sludge, toxic metals, mobility.

INTRODUCTION

Municipal and industrial sewage sludges from water treatment plants are frequently applied to soils to provide plant nutrients for crop production. However this practice has the potential of creating environmental pollution problems because many sludges have high contents of toxic heavy metals. Although there are strict guidelines in both North America and Europe on the maximum amounts of metals that can be added to agricultural land through the application of sewage sludges, current regulations do not generally define the soil management practises that should be followed once these maximum application values have been attained.

Soils are particularly important in the attenuation of heavy metals in the environment because they contain surface-active mineral and humic constituents that are involved in metal retention[1]. These surface-active sites include both constant negative charge sites associated with phyllosilicate clay minerals as well as variable charge sites associated with oxides, (oxy)hydroxides and humic material. Both inner- and outer-sphere complexes can be formed between the metallic ions and these reactive sites on soil particles.

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Studies have shown that if the pH of sewage sludge amended soils is maintained at neutral or slightly alkaline pH's then the toxic metals and non-metals present are relatively immobile[2,3]. However, a number of soil management practices can remobilize metals in sludge-amended soils after the addition of sewage sludges has ceased. For instance, decreases in soil acidity brought about by the oxidation of NH_4^+-N fertilizers can have a dramatic effect on metal solubility. Metal availability to plants may be increased by the addition of complexant ligands, such as Cl^- ions added as KCl fertilizer, or organic anions added as organic amendments, such as food processing wastes.

Pollution problems may arise if toxic heavy metals are mobilized into the soil solution and are either taken up by plants or transported in drainage waters to associated water supplies. The metals may then enter the human food chain through the consumption of such plants or through intake of contaminated waters. As toxic heavy metals can form strong complexes with biomolecules, their presence, in even small amounts, can be hazardous to the health of both plants and animals.

The primary objective of this research was to investigate the mobility of the toxic heavy metals Cd, Cr, Cu, Co, Pb, Ni, V and Zn in sewage-sludge amended soils. The mobility of the metals was investigated by a series of laboratory experiments in which the pH of the soils was adjusted by addition of appropriate amounts of acid or base to give a range in pH's from 3.5 to 8. In addition to changes in pH, the mobility of the metals was investigated in the presence of two different background electrolytes – LiCl, containing the complexant Cl^- ion, and $LiClO_4$ containing the non-complexant ClO_4^- ion.

MECHANISMS OF HEAVY METAL RETENTION BY SOILS

Metal speciation in solution

As many cationic metals undergo hydrolysis reactions in water, the concentration of the free metal, $[Me^{z+}]$, in solution depends on pH and on the magnitude of the various hydrolysis constants involved in the reactions. A general equation for the formation of mono-nuclear hydrolysed metal complexes is:-

$$pH^+ + Me^{z+} + rH_2O \rightleftarrows H_pMe(H_2O)_r^{p+z}; \quad \beta_{p,1,r} = \frac{\{H_pMe(H_2O)_r^{p+z}\}}{\{H^+\}^p\{Me^{z+}\}} \tag{1}$$

where $\beta_{p,1,r}$ is the overall formation constant for the hydrolysed species and { } represents activities.

Soluble complexes can also be formed with carbonate, CO_3^{2-}, species found in soil solutions. These complexes are generally with divalent metals.

$$Me^{2+} + rCO_3^{2-} \rightleftarrows Me(CO_3)_r^{2-2r}; \quad \beta_{0,1,r}^{CO_3} = \frac{\{Me(CO_3)_r^{2-2r}\}}{\{Me^{2+}\}\{CO_3^{2-}\}^r} \tag{2}$$

The content of CO_3^{2-} ions in soil solutions can be calculated from:-

$$CO_3^{2-} = \frac{K_{a1}\,K_{a2}\,K_H\,pCO_{2(g)}}{\{H^+\}^2} \tag{3}$$

where K_{a1} and K_{a2} are the dissociation constants for carbonic acid, HCO_3^*; K_H is the Henry's constant for CO_2; and $pCO_{2(g)}$ is the partial pressure for gaseous CO_2.

The Cl^- ion is also a complexant ligand for many metallic cations and its overall reaction with a metal can be described by:-

$$Me^{z+} + rCl^- \rightleftarrows MeCl_r^{z-r}: \quad \beta_{0,1,r}^{Cl} = \frac{\{MeCl_r^{z-r}\}}{\{Me^{z+}\}\{Cl^-\}^r} \tag{4}$$

Generally up to four hydrolysed species, two carbonate species and four chloride species can be formed with most metallic cations.

The total concentration of metal in solution, $[Me]_T$, is thus the sum of the free metal content plus each of the complexed species in solution.

$$\begin{aligned}[Me]_T = {} & [Me^{z+}] + [MeOH^{z-1}] + [Me(OH)_2^{z-2}] + [Me(OH)_3^{z-3}] + [Me(OH)_4^{z-4}] \\ & + [MeCO_3^0] + [Me(CO_3)_2^{2-}] + MeCl^{z-1} + MeCl_2^{z-2} + MeCl_3^{z-3} + MeCl_4^{z-4}\end{aligned} \tag{5}$$

By including activity coefficients, γ, equation (5) becomes:-

$$[Me]_T = [Me^{2+}]\left\{\begin{aligned} & 1 + \frac{\gamma_2\beta_{-1,1,1}}{\gamma_1^2\{H^+\}} + \frac{\gamma_2\beta_{-2,1,2}}{\gamma_1^2\{H^+\}^2} + \frac{\gamma_2\beta_{-3,1,3}}{\gamma_1^4\{H^+\}^3} + \frac{\beta_{-4,1,4}}{\gamma_1^4\{H^+\}^4} \\ & + \gamma_2^2\beta_{0,1,1}^{CO_3}\{CO_3^{2-}\} + \gamma_2^2\beta_{0,1,2}^{CO_3}\{CO_3^{2-}\}^2 + \gamma_2\beta_{0,1,1}^{Cl}\{Cl\} \\ & + \gamma_1^2\gamma_2\beta_{0,1,2}^{Cl}\{Cl\}^2 + \gamma_1^2\gamma_2\beta_{0,1,3}^{Cl}\{Cl\}^3 + \gamma_1^4\beta_{0,1,4}^{Cl}\{Cl^4\}\end{aligned}\right\} \tag{6}$$

The inorganic speciation of the metals examined here can be summarized as follows - Cr(III) is the most hydrolysable while Cd(II) is the least; both Pb(II) and Cu(II) form strong complexes with CO_3^{2-} ions; and Cd(II) and Pb(II) strong complexes with Cl^- ions (Table 1).

Cr(VI) and V(V) are fully hydrolysable metals and exist in water in the form of oxyanions. The content of the weak acids and their conjugate bases is dependent on the dissociation constants,K_a's, of the acids and their oxyanions.

$$HCrO_4^- \rightleftarrows CrO_4^{2-} + H^+; \quad pK_{a2} = 6.51 \tag{7}$$

$$H_3VO_4 \rightleftarrows H_2VO_4^- + H^+; \quad pK_{a1} = 4.00 \tag{8}$$

$$H_2VO_4^- \rightleftarrows HVO_4^{2-} + H^+; \quad pK_{a2} = 8.55 \tag{9}$$

Adsorption on mineral surfaces

The surfaces of many soil particles, particularly those in the clay-sized fraction, are electrically charged. The intrinsic charges responsible for both cation and anion adsorption reactions in soils arise from two different mechanisms of charge generation. Permanent charges arise from structural imperfections within the unit structures of clay

Table 1 Hydrolysis, carbonate and chloride formation constants, pβ, of studied metals.†

Metal	*OH*	*$(OH)_2$*	*$(OH)_3$*	*$(OH)_4$*	*CO_3*	*$(CO_3)_2$*	*Cl*	*Cl_2*	*Cl_3*	*Cl_4*
Cr^{3+}	4.00	9.70	18.00	27.40	–	–	0.62	–	–	–
Cd^{2+}	10.08	20.35	33.30	47.35	4.35	–	1.97	2.59	2.40	1.47
Co^{2+}	9.65	18.80	31.50	46.30	4.91	–	0.57	–	–	–
Cu^{2+}	8.00	17.30	27.80	39.60	6.75	10.69	0.40	–	–	–
Pb^{2+}	7.71	17.12	28.06	–	7.00	10.29	1.58	1.82	1.71	1.40
Ni^{2+}	9.86	19.00	30.00	44.00	5.37	–	0.72	–	–	–
Zn^{2+}	8.96	16.90	28.40	41.20	4.75	–	0.49	0.62	0.51	0.20

†Taken from Turner *et al.*,[4]

minerals, whereas pH-dependent charges are generated by proton association-dissociation reactions at the edges and surfaces of minerals.

The variable charge mineral surfaces in soils are usually associated with the oxides and (oxy)hydroxides of Fe, Al and Mn. At the point of net zero proton charge, PNZPC, of the mineral the surfaces or edges are neutral [$\equiv$ Me-OH^0], whereas at pH's below the PNZPC the sites are positively charged [$\equiv$ Me-OH_2^+] and negatively charged [$\equiv$ Me-O^-] at pH's above the PNZPC.

The proton dissociation reactions and the intrinsic equilibrium constants for these reactions at the surfaces or edges of minerals can be represented by two surface acidity reactions:-

$$\equiv \text{Me–OH}_2^+ \rightleftarrows \equiv \text{Me–OH}^0 + \text{H}^+; \quad {}^c\text{K}_{a1}^{int} = \frac{[\equiv \text{Me–OH}^0]\{\text{H}^+\}}{[\equiv \text{Me–OH}_2^+]} \exp(-\psi_s F/RT) \quad (10)$$

$$\equiv \text{Me–OH}^0 \rightleftarrows \equiv \text{Me–O}^- + \text{H}^+; \quad {}^c\text{K}_{a2}^{int} = \frac{[\equiv \text{Me–O}^-]\{\text{H}^+\}}{[\equiv \text{Me–OH}^0]} \exp(-\psi_s F/RT) \quad (11)$$

where ${}^c\text{K}_{a1}^{int}$ and ${}^c\text{K}_{a2}^{int}$ are the first and second intrinsic conditional equilibrium constants for the surface acidity reactions and ψ_s is the electrical potential at the charged surface.

Specific adsorption of metallic cations onto mineral surfaces involves the formation of an inner-sphere complex between the metal and the negatively charged deprotonated surface site and occurs most readily for those metals that hydrolyse in water at relatively low pH's.

For the reaction of metallic cations, Me^{z+}, at variable charged surfaces,

$$\equiv \text{Me–OH}^0 + \text{Me}^{z+} \rightleftarrows \equiv \text{Me–O–Me}^{z-1} + \text{H}^+ \quad (12)$$

At equilibrium,

$${}^c\text{K}_{Me}^{int} = \frac{[\equiv \text{Me–O–Me}^{z-1}]\{\text{H}^+\}}{[\equiv \text{Me–OH}^0]\{\text{Me}^{z+}\}} \exp(\psi_{is} F/RT) \quad (13)$$

where ${}^c\text{K}_{Me}^{int}$ is the conditional intrinsic formation constant for the surface complex and ψ_{is} is the electrical potential at the plane of adsorption of the inner-sphere complexes.

The extent of the reaction is dependent on pH, and increases to a maximum as the pH is raised. The maximum amount of adsorption occurs at a pH about 3 units below that of the first hydrolysis constant of the metal.

The retention of metallic anions also involves the formation of covalent bonds with surface mineral sites through a process of ligand exchange. The extent of adsorption is generally at a maximum at or near the pK_a of the weak acid or oxyanion and then declines with increasing pH.

For the adsorption of metallic anions, L^{n-}, onto variable charge mineral sites,

$$\equiv \text{Me–OH}^0 + L^{n-} + H^+ \rightleftarrows \equiv \text{Me–L}^{1-n} + H_2O \qquad (14)$$

At equilibrium,

$$^cK_L^{int} = \frac{[\equiv \text{Me–L}^{1-n}]}{[\equiv \text{Me–OH}^0]\{L^{n-}\}\{H^+\}} \exp(\psi_{is} F/RT) \qquad (15)$$

where $^cK_L^{int}$ is the conditional intrinsic formation constant for the surface complex.

Intrinsic complexation constants for metallic cations and anions onto hydrous ferrous oxide are shown in Table 2[5]. The adsorption of Cd(II), Cr(VI), Cr(III), Co(II), Cu(II), Pb(II), Ni(II), V(V) and Zn(II) onto hydrous ferric oxide are shown in Figure 1.

Adsorption on humic surfaces

Much less in known about the complexation of heavy metals with soil organic matter than for variable charge minerals, such as goethite or hydrous ferric oxide. Multi-ligand representations of the humic material have been used to empirically fit titration data using both discrete and continuous multi-ligand models[6,7]. Although the complexity of humic materials suggests that a large number of types of sites may be involved in metal binding and that these sites are best characterized by a continuous distribution of complexation constants, it has been shown that titration data can be adequately described using only two or three discrete complexant ligands[1].

Table 2 Complexation reactions and constants for metals with hydrous ferric oxide.[†]

	Intrinsic complexation reaction			$p^cK^{int}_{Me}$
Cations				
Cd(II)	$\equiv \text{Fe-OH}^0 + \text{Cd}^{2+}$	$\rightleftarrows$	$\equiv \text{Fe-OCd}^+ + H^+$	-0.47
Cr(III)	$\equiv \text{Fe-OH}^0 + \text{Cr}^{3+} + H_2O$	$\rightleftarrows$	$\equiv \text{Fe-OCrOH}^+ + 2H^+$	-2.06
Co(II)	$\equiv \text{Fe-OH}^0 + \text{Co}^{2+}$	$\rightleftarrows$	$\equiv \text{Fe-OCo}^+ + H^+$	0.46
Cu(II)	$\equiv \text{Fe-OH}^0 + \text{Cu}^{2+}$	$\rightleftarrows$	$\equiv \text{Fe-OCu}^+ + H^+$	-2.89
Pb(II)	$\equiv \text{Fe-OH}^0 + \text{Pb}^{2+}$	$\rightleftarrows$	$\equiv \text{Fe-OPb}^+ + H^+$	-4.65
Ni(II)	$\equiv \text{Fe-OH}^0 + \text{Ni}^{2+}$	$\rightleftarrows$	$\equiv \text{Fe-ONi}^+ + H^+$	-0.37
Zn(II)	$\equiv \text{Fe-OH}^0 + \text{Zn}^{2+}$	$\rightleftarrows$	$\equiv \text{Fe-OZn}^+ + H^+$	-0.99
Anions				
Cr(VI)	$\equiv \text{Fe-OH}^0 + \text{CrO}_4^{2-}$	$\rightleftarrows$	$\equiv \text{Fe-CrO}_4^- + H_2O$	-10.85
V(V)	$\equiv \text{Fe-OH}^0 + \text{VO}_4^{3-}$	$\rightleftarrows$	$\equiv \text{Fe-OHVO}_4^{3-}$	-13.57

[†]Taken from Dzombak and Morel,[5].

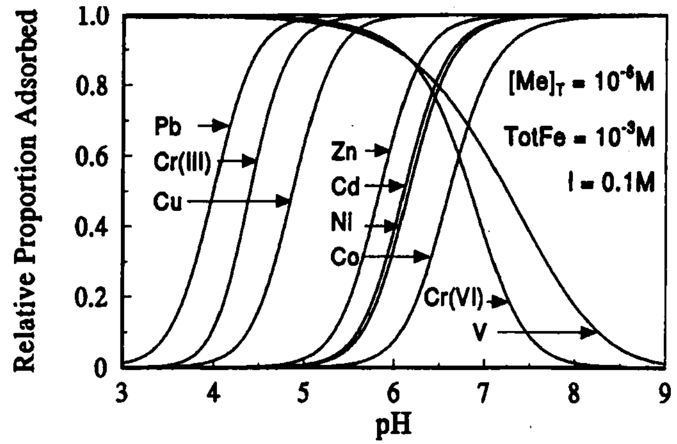

Figure 1 Adsorption of Cd(II), Cr(VI), Cr(III), Co(II), Cu(II), Pb(II), Ni(II), V(V) and Zn(II) onto hydrous ferric oxide.

Hence, the complexation of metals by humic materials is thus often represented as the interaction between a metal and a simple diprotic acid[8]:-

$$Me^{2+} + H_2L \rightleftarrows MeL^{z-2} + 2H^+; \quad \beta_{-2,1,1} = \frac{\{MeL^{z-2}\}(H^+\}^2}{\{Me^{z+}\}\{H_2L\}} \qquad (16)$$

As humic materials differ widely in their chemical structures, it is difficult to compare complexation constants for metals with different humic materials. However, as an example of metal complexation with humic material, the complexation reactions of Cd^{2+} and Cu^{2+} with the same humic material are shown in Figure 2.

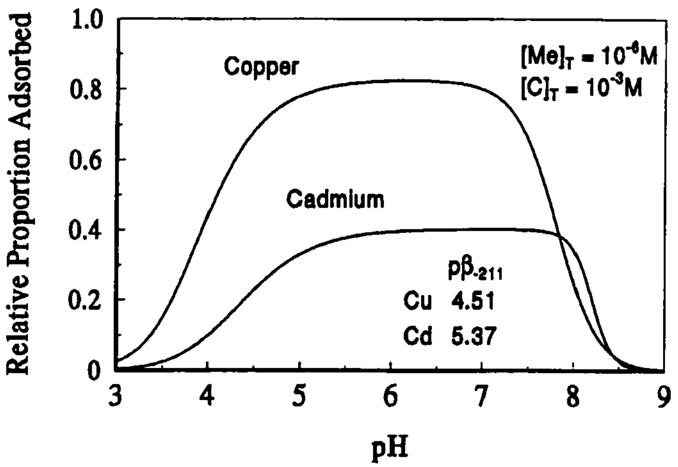

Figure 2 Complexation of Cd^{2+} and Cu^{2+} with humic material.

Precipitates

The maximum amount of any element in soil solutions is controlled by the solubility of precipitates which contain that element. The most important of these precipitates are the hydroxides, carbonates and sulphides, and to a lesser extent, phosphates. However, sulphide precipitates are only important in soils which experience reducing conditions as sulphides readily oxidize in soils containing sufficient O_2.

For the dissolution of hydroxides, $Me(OH)_z$, to release metallic cations, Me^{z+},

$$Me(OH)_z + zH^+ \rightleftarrows Me^{z+} + zH_2O; \quad {}^*K_{so} = \frac{\{Me^{z+}\}}{\{H^+\}^z} \tag{17}$$

where ${}^*K_{so}$ is the solubility product of the hydroxide precipitate.

Taking negative logarithms,

$$pMe^{z+} = zpH + p^*K_{so} \tag{18}$$

The extent of dissolution reactions of carbonates in soil solutions is controlled not only by the solubility products of the individual carbonates but also by the partial pressure of carbon dioxide gas, pCO_2. This is because the content of the carbonate anion, CO_3^{2-}, is controlled by the partial pressure of carbon dioxide, pCO_2, present in the soil atmosphere.

The dissolution of divalent metallic carbonates, $MeCO_3$, can be described by:-

$$MeCO_3 \rightleftarrows Me^{2+} + CO_3^{2-}; \quad K_{so} = \{Me^{2+}\}\{CO_3^{2-}\} \tag{19}$$

Taking negative logarithms,

$$pMe^{z+} = zpH + pK_{so} - pK_{a1} - pK_{a2} - pK_H - ppCO_{2(g)} \tag{20}$$

Using the p^*K_{s0} values given in Table 3, In addition to Equations (20) and (6), the relationships between the negative logarithms of the concentrations of total metal, pMe_T, and pH for the hydroxides of Cd, Co, Cr, Ni, Pb and Zn (Figure 3a) and for the carbonates of Cd, Ni, Pb and Zn (Figure 3b) were calculated.

Table 3 Solubility reactions and products for metallic hydroxides and carbonates.[†]

Dissolution reaction			p^*K_{s0}	*Dissolution reaction*			p^*K_{s0}
Hydroxides							
$Cr(OH)_3 + 2H^+$	$\rightleftarrows$	$CrOH^{2+} + 2H_2O$	-5.78	$Zn(OH)_2 + 2H^+$	$\rightleftarrows$	$Zn^{2+} + 2H_2O$	-11.83
$Ni(OH)_2 + 2H^+$	$\rightleftarrows$	$Ni^{2+} + 2H_2O$	-6.83	$Co(OH)_2 + 2H^+$	$\rightleftarrows$	$Co^{2+} + 2H_2O$	-12.36
$Pb(OH)_2 + 2H^+$	$\rightleftarrows$	$Pb^{2+} + 2H_2O$	-8.14	$Cd(OH)_2 + 2H^+$	$\rightleftarrows$	$Cd^{2+} + 2H_2O$	-13.71
Carbonates							
$PbCO_3$	$\rightleftarrows$	$Pb^{2+} + CO_3^{2-}$	12.84	$ZnCO_3$	$\rightleftarrows$	$Zn^{2+} + CO_3^{2-}$	9.93
$CdCO_3$	$\rightleftarrows$	$Cd^{2+} + CO_3^{2-}$	11.21	$NiCO_3$	$\rightleftarrows$	$Ni^{2+} + CO_3^{2-}$	6.85

[†] Calculated from the thermodynamic data base of Wagman *et al.*,[9].

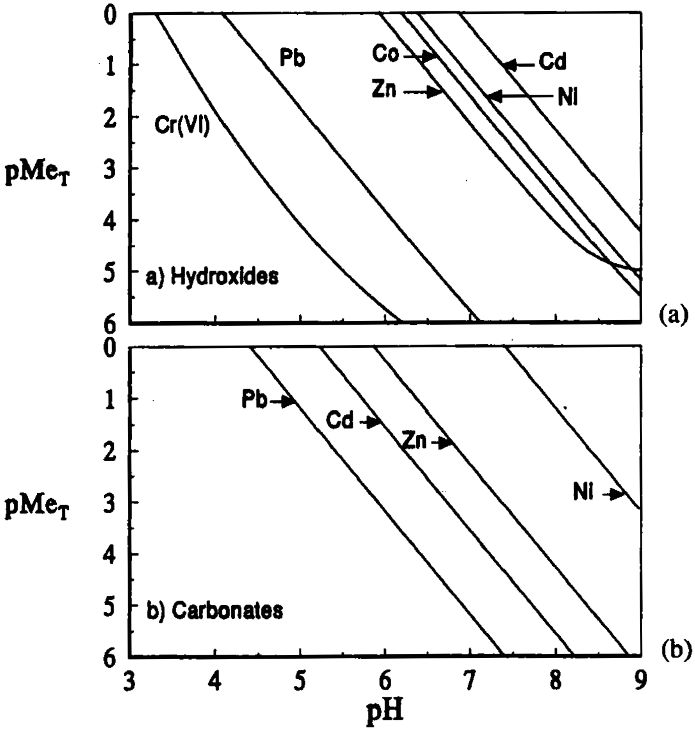

Figure 3 The solubility of a) metallic hydroxides and b) carbonates

EXPERIMENTAL

Materials

The soils used for the experiments were taken from the University of Guelph, Elora Research Station, Ontario, from plots to which sewage sludge was applied between 1972–1980. The soil used for the trials was a Conestogo loam (Gleyed Melanic Brunisol; Aquic Eutrochrept). To these plots were applied three different sludges – a Ca-sludge, an Al-sludge and an Fe-sludge. Details of the treatments are reported in Soon and Bates[10].

Although nine soil samples were taken from the experimental plots representing each of the three sludge treatments at three different rates of application, only the results of the Al-sludge application at a rate of four times the lowest application will be discussed. The contents of DTPA-extractable metals in the soil from this treatment were 0.16 mg kg^{-1} for Co, 1.75 for Cd, 0.1 for Cr, 8.8 for Pb, 67.5 for Zn, 26.8 for Cu and 1.0 for Ni.

Incubation experiments

Approximately 2.5 g of soil sample was weighed into a 50 ml centrifuge tube containing 20 ml of either 0.01 M $LiClO_4$ or LiCl. To lower the pH of the soil containing $LiClO_4$, 1 ml of $HClO_4$ with differing acid strengths was added to reach the required pH values. Similarly for those soils incubated with 0.01 M LiCl, 1 ml of various HCl solutions was added. To raise the pH of the soils, 1 ml of LiOH with increasing strengths was added to both soils incubated with either LiCl or $LiClO_4$. A pH range from 3 to 9 was used in the incubation experiments. The suspensions were shaken for six days to reach equilibration, centrifuged at 10,000 rpm for 15 minutes, to obtain supernatants which were filtered through 0.22 μm Millipore filters. The pH's of the filtrates were then measured.

Analytical procedures

The amount of Pb remaining in the filtered solutions was measured by potentiometric stripping analysis using a Radiometer Trace-Lab®, a Hg film-plated electrode, an electolysis time of 3 min and a stripping potential of -450 mv.

The other metals, Cr, Cu, Ni, Zn, Co, V, were analyzed of ICP-AE spectrometry. The LECO Plasmarray® spectrometer[11-13] utilised for the current study incorporates the major advantages of both simultaneous and sequential systems; the simultaneous multi-element capability, together with the flexibility to select the analytical lines of interest. Selection of analytical wavelength regions (Table 5) for this study was achieved through the use of a "spectral mask" situated on the Rowland circle of a concave grating. The operational settings for the instrument, together with the selected wavelengths for analysis are listed in Table 4.

A CETAC U-5000® ultrasonic nebulisation system consisting of a sample nebulizer plus a closed cycle cooling system was utilised for sample introduction to the spectrometer with a peristaltic pump delivering the solution at 0.9 ml min^{-1} to a transducer face vibrating at 1.40 MHz. The aerosol mist is carried by an argon stream that enters a "U" shaped tube heated to 160 C to desolvate the aerosol. Upon entering the cold (2°C) desolvation chamber, the water component is "stripped" from the sample aerosol. The final sample path extends between the nebulizer and the ICP-AES instrument. This introduction system to the ICP-AES enables more than an order of magnitude improvement in detection limits.

RESULTS AND DISCUSSION

The contents of metals released from the soils as a result of the addition of acid or base determined in the presence of $LiClO_4$ or LiOH ranged considerably from a low of less

Table 4 Instrument settings for ICP-AES analysis of metals utilising the LECO Plasmarray® spectrometer.

		Element	*Wavelength (nm)*
Forward power	1.9 kw	Cd	228.802
Reflected power	< 5 kw	Cr	267.716
Coolant flow rate	18 L min^{-1}	Co	345.350
Auxiliary flow rate	1.6 L min^{-1}	Cu	324.754
Nebulizer flow rate	1.0 L min^{-1}	Ni	231.604
Sample delivery rate	0.85 ml min^{-1}	V	309.311
Viewing height	12 mm	Zn	213.856
Slit width	50 μm		
Camera temperature	–40°C		
Torch	Hi-solids		

than 1 µmol L^{-1} for V, up to 5 µmol L^{-1} for Cd, Cr, Co and Pb, up to 7 µmol L^{-1} for Ni, up to 15 µmol L^{-1} for Cu and up to 500 µmol L^{-1} for Zn (Figures 4 and 5).

For all the metals studied, contents in solution increased rapidly as the pH decreased below a value of about pH 5. As all the measured metal contents were considerably undersaturated with respect to their respective hydroxide or carbonate precipitates, the changes in their concentrations were probably related to desorption from variable charge sites on mineral and/or humic surfaces. For V, Cr, Cu and Pb there were significant increases in their solution concentrations above pH 7. The increases in the contents of Cu and Pb as the pH increased probably result from the formation of soluble CO_3^{2-} complexes, whereas those for V and Cr probably result from the desorption of HVO_4^{2-} and CrO_4^{2-} respectively. The increase in Cr content at low pH values suggests that at least part of the Cr in the soil exists as Cr(III).

For all the metals, contents were greater in the presence of Cl^- ions, presumably because of the formation of soluble Cl^- complexes in the case of Cd, Co, Cu, Pb, Ni and Zn; and for V and Cr, displacement of their respective anions by Cl^- ions from variable charged mineral surfaces.

CONCLUSIONS

The results from this study have shown that both pH and the presence of elevated contents of Cl^- ions have an influence on the content of a number of toxic heavy metals

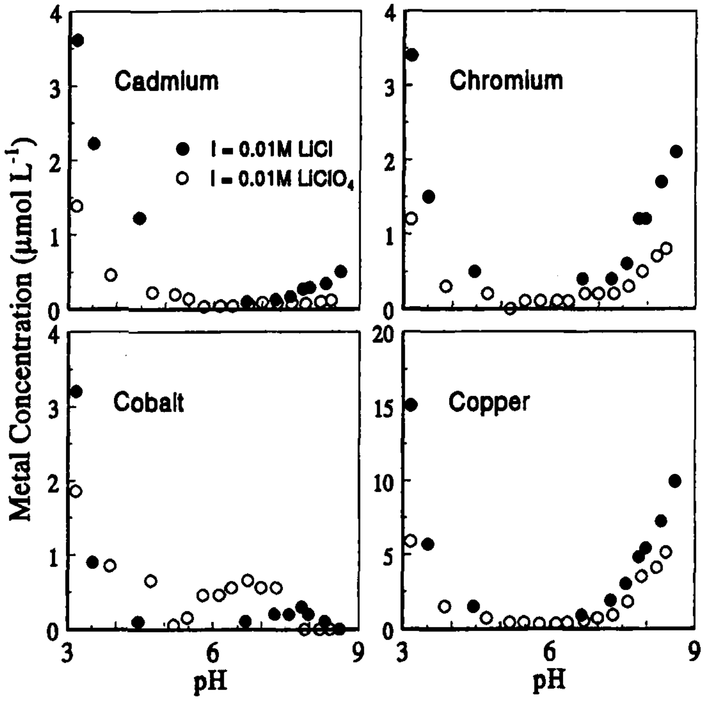

Figure 4 Concentrations of soluble Cd, Cr, Co and Co in a sewage sludge amended soil as a function of pH and different electrolyte.

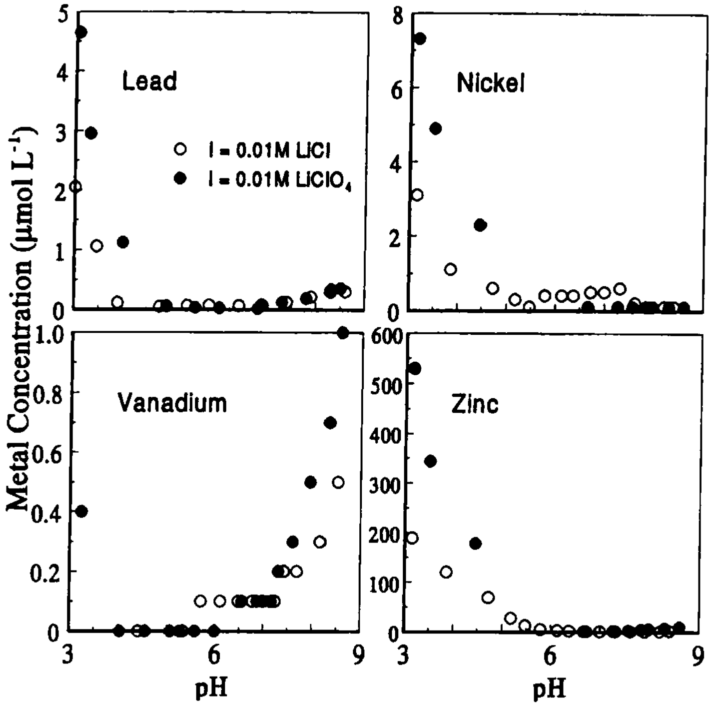

Figure 5 Concentrations of soluble Ni, Pb, V and Zn in a sewage sludge amended soil as a function of pH and different electrolyte.

added to soils as constituents of sewage sludge. Although current guidelines for the application of sewage sludge to agricultural land emphasize the metal content of the sludge and the soil, in addition to soil pH, other soil properties are known to influence the retention and mobility of toxic elements. These properties include the amount and nature of the clay fraction; the content of variable charge minerals, such as goethite and ferrihydrite; and the content and nature of the organic fraction.

An evaluation, and possible revisions, to current guidelines are probably needed due to our increased understanding of the behaviour of toxic elements in sewage sludge amended soils. In addition, there is very little emphasis in the current guidelines to soil management practices that might result in changes to soil pH or their contents of Cl$^-$ ions after the application of sludges.

Results from this study will therefore be of value in providing information on the soil chemistry of toxic elements to aid in the development of useful, and scientifically sound, guidelines for the application of industrial and municipal wastes onto land. The results should also aid in the development of strategies for the remediation of contaminated soils.

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