Metal Retention and Mobility as Influenced by Some Organic Residues Added to Soils: A Case Study

Luis Madrid

INTRODUCTION

This chapter provides a review of the present knowledge of how retention and mobility of metals in soils and other environmental systems are influenced by organic substances, especially those present in residues added to soils for recycling purposes, and is further illustrated with examples of recent research carried out with an agricultural residue which represents a major concern in Mediterranean countries.

Soil as a Sink for Trace Metals

As Domergue and Védy (1992) say, "mobility is a concept frequently used in soil science to estimate the risk of contamination of other environmental compartments by toxins, and especially by heavy metals." However, the definition of mobility depends to a large extent on the scientific field where it is used. In the following text, we shall use this term in the context of the dissolved metal forms in opposition to those bound to solid phases, as the former are likely to be those responsible for immediate environmental risks. Nevertheless, it must be kept in mind that long distance transport of heavy metals occurs largely as part of fine solid particles of earth materials, causing a slow buildup of soil pollution (Tiller, 1989).

Soils receive trace metals from various sources, mostly from lithogenic origin, i.e., from the parent material, or from anthropogenic origin; e.g., present in fertilizers, as part of wastes (industrial, agricultural, or otherwise), irrigation waters, etc. (Singh and Steinnes, 1994). When metals enter the soils, they undergo a number of reactions, namely dissolution/precipitation, adsorption/desorption, complexation, inclusion in minerals through formation of solid solutions (Alloway, 1990), which determine their "final" distribution in various chemical forms in the soil with very different solubilities. This final

distribution is frequently described in terms of several fractions, operationally defined according to a sequential extraction technique. Although different fractionation techniques have been proposed, most of them distribute the soil metals in fractions called "soluble," "exchangeable," "bound to carbonates," "bound to iron/manganese oxides," "bound to organic matter," or similar names, and that part of the metal content which cannot be extracted but by strong concentrated acids is called "residual." Although these names refer to a given chemical nature, in fact the fractions cannot usually be identified with a definite group of chemical compounds. In the past, the term "speciation" was used for the process of distinguishing different species of an element, and such species could be defined either operationally (by the procedure or extractant used) or functionally (bioavailable, exchangeable, etc.). Nowadays, the term "speciation" is preferred to be applied to the distinction of specific chemical forms of an element (Ure et al., 1993). Figure 10.1 is an example of the fractionation of some metals in Polish soils, where the solubility or availability of each fraction increases from bottom to top (data from Kabata-Pendias, 1995). Regardless of how the fractions are called, those fractions that are more easily released usually account for a minor proportion of the metal content. Therefore, as a consequence of the set of reactions mentioned above, soil acts as a geochemical sink for metals and controls their transport to other media (Kabata-Pendias, 1995), so that their persistence in soils is high: while the residence time of easily leachable elements like Ca, Mg, etc., is usually below 300 years, for many heavy metals residence times of several millennia have been reported (Bowen, 1979). Consequently, the budgets for some trace metals in soils are positive in many cases. Table 10.1 gives some examples for European soils (from Kabata-Pendias, 1995). Only in the case of some acid forest soils, losses of Mn or Zn are found.

Summarizing, metals tend to accumulate in soils, either by long-distance transport of fine solid particles or by immobilization of the soluble forms, so that a sort of "chemical time bomb" is building up. The environmental risk of such a chemical time bomb depends on whether various chemical "fuses" may cause a more or less sudden increase in solubility, passing to ground or surface waters, or becoming available to plants.

Modeling Approaches for Retention of Metals by Soils

The use of mathematical models for a quantitative description of the various reactions involved in a given process is a common practice in the study of environmental problems (Basset and Melchior, 1990). Various models have been specifically developed for understanding surface reactions involving metals or other ionic species. Some of them, which can be illustrated by those used by Davis and Leckie (1978) and by Barrow et al. (1981), assume some "mechanistic" characteristics of the retention process, e.g., pairwise association between adsorbing ions and oppositely charged surface groups, or location of adsorbing ions in planes of a given value of the electric potential. In both models, a number of parameters that usually cannot be estimated by independent experiments have to be adjusted by some iterative procedure.

Another group of models (Amacher et al., 1986) do not assume any particular mechanism for the retention reaction. Some of them use simple equations to describe equilibrium situations, e.g., one- or two-surface Langmuir equation, Freundlich equation, etc. Others try to describe the time dependence of the solution concentration of the sorbing
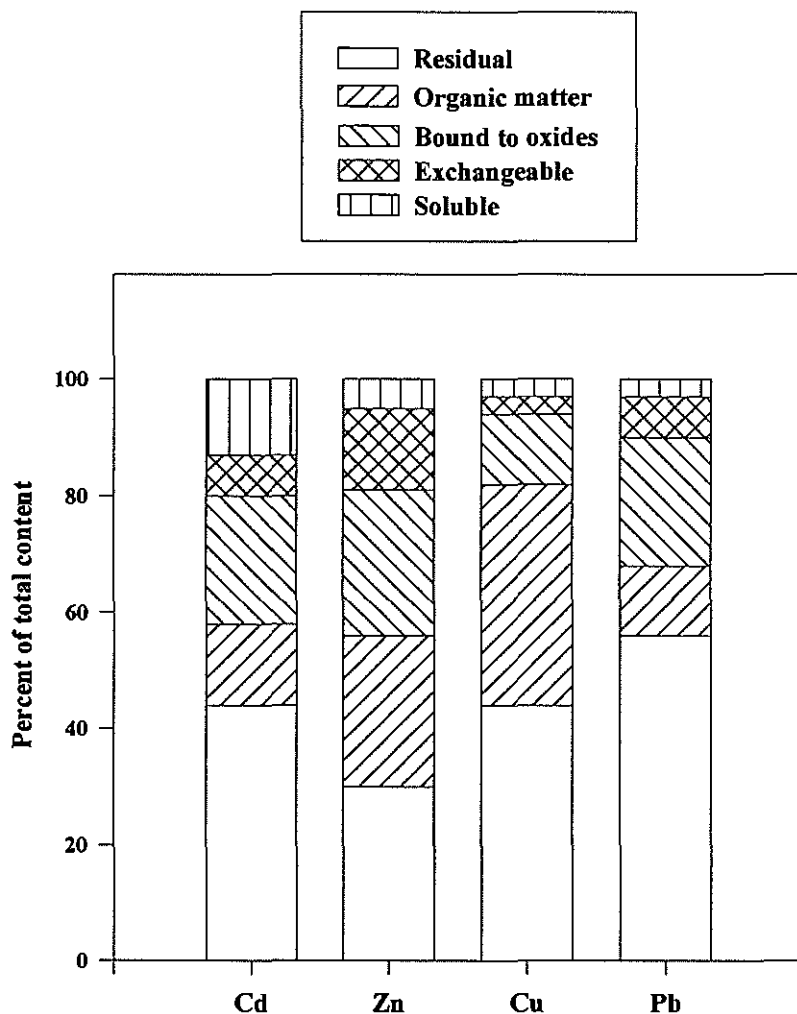
Figure 10.1. Example of fractionation of some metals in soils (from Kabata-Pendias, 1995, with permission).

Table 10.1. Metal Budgets of Surface Soils in Europe (g ha⁻¹ yr⁻¹)[a]

Ecosystem (Method)	Country	Cd	Cu	Mn	Pb	Zn
Pine forest (seepage water)	W. Germany	3	10	−360	104	134
Spruce forest (lysimeter)	Sweden	−1	5	−600	75	−130
Farmland (drainage water)	Denmark	3	—	—	260	130
Farmland (seepage water)	Poland	2	14	90	160	360

[a] From Kabata-Pendias, A., in *Heavy Metals, Problems and Solutions*, W. Salomons, U. Förstner, and P. Mader, Eds., Springer-Verlag, Berlin, 1995, pp. 3–18, with permission.

species, assuming reversibility or irreversibility and a given reaction order. In general, these models are too simple and are not likely to represent the experimental data of retention of metals by soils satisfactorily, probably because such retention is due to many

different reactions, as mentioned above. That is why models considering the contribution of various simultaneous, concurrent reactions are probably more realistic. In an exhaustive review, Selim (1992) described a number of multireaction kinetic models, empirical in nature, based on the assumption that a fraction of the total sites are highly kinetic, and the remaining sites interact slowly, irreversibly, or instantaneously with the adsorbing species. Some models include concurrent and concurrent-consecutive processes. Many metal retention processes are well described by this kind of model (Selim et al., 1990).

METAL CONCENTRATIONS IN THE SOIL SOLUTION

The various metal retention processes that may occur in soils cause the solution concentration of many metals to be generally below the values corresponding to the solubility of pure components. A detailed description of the reactions controlling heavy metal solubility can be found elsewhere (McBride, 1989). The occurrence of coprecipitation of metals with the major metal oxides from soil solutions is accepted, but the nature of the precipitate is not well defined. It can be easily shown (Driessens, 1986) that the solubility of a metal can be lowered in a mixed ionic compound relative to the solubility of the pure compound, and the activity of the metal compound is a function of its mole fraction. That means that when a metal is incorporated in an iron or aluminum oxide in trace proportions, the solution concentration of the former may be several orders of magnitude below that expected from the solubility of the trace metal compound *alone* (McBride, 1989).

Various observations suggest that metals retained by oxides are concentrated at solid surfaces (McBride, 1978), and little or no difference is found whether they are "coprecipitated" or adsorbed on preexisting oxide surfaces. Formation of surface solid solutions has been shown to be the cause for Cu adsorption by calcium carbonate (Papadopoulos and Rowell, 1989), and by soils rich in lime (Madrid and Diaz-Barrientos, 1992), and in both cases the resulting equilibrium concentrations are several orders of magnitude below that corresponding to the solubility of Cu carbonate. Figure 10.2 shows that, while Ca solutions in the presence of $CaCO_3$ produced equilibria located close to the solubility line of $CaCO_3$ in solubility diagrams, Cu solutions showed a definite tendency to be in equilibrium with $Cu(OH)_2$, considerably less soluble than the metal carbonate. Madrid and Diaz-Barrientos (1992) treated calcareous soils with acetate buffer at pH 5 to eliminate carbonates and equilibrated the original and treated soils with Cu solutions and subsequently with Cu-free solutions, and found that all the equilibria with the original samples corresponded with solubilities considerably below those of the oxide, hydroxide or basic carbonate, while the equilibria with treated soils were close to the line for CuO (Figure 10.3). Lindsay (1979) estimated that the solubility of Cu in soils could be described by an equilibrium:

$$\text{Soil-Cu} + 2H^+ \rightleftharpoons Cu^{2+}$$
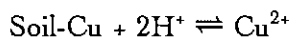
which causes a value of the ratio $Cu^{2+}/(H^+)^2$ of $10^{2.8}$, giving Cu^{2+} concentrations several orders of magnitude lower than those corresponding to the solubility of most Soil-Cu minerals. Lindsay (1979) considered it likely that "soil-Cu" could correspond to cupric ferrite, $CuFe_2O_4$, and suggested that the corresponding Zn compound, Zn-ferrite, could
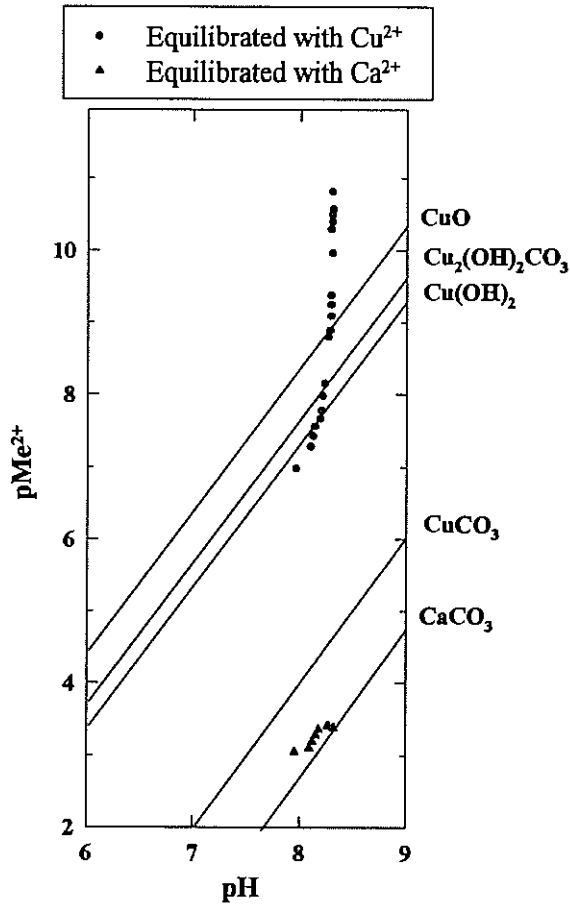
Figure 10.2. Solubility diagrams for Cu^{2+} or Ca^{2+} solutions equilibrated with A.R. $CaCO_3$ (from Papadopoulos and Rowell, 1989, with permission).

also account for the solubility of Zn in soils. However, other authors (Baker, 1990; McBride, 1989) believe that formation of mixed oxides similar to cupric ferrite is unlikely in the conditions found in soils. There is general consensus that adsorption on the various surfaces present in soils is the main process responsible for the low metal solution concentrations often found in many soils. Only in some cases with high metal loadings do some solid phases determine metal solubility; e.g., malachite in soils with very high Cu contents (McBride and Bouldin, 1984; Lund and Fobian, 1991).

FACTORS CAUSING A REVERSAL OF IMMOBILIZATION

Although, on a large scale, soils tend to immobilize trace metals, some conditions of the soil environment can undergo changes driving to a localized reversal of the process. Metals with different valences are frequently more soluble in their lower oxidation states, so that reductive conditions may cause a local increase in solubility, and a decrease in pH will also cause an enhanced solubilization of heavy metals. A decrease in pH also causes a decrease in negative electric charge of variable-charge surfaces, so that a decrease in
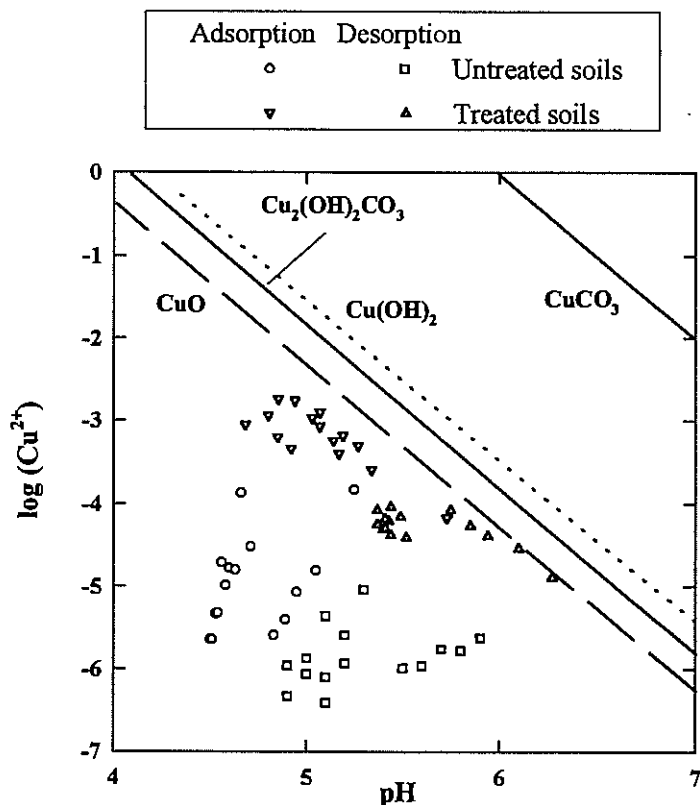
Figure 10.3. Solubility diagrams for adsorption and desorption equilibria of Cu with soils rich in lime, before and after being treated with acetate buffer at pH 5 (from Madrid and Díaz-Barrientos, 1992, with permission).

adsorption of cations also contributes to an increase in the presence of metals in solution (McBride, 1989). Such effects are usually localized and easily reversed when the cause disappears. An example of such reversible solubilizations can be found in the case of some rivers close to mining areas, which may show low pH values and high concentrations of several metals immediately downstream from the mining site, but a short distance further downstream the pH increases several units, metal concentrations decrease sharply and the bank sediments show high contents in metal compounds of low solubility (Arambarri et al., 1984).

The presence of organic compounds with functional groups with ability to form stable complexes with transition elements is another factor which may increase the solution concentration of heavy metals, and is a known fact since the end of the past century. In contrast with acidification or with reducing conditions, formation of soluble complexes may enhance the transport of metals in solution to long distances, due to the high stability frequently shown by such complexes. Frequently a high selectivity is found in the interaction of complexants with metals, as shown by Xue et al. (1995), who found that the concentration of free Cu^{2+} in a eutrophic lake was about 10^6 times lower than total Cu concentration, whereas a substantial part of Zn was present as free Zn ions and weak complexes.

The presence of a complexing agent in waters in contact with soils or sediments may actively desorb metals from the solids, or hinder the adsorption processes responsible for metal retention. This was shown to happen in the case of synthetic complexants added to waters: in a study of nitriloacetic acid (NTA) as a possible alternative to polyphosphate in detergents, it was found that the presence of NTA in waters resulted in a significant increase in solubility of metals in river sediments and a decrease in their metal-sorbing ability (Salomons and Förstner, 1984). Also, Davis and Singh (1995) found that when soil columns contaminated with Zn were leached with EDTA solutions, the metal retained was almost quantitatively removed. Recently, we have seen that Cu added to soil columns is strongly removed by glyphosate, a herbicide with zwitterion structure.

INTERACTION WITH NATURAL ORGANIC MATTER

The behavior of natural organic polymers as humic or fulvic acids is not as straightforward as that of simple complexants like NTA. Their action on heavy metals is twofold: on the one hand, soluble components of the humic substances can form complexes which will be responsible for an enhanced solubility of metals, and, on the other hand, fine solid particles of humic substances or organic coatings of minerals often contribute to the retention (and immobilization) of metals. In either case, the interaction with the metal ions occurs through various kinds of functional groups present in the organic polymers (Senesi, 1992), and whether the interaction results in metal mobilization or immobilization is strongly related with the size and solubility of the organics rather than with the functional groups involved. Fulvic acids play an important role in the transport of heavy metals in water, due to their lower molecular mass and much greater solubility as compared to humic acids (Förstner and Wittman, 1983, and references therein). The stability sequence of the complexes for some selected cations is considered to be (Klamberg et al., 1989)

$$Fe^{3+} > Al^{3+} > Cu^{2+} > Pb^{2+} > Fe^{2+} > Ni^{2+} > Cd^{2+} > Zn^{2+} > Mn^{2+}$$
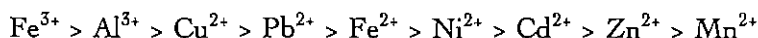
Therefore, organic matter/heavy metal interactions determine three broad, dynamically interrelated groups of species with different influence on the availability of the metals for the living organisms (Figure 10.4):

(a) Solid organic surfaces can retain metals, which are not immediately available to plants. From this point of view, metals retained in this way behave similarly to those retained by inorganic solid surfaces. However, some metals, e.g., cadmium, may show a preferential association with aqueous solution components as compared to solid surfaces (Neal and Sposito, 1986).

(b) Some components of the natural organic matter can eventually be dissolved and form metal complexes in solution, which in turn will be affected by adsorption/desorption equilibria with the solid surfaces. Monomeric organic molecules (e.g., released from plant roots) or large polymers can contribute to these equilibria. If such complexes are strong enough, usually the toxic effects of the metal are ameliorated, but it has been observed that some lipid-soluble complexes can rapidly penetrate a biomembrane, so that substances forming
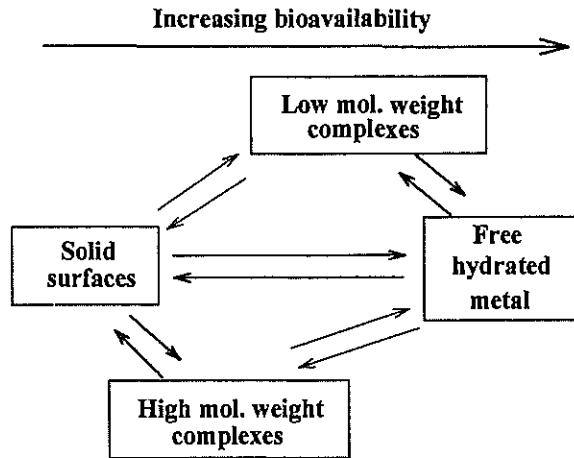
Increasing bioavailability

Figure 10.4. Schematic distribution of metal species from the point of view of their availability to biological systems.

this kind of complexes can cause an enhanced toxicity of the metal (Carlson-Ekvall and Morrison, 1995).

(c) The free or weakly complexed metal ions will usually be the most bioavailable species. Their concentration will be influenced by the various equilibria with complexing species in solution and by adsorption/desorption reactions on organic as well as inorganic solid surfaces.

Another important feature that distinguishes natural organic matter is the heterogeneity of its complexing sites. Figure 10.5 shows schematically the dependence of the cumulative distribution of complexing sites of fulvic acid upon their stability constants (based upon data of Buffle, 1988). Therefore, a single value for the stability constant cannot be defined, although different graphical approaches for estimating apparent or "average" constants have been proposed (Fitch and Stevenson, 1984). Another useful parameter in this context is the *complexation capacity*, defined as the maximum quantity of a given metal that can be bound per gram of the substance (Perdue, 1988). The amount and distribution of complexing sites of natural complexants have been estimated by various techniques, especially those able to distinguish free from complexed metals. The use of ion-selective electrodes (e.g., Buffle et al., 1977, 1980; Gamble et al., 1980; Stevenson and Chen, 1991; Stevenson et al., 1993) appeared to give reliable results in terms of applicability and sensitivity (Sterrit and Lester, 1984). Polarographic techniques have proved to give information of the lability of the complexes, and have been successfully applied to the characterization of metal complexes with humic and fulvic substances (Greter et al., 1979; Wilson et al., 1980; Filella et al., 1990; Pinheiro et al., 1994). Equilibration with ion exchangers has also been used for studying metal complexation with organic matter. The method proposed by Schubert (1948) could be used only for mononuclear complexes with respect to the metal ion, but Zunino et al. (1972a,b) proposed some changes in the equations involved that allowed them to be applied to complexes of the type $M_a(\text{ligand})_b$, where a and b are integers ≥ 1.
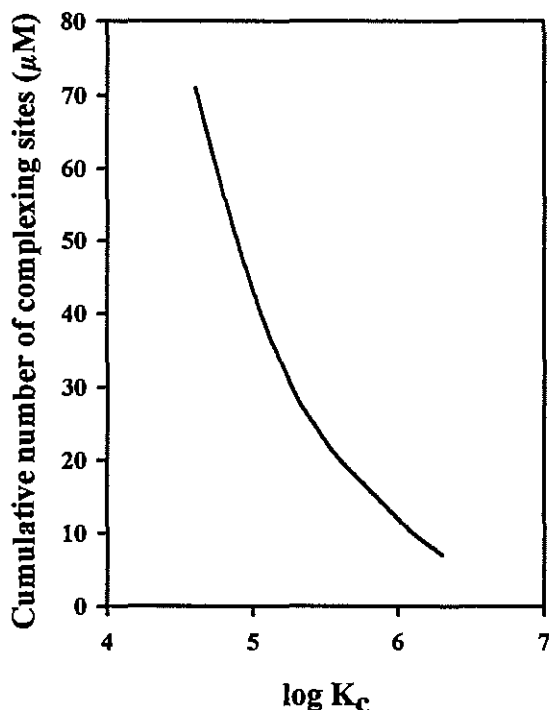
Figure 10.5. Example of cumulative distribution of metal complexing sites in a solution of fulvic acid as a function of their stability constants.

EFFECT OF ORGANIC RESIDUES ON METAL SOLUBILITY

Land application is a widely used practice for disposal of many organic wastes. They frequently contain substances which improve soil fertility, although other components can have undesirable consequences for crops, so that research on many different aspects of their addition to soils has increased in the last few years. One of the points that must be carefully considered when such wastes are added to soils is their possible effect on metal mobility or solubility: such organic residues are likely to contain polymers with not very different properties from those of natural humic or fulvic substances, and there-fore it can be expected that metal complexes similar to those known to form with the latter will also be formed with such residues. In soils receiving dairy cattle-manure slurry, Del Castilho et al. (1993) found significant increases in the concentrations of Cd, Zn, and Cu in soil solutions. In the case of Cu, its concentrations were correlated with the dissolved organic carbon, while Zn and Cd were also influenced by low pH and high levels of electric conductivity. They concluded that Cu complexes showed high stability, and a considerable part were of high molecular weight and nonlabile. Japenga et al. (1992) also studied the effect of the liquid fraction of animal manure on heavy metal solubilization in soil, and found a significant relationship between dissolved organic car-bon and Cu concentrations in aqueous extracts (Figure 10.6). They concluded that, to-gether with pH, complexation involving dissolved, high molecular weight organic matter is the most important driving force for heavy metal solubilization. Metal complexation was also considered to be one of the causes of metal leaching from a soil in a reed bed
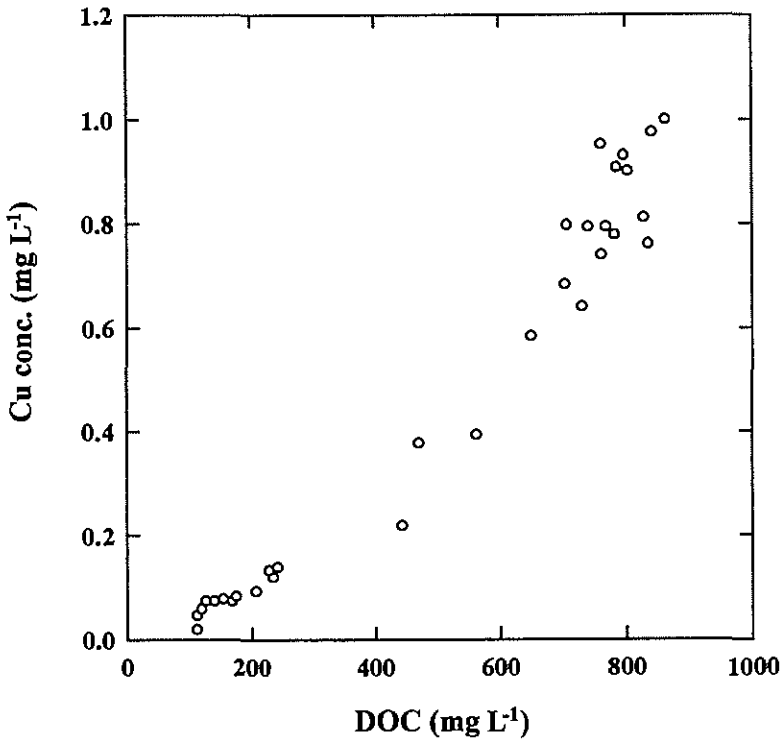
Figure 10.6. Relationship between dissolved organic carbon and Cu in aqueous extracts of a soil mixed with liquid animal manure (selected data from Japenga et al., 1992).

system continuously flooded with sewage (Wenzel et al., 1992). Barrado et al. (1995) also concluded that extracts from eucalyptus and oak leaf litter showed complexation ability for metals, and could estimate the complexing constants for various metals.

THE CASE OF SEWAGE SLUDGE

Addition of sewage sludge to soils was found to decrease the sorption of Cd at low concentrations of this metal (Neal and Sposito, 1986). In soils treated with sewage sludge and artificially contaminated with high doses of Cu in the form of Cu carbonate, Cheshire et al. (1994), using electron magnetic resonance, found evidence of Cu solubilization through complexation. The results for organically bound Cu in the soil solution indicate oxygen ligand coordination in equatorial arrangement. Keefer et al. (1994) also found significant metal-organic association in soils amended with sewage sludge, and McGrath and Cegarra (1992) observed large increases in the most soluble fractions of metals in a soil with long-term applications of sewage sludge. They found that the fractionation of metals in the original sewage sludge differed from that observed in the soil treated with the residue.

Frequently, sewage sludges have relatively high metal contents, so that their effect on metal mobility in soils has been often attributed to the metals present in the residue itself: Sposito et al. (1982) concluded that the accumulation of metals in soils amended with sewage sludge was governed by the metal content in the sludge, and Cavallaro et al.

Table 10.2. Examples of Maximum Permissible Concentrations of Some Metals in Soil after Application of Sewage Sludge (mg kg^{-1})

Soil pH	Country	Cd	Cu	Ni	Pb	Zn
5.0–5.5	UK[a]	—	80	50	—	200
5.5–6.0	UK[a]	—	100	60	—	250
6.0–7.0	UK[a]	—	135	75	—	300
> 7.0	UK[a]	—	200	110	—	450
> 5.0	UK[a]	3	—	—	300	—
< 7.0	Spain[b]	1	50	30	50	150
> 7.0	Spain[b]	3	210	112	300	450

[a] Data selected from Department of the Environment, *Code of Practice for Agricultural Use of Sewage Sludge*, HMSO Publications, London, 1992, p. 6.
[b] Data selected from *Boletin Oficial del Estado*, No. 262, Madrid, 1990, p. 3234.

(1993) found that increases in Mehlich-3 extractable Cu and Zn in soils treated with sewage sludge were similar to the amounts of these metals added in the residue. Most countries have established regulations concerning the use of sewage sludge on the basis of the maximum permissible contents of potentially toxic elements in soil after application of sewage sludge (Table 10.2) and annual rate of addition of such toxic elements, so that no legal limit exists if the sewage sludge added to a soil shows a low content in toxic metals. It is thus forgotten that solubilization of the metals already present in the soil can be enhanced by complexation, as shown by some of the authors quoted in the previous paragraph. This lack of attention paid to the effect of soil management practices, especially the use of sewage sludge, on the solubility of the metals present in amounts below the legal limits in the soil has been claimed by several authors (McBride, 1994; Evans et al., 1995), and has been favored by the conclusions of some authors, who even found a decrease in metal mobility in some cases (Emmerich et al., 1982; Saviozzi et al., 1983; Hooda and Alloway, 1994).

A MEDITERRANEAN CONCERN: OLIVE MILL WASTEWATER

Setting Up the Problem

In areas with extensive production of olive oil, disposing of the residues from manufacturing plants for this agricultural product represent a major concern. The traditional procedure implies generating large amounts of wastewater (called *alpechin*, from now on OMW) with extremely high BOD and other undesirable properties which have caused the existence of regulations prohibiting its disposal in rivers since 1981. Every year, about 10 million tons of this waste have to be disposed of in the Mediterranean countries, mainly by storing them in evaporation ponds, composting the resulting sludge with other plant refuse or, in countries where the production of this residue is not especially high, discharging them into watercourses. In recent years, olive oil production plants are being adapted for new techniques using much smaller volumes of water, so that production of OMW is decreasing sharply, but its disposal must still be considered until total substitution of the old manufacturing plants, and the existence of small factories which cannot afford the changes cannot be forgotten, at least during several years in the near future.

While the effect of sewage sludge on heavy metal availability has been extensively studied, as summarized in the previous section, literature on the relationships between heavy metals and OMW is scarce, although in the last few years some authors have found evidence of significant metal solubilizing effects of this residue, both when added to soils and when present in freshwaters. OMW is a slightly acid (pH 4–5), dark-colored aqueous phase with highly variable composition, containing 10–15% organic matter and 1–2% of mineral salts. Its contents in heavy metals is usually negligible, except Fe (10–20 mg L^{-1}), Mn (< 5 mg L^{-1}), and Zn (< 2 mg L^{-1}). Several authors have given detailed descriptions of the composition of this waste (e.g., Gonzalez-Vila et al., 1992; Martinez-Nieto and Garrido-Hoyos, 1994).

Effect of OMW on Metal Retention Properties of Soils

As with other organic wastes, one of the first ideas that emerge when recycling OMW is considered is its application to soils as fertilizer, and it has been frequently used to irrigate olive trees. Considering previous knowledge of the nature of this residue, Saiz-Jiménez et al. (1987) deemed it of interest to carry out a detailed study of its chemical composition in order to evaluate its potential value as soil fertilizer. They concluded that the composition of the humic fraction was different from soil humic acids, but still suggested that the residue had good properties as fertilizer. On a relatively short-term basis, applications of a composted olive mill sludge to soils have been found to cause no harmful effects on plants, the improvement of soil physical properties is apparent, and significant increases are found in soil organic N. Also, increases in available Cu, Zn, Mn, and Fe determined by DTPA extraction have been observed (Martín-Olmedo et al., 1995). In a study specifically oriented toward the effect of OMW on metal availability, Pérez and Gallardo-Lara (1993) found that although OMW initially caused a slight decrease in Zn availability and hardly any effect on Cu availability, a significant residual increase in Cu availability was observed after growing barley and ryegrass.

A fundamental aspect that must be considered is whether the presence of OMW affects the action of soils as a sink of heavy metals which are added in soluble forms. Madrid and Díaz-Barrientos (1994) chose three soils (called A, B, and C) with widely differing contents in organic matter, carbonate, and clay fraction and CECs for that purpose. Soil A had been manured in the field with 150,000 kg ha^{-1} of a compost obtained from OMW and other plant refuse, and soil B had received a similar dose of raw OMW. Soil C was untreated. Moreover, samples of the three soils were aged in vitro with freeze-dried OMW in a proportion corresponding to twice the dose received by soils A and B in the field. The reaction of several metals with the original, manured, and aged samples was studied. Figure 10.7 shows the results for the adsorption isotherms obtained for Cu and Zn.

The adsorption of these two metals was strongly decreased by mixing and aging the soils with OMW, while manuring with OMW or compost obtained from it only caused a significant decrease in the case of Zn. Manuring even caused a slight increase in Cu adsorption by soil A. The pH values of the adsorption experiments did not show differences large enough to explain the differences in adsorption. The authors suggested that the decrease in adsorption when OMW was added in large doses could be the result of coating the sorbing surfaces with organic matter. However, in the samples containing
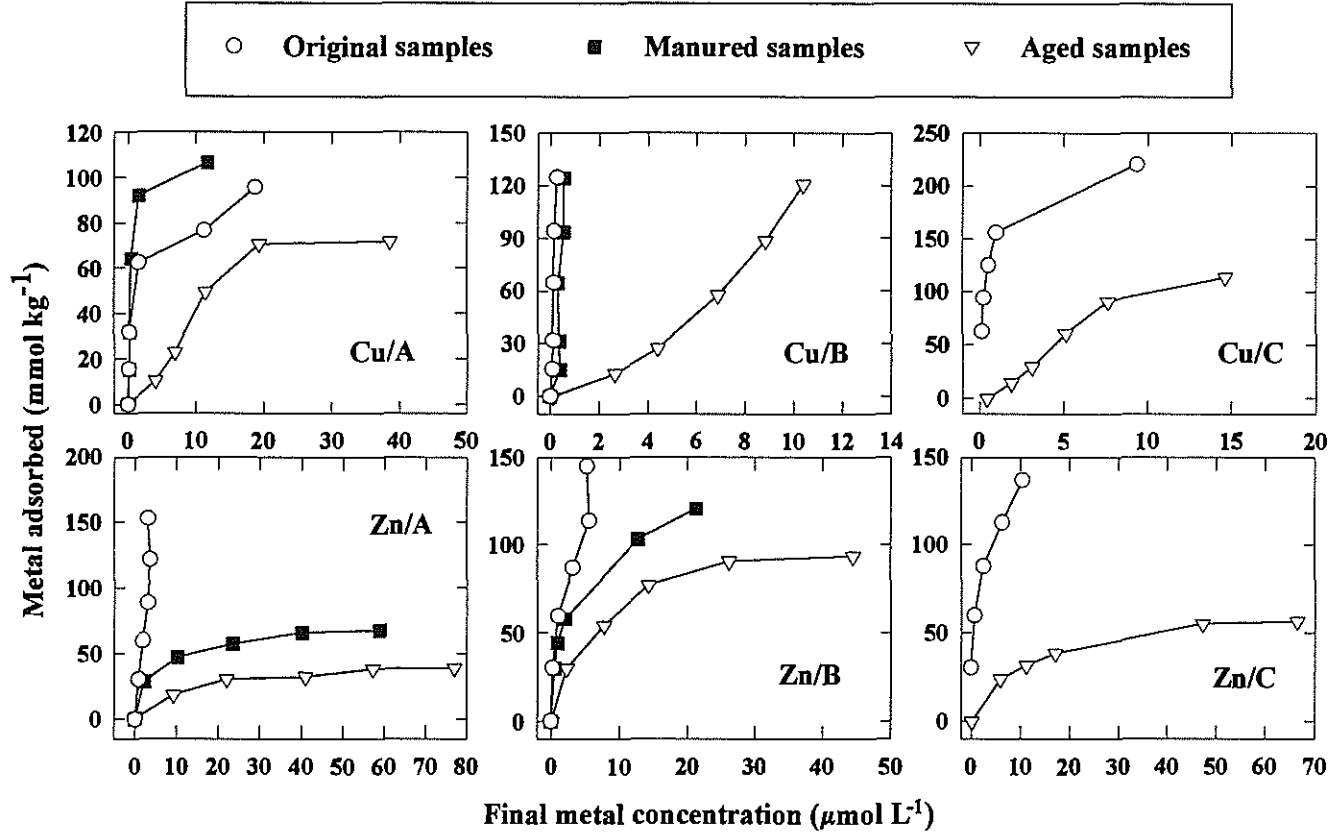
Figure 10.7. Adsorption isotherms of Cu and Zn by three soils (A, B, and C), before and after different treatments: Soils A and B were manured with composted and raw OMW, respectively, and the three soils were aged in vitro with a high dose of freeze-dried OMW (from Madrid and Díaz-Barrientos, 1994, with permission).

OMW some oversaturation was found in Cu experiments with two of the soils, both in the adsorption and the desorption steps, with respect to the Cu compounds likely to form. This result suggests that formation of soluble complexes could also contribute to the decrease in adsorption of this metal.

Selim et al. (1990) considered the adsorption reactions caused by several kinds of surfaces, with different kinetic characteristics. Madrid and Díaz-Barrientos (1996) examined whether the effect of OMW on the metal-sorbing properties of soils manifested itself when the multireaction model (MRM) of Selim et al. (1990) was applied to kinetic data of Cu adsorption by two soils which had received OMW compost. The MRM model distinguished several fractions in the amount sorbed: s_e, that reacts "instantaneously" with the sorbate in solution, described by a Freundlich equation with a distribution coefficient K_d and exponent b (Equation 1); s_1 and s_2, which react kinetically and reversibly with the solution at different rate, described by the forward and backward rate coefficients k_1 and k_2 for s_1 and k_3 and k_4 for s_2, and reaction orders n and m respectively (Equations 2 and 3); and finally s_{irr}, which reacts kinetically and irreversibly with the solution by a first order reaction, described by a rate coefficient k_s (Equation 4). The original model considered that some of the fractions could undergo other consecutive reactions, generating further fractions, but Madrid and Díaz-Barrientos (1996) found out that this latter assumption did not increase the percentage of variance explained when the model was applied to their data. The mathematical structure of the model as used by Madrid and Diaz-Barrientos (1996) is summarized below, where ρ and θ represent the bulk density and water content of the soil in the experiments.

$$s_e = K_d \, c^b \tag{1}$$

$$\rho(\partial s_1/\partial t) = \Theta k_1 c^n - \rho k_2 s_1 \tag{2}$$

$$\rho(\partial s_2/\partial t) = \Theta k_3 c^m - \rho k_4 s_2 \tag{3}$$

$$\rho(\partial s_{irr}/\partial t) = \Theta k_s c \tag{4}$$

Table 10.3 shows the parameters estimated by Madrid and Díaz-Barrientos (1996) for their original samples and those treated with OMW compost. It can be observed that addition of OMW to the soils causes significant changes on some of the parameters: the instantaneous distribution coefficient K_d is strongly increased by a factor of 50 in both soils; the irreversible fraction s_{irr} becomes irrelevant, and the rate coefficients of the kinetic fraction s_1 are significantly decreased. s_2 does not show any significant effect. Madrid and Díaz-Barrientos (1996) concluded that the Cu-immobilizing action of the soils was altered by the presence of composted OMW, probably by the presence of new solid, organic surfaces, which react instantaneously with the metal in solution. The dependence of the instantaneous fraction upon the solution concentration of Cu means that the metal adsorbed by the soil with OMW must easily come into solution if its concentration decreases, in contrast with the behavior of the untreated soils, which hardly release Cu by dilution. The disappearance of fraction s_{irr} also means a decrease in the immobilization of the metal.

Table 10.3. Average Values of the Model Parameters. k_1 to k_4 and k_5, h^{-1}; b, n and m, dimensionless; K_d, mg kg^{-1} [a]

Soil	Parameters of Each Fraction of the Model									
	s_e		s_1				s_2		s_{irr}	
	K_d	b	k_1	k_2	n	k_3	k_4	m	k_5	R^2
A orig.	9	0.4	24.5	2.79	0.3	0.33	0.13	0.7	0.04	0.998
A comp.	440	0.4	1.82	0.79	0.4	0.50	0.04	0.5	0	0.997
C orig.	18	0.4	28.4	1.15	0.4	0.61	0.08	0.7	0.15	0.995
C comp.	925	0.9	9.7	0.45	0.4	0.77	0.05	0.4	0	0.994

[a] From Madrid, L. and E. Díaz-Barrientos, *Toxicol. Environ. Chem.* 54, pp. 93–98, 1996, with permission.

OMW in the Aqueous Phase as a Mobilizing Agent of Insoluble Metal Forms

Although discharges of OMW in watercourses is prohibited, its accumulation in ponds may cause a slow migration of its soluble components to groundwaters. Moreover, accidental releases of significant amounts into rivers do occur. Thus, another important point that must be considered is the solubilization of metals in "immobile" forms when in contact with water containing OMW. Bejarano and Madrid (1992, 1996a) studied the solubilization of heavy metals from river sediments, with high metal contents due to their location close to mining sites, when treated in vitro with dilute solutions of OMW. These solutions were prepared from freeze-dried OMW and adjusted at pH values between 3 and 5, considering the slightly acid pH of the residue. They found that some metals, e.g., Mn or Zn, were not solubilized by the residue, and in the case of Mn the sediment even retained part of the metal originally present in the OMW. On the contrary, Cu, Fe, and Pb from the sediments were solubilized when in contact with OMW solutions. The presence of OMW favored Pb solubilization at any pH, while Cu and Fe were dissolved to a greater extent than in the absence of OMW only at the higher pH tested. Considering that the solubility of these metals usually increases at lower pH values, this result suggests that the solubilization of these two metals can be related with the formation of soluble complexes with OMW components. Figure 10.8 shows a summary of the results obtained by the authors for Pb and Cu. In the second paper mentioned (Bejarano and Madrid, 1996a) the authors showed that the amounts solubilized by OMW were comparable with the metals originally present in the sediments in forms bound to carbonates and to oxides, according to a conventional fractionation technique.

The hypothesis of complexation by OMW components had been previously checked by Cabrera et al. (1986). Using the cation-exchange resin method of Zunino et al. (1972b), they found that the freeze-dried residue showed a complexing ability of 0.66 mmol of Cu per gram of OMW. Bejarano and Madrid (1996b) studied the time-dependence of the release of several metals by solutions with three different OMW concentrations from a river sediment, and the resulting solutions were filtered through C-18 reverse-phase cartridges. The metals complexed by polymers present in the OMW, especially those forming less labile complexes, were supposed to be retained by the cartridges, together with the uncomplexed organic polymers. Previously they checked that no free metal was retained in the cartridges. Figure 10.9 summarizes the results for Cu, Mn, and Zn. The
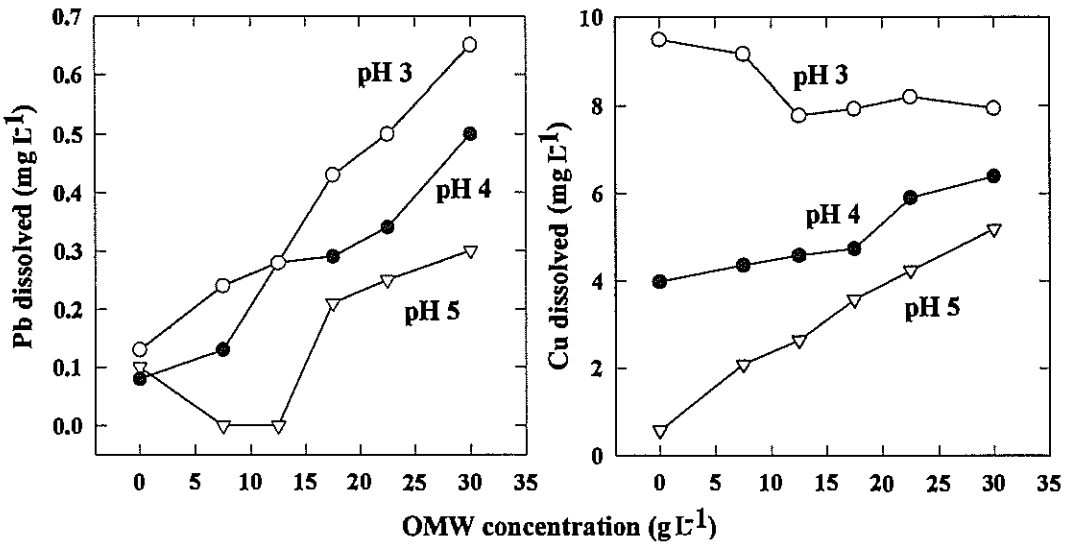
Figure 10.8. Pb and Cu dissolved from a river sediment by solutions of various OMW concentrations and pH values (from Bejarano and Madrid, 1992, with permission).

authors concluded that most of the Cu and Zn released into solution by the OMW was in complexed forms, as nearly 100% of both metals were retained by the cartridges. In the case of Mn, only about 50% of the metal dissolved by OMW was retained by the cartridges, suggesting that complexation was less complete or that the complexes formed were more labile.

Considering that some of the results commented on in this and the previous section suggest that some components of OMW do form complexes with several metals, Bejarano and Madrid (1996c) applied the techniques of Zunino et al. (1972a,b) to determining the complexation parameters of this residue for several metals. They found that the maximum complexing ability (MCA) was inversely related with the ionic radii of the metal ions, and a direct dependence between the logarithm of the conditional stability constants and the metal electronegativity (Figure 10.10). This latter result agrees with the fact that the stability of complexes formed by a given ligand with a series of metals is expected to increase with the electronegativity of the metals (Irving and Williams, 1948), thus showing indirectly that complexation by OMW does occur. The authors concluded that the "average" complex formed is mono-nuclear, with a bidentate bond for Cu^{2+}. For other larger M^{2+} ions, a progressive steric hindrance seems to exist.

This simple model of a mono-nuclear, bidentate complex between the "average" component of OMW and a metal ion was further developed elsewhere (Bejarano and Madrid, 1996d). The reaction was assumed to be
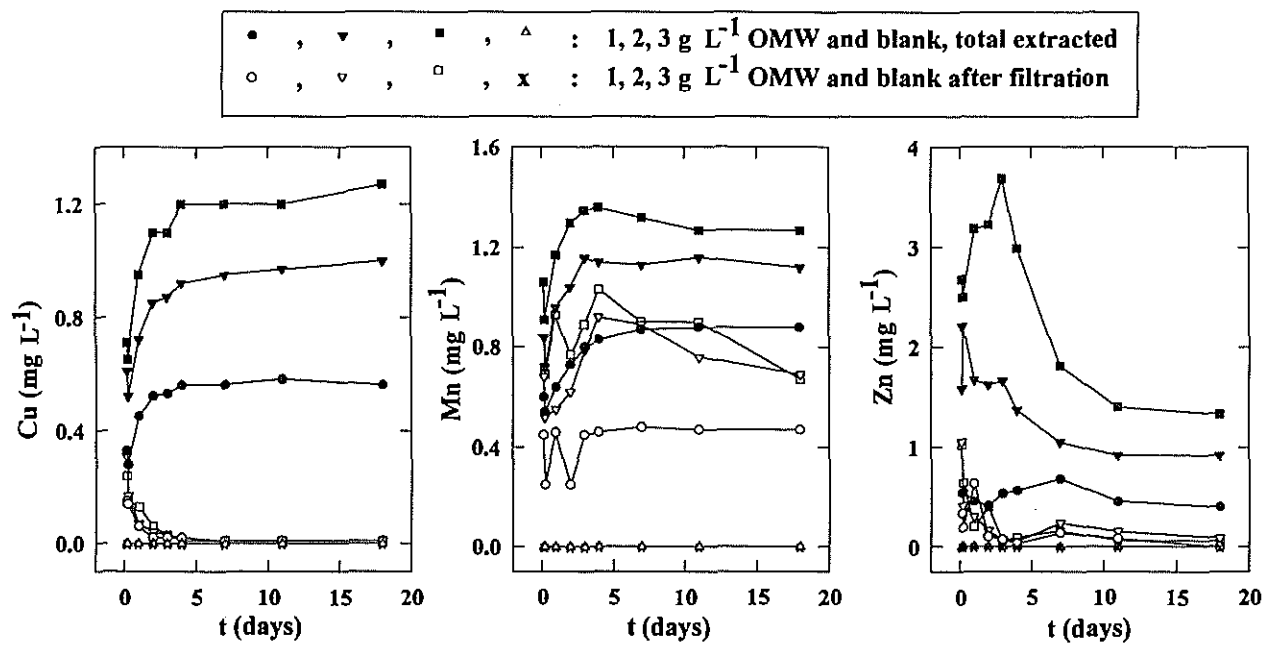
$$L^{2-} + M^{2+} \rightleftharpoons ML \qquad K_{ML} = \frac{[ML]}{[L^{2-}][M^{2+}]}$$
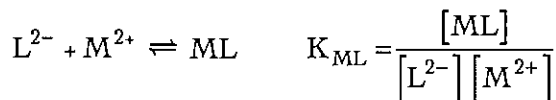
Figure 10.9. Time dependence of metals found in solutions of OMW in contact with a river sediment, and effect of filtering the solutions through C-18 reverse-phase cartridges (from Bejarano and Madrid, 1996, with permission).
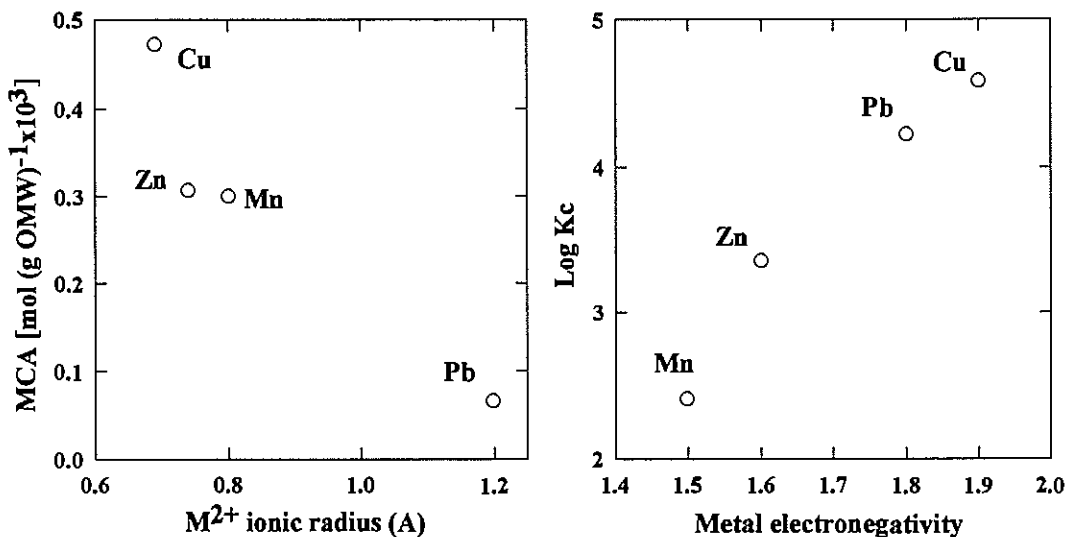
Figure 10.10. Relationship between maximum complexing ability of OMW and the radius of each metal ion, and dependence of the stability constant on the metal electronegativity (from Bejarano and Madrid, 1996, with permission).

A double acid dissociation was assumed for the organic ligand, defined by two acid dissociation constants. From Cu^{2+} and Zn^{2+} data of experiments similar to those mentioned above with reverse-phase cartridges, estimates of free metal concentration $[M^{2+}]$ and, by difference, of complexed metal $[ML]$ were obtained. Total ligand concentrations were considered to be those of the residue (in g L^{-1}). By an iterative, computer simplex method the authors obtained values for the conditional constant K_{ML} and the two acid dissociation constants. The graphs in Figure 10.11 show the experimental data and the corresponding calculated solution compositions. As can be seen, the model was a good approximation to the behavior of OMW as complexant. The values of the stability constants obtained by this model (Bejarano and Madrid, 1996d) and by a cation exchange resin (Bejarano and Madrid, 1996c) were reasonably congruent despite the different techniques and conditions, and agreed with that previously obtained for Cu^{2+} by Bejarano et al. (1994) using voltammetric techniques.

SUMMARY

During the last decades, the view of land as a sink for any waste has been ruled out as erroneous, and concern for the long-term environmental hazards of accumulation of wastes has gained increasing importance. In the preceding pages we have tried to show that, even though soils can "fix" large quantities of potentially toxic metals, acting as a barrier against metal pollution of ground and surface waters, organic matter, either natural or, especially, added to soils, is a very important factor able to change the status of the metals in the system. Whether such change is in the direction of increasing the fixation of metals or of mobilizing them depends on several circumstances, but many studies suggest that the presence of soluble organic matter generally increases metal mobility through formation of soluble complexes. Therefore, those processes for maturing organic wastes
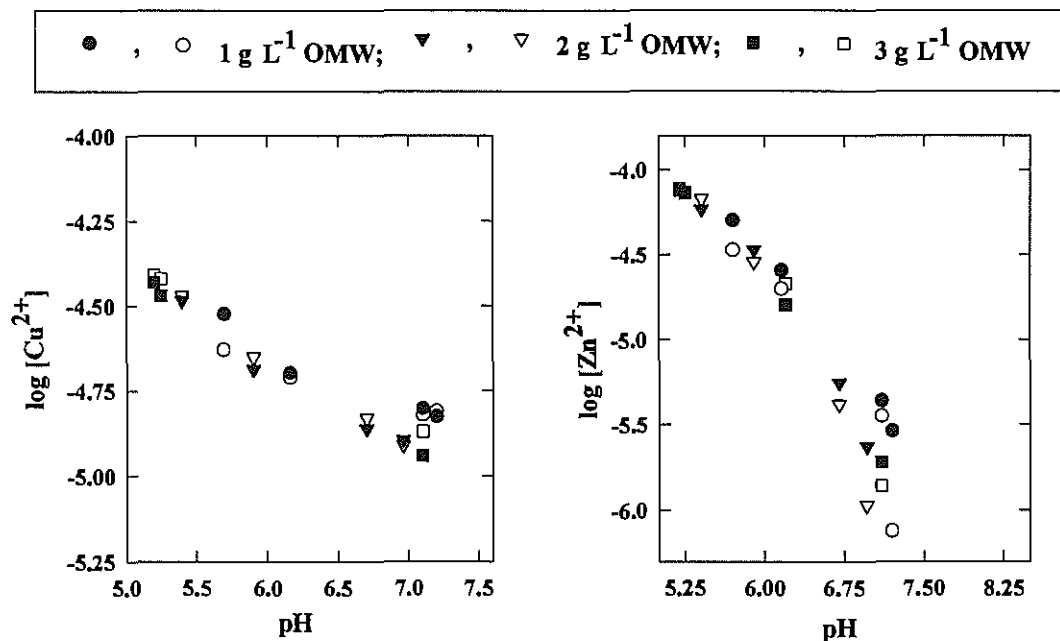
● , ○ 1 g L^{-1} OMW;   ▼ , ▽ 2 g L^{-1} OMW;   ■ , □ 3 g L^{-1} OMW

Figure 10.11. Comparison of the metal concentrations found in solutions of OMW equilibrated with a river sediment and subsequently filtered through C-18 reverse-phase cartridges (hollow symbols) and values calculated by a simple model of mono-nuclear bidentate complexation (filled symbols) (From Bejarano and Madrid, 1996, with permission).

previous to their use as soil amendments must be aimed, among other purposes, at minimizing the proportion of soluble components. Thus, the mobilizing action will also be minimized and the resulting highly polymerized, sparingly soluble organic wastes will contribute to immobilize metals and consequently will help to keep a low bioavailability of such potentially toxic elements.

REFERENCES

Alloway, B.J. Soil Processes and the Behaviour of Metals, in *Heavy Metals in Soils*, B.J. Alloway, Ed., Blackie and Son, Glasgow, 1990, pp. 261–279.

Amacher, M.C., J. Kotuby-Amacher, H.M. Selim, and I.K. Iskandar. Retention and release of metals by soils—Evaluation of several models. *Geoderma*, 38, pp. 131–154, 1986.

Arambarri, P., F. Cabrera, and C.G. Toca, *La Contaminación del Río Guadiamar y su Zona de Influencia, Marismas del Guadalquivir y Coto Doñana, por Residuos de Industrias Mineras y Agrícolas*. CSIC, Madrid, 1984.

Baker, D.E. Copper, in *Heavy Metals in Soils*, B.J. Alloway, Ed., Blackie and Son, Glasgow, 1990, pp. 151–176.

Barrado, E., M.H. Vela, R. Pardo, and F. Rey. Determination of acidity and metal ion complexing constants for eucalyptus and oak extracts. *Commun. Soil Sci. Plant Anal.*, 26, pp. 2067–2078, 1995.

Barrow, N.J., J.W. Bowden, A.M. Posner, and J.P. Quirk. Describing the adsorption of copper, zinc and lead on a variable charge mineral surface. *Austral. J. Soil Res.*, 19, pp. 309–321, 1981.

Basset, R.L. and D.C. Melchior, Chemical Modeling of Aqueous Systems: An Overview, in *Chemical Modeling of Aqueous Systems II*, D.C. Melchior and R.L. Basset, Eds., ACS Symposium Series No. 416, American Chemical Society, Washington, DC, 1990, pp. 1–14.

Bejarano, M. and L. Madrid. Solubilization of heavy metals from a river sediment by a residue from olive oil industry. *Environ. Technol.*, 13, pp. 979–985, 1992.

Bejarano, M. and L. Madrid. Solubilization of heavy metals from a river sediment by an olive mill effluent at different pH values. *Environ. Technol.*, 17, pp. 427–432, 1996a.

Bejarano, M. and L. Madrid. Release of heavy metals from a river sediment by a synthetic polymer and an agricultural residue: Variation with time of contact. *Toxicol. Environ. Chem.*, 55, pp. 95–102, 1996b.

Bejarano, M. and L. Madrid. Complexation parameters of heavy metals by olive mill wastewater determined by a cation exchange resin. *J. Environ. Sci. Health*, B31, pp. 1085–1101, 1996c.

Bejarano, M. and L. Madrid. Solubilization of Zn, Cu, Mn and Fe from a river sediment by olive mill wastewater: Influence of Cu or Zn. *Toxicol. Environ. Chem.*, 55, pp. 83–93, 1996d.

Bejarano, M., A.M. Mota, M.L.S. Gonçalves, and L. Madrid. Complexation of Pb(II) and Cu(II) with a residue from the olive-oil industry and a synthetic polymer by DPASV. *Sci. Total Environ.*, 158, pp. 9–19, 1994.

Boletín Oficial del Estado, Madrid, No. 262, p. 3234, 1990.

Bowen, H.J.M. *Environmental Chemistry of the Elements*. Academic Press, London, 1979, p. 333.

Buffle, J. *Complexation Reactions in Aquatic Systems: An Analytical Approach*. Ellis Horwood, Chichester, 1988, p. 33.

Buffle, J., F.-L. Greter, and W. Haerdi. Measurement of complexation properties of humic and fulvic acids in natural waters with lead and copper ion-selective electrodes. *Anal. Chem.*, 49, pp. 216–222, 1977.

Buffle, J., P. Deladoey, F.L. Greter, and W. Haerdi. Study of the complex formation of copper(II) by humic and fulvic substances. *Analytica Chimica Acta*, 116, pp. 255–274, 1980.

Cabrera, F., M. Soldevilla, F. Osta, and P. Arambarri. Interacción de Cobre y Alpechines. *Limnética*, 2, pp. 311–316, 1986.

Carlson-Ekvall, C.E.A. and G.M. Morrison. Toxicity of copper in the presence of organic substances in sewage sludge. *Environ. Technol.*, 16, pp. 243–251, 1995.

Cavallaro, N., N. Padilla, and J. Villarrubia. Sewage sludge effects on chemical properties of acid soils. *Soil Sci.*, 156, pp. 63–70, 1993.

Cheshire, M.V., D.B. McPhail, and M.L. Berrow. Organic matter-copper complexes in soils treated with sewage sludge. *Sci. Total Environ.*, 152, pp. 63–72, 1994.

Davis, A.P. and I. Singh. Washing of zinc(II) from contaminated soil column. *J. Environ. Eng.*, 121, pp. 174–185, 1995.

Davis, J.A. and J.O. Leckie. Surface ionization and complexation at the oxide/water interface. 2. Surface properties of amorphous iron oxyhydroxide and adsorption of metal ions. *J. Colloid Interface Sci.*, 67, pp. 90–107, 1978.

Del Castilho, P., W.J. Chardon, and W. Salomons. Influence of cattle-manure slurry application on the solubility of cadmium, copper, and zinc in a manured acidic, loamy-sand soil. *J. Environ. Qual.*, 22, pp. 689–697, 1993.

Department of the Environment, *Code of Practice for Agricultural Use of Sewage Sludge*. HMSO Publications, London, 1992, p. 6.

Domergue, F.-L. and J.-C. Védy. Mobility of heavy metals in soil profiles. *Int. J. Environ. Anal. Chem.*, 46, pp. 13–23, 1992.

Driessens, F.C.M. Ionic Solid Solutions in Contact with Aqueous Solutions, in *Geochemical Processes at Mineral Surfaces*, J.A. Davis and K.F. Hayes, Eds., ACS Symposium Series No. 323, American Chemical Society, Washington, DC, 1986, pp. 524–560.

Emmerich, W.E., L.J. Lund, A.L. Page, and A.C. Chang. Solid phase forms of heavy metals in sewage sludge-treated soils. *J. Environ. Qual.*, 11, pp. 178–181, 1982.

Evans, L.J., G.A. Spiers, and G. Zhao. Chemical aspects of heavy metal solubility with reference to sewage sludge amended soils. *Int. J. Environ. Anal. Chem.*, 59, pp. 291–302, 1995.

Filella, M., J. Buffle, and H.P. van Leeuwen. Effect of physico-chemical heterogeneity of natural complexants. Part I. Voltammetry of labile metal-fulvic complexes. *Analytica Chimica Acta*, 232, pp. 209–223, 1990.

Fitch, A. and F.J. Stevenson. Comparison of models for determining stability constants of metal complexes with humic substances. *Soil Sci. Soc. Am. J.*, 48, pp. 1044–1050, 1984.

Förstner, U. and G.T.W. Wittman. *Metal Pollution in the Aquatic Environment*, 2nd ed., Springer-Verlag, Berlin, 1983, p. 223.

Gamble, D.S., A.W. Underdown, and C.H. Langford. Copper(II) titration of fulvic acid ligand sites with theoretical, potentiometric, and spectrophotometric analysis. *Anal. Chem.*, 52, pp. 1901–1908, 1980.

Gonzalez-Vila, F.J., T. Verdejo, and F. Martin. Characterization of wastes from olive and sugarbeet processing industries and effects of their application upon the organic fraction of agricultural soils. *Int. J. Environ. Anal. Chem.*, 46, pp. 213–222, 1992.

Greter, F.-L., J. Buffle, and W. Haerdi. Voltammetric study of humic and fulvic substances. Part I. Study of the factors influencing the measurement of their complexing properties with lead. *J. Electroanal. Chem.*, 101, pp. 211–229, 1979.

Hooda, P.S. and B.J. Alloway. Sorption of Cd and Pb by selected temperate and semi-arid soils: Effects of sludge application and aging of sludged soils. *Water Air Soil Pollut.*, 74, pp. 235–250, 1994.

Irving, H. and R.J.P. Williams. Order of stability of metal complexes. *Nature*, 162, pp. 746–747, 1948.

Japenga, J., J.W. Dalenberg, D. Wiersma, S.D. Scheltens, D. Hesterberg, and W. Salomons. Effect of liquid animal manure application on the solubilization of heavy metals from soil. *Int. J. Environ. Anal. Chem.*, 46, pp. 25–39, 1992.

Kabata-Pendias, A. Agricultural Problems Related to Excessive Trace Metal Contents of Soils, in *Heavy Metals, Problems and Solutions*, W. Salomons, U. Förstner, and P. Mader, Eds., Springer-Verlag, Berlin, 1995, pp. 3–18.

Keefer, R.F., S.M. Mushiri, and R.N. Singh. Metal-organic associations in two extracts from nine soils amended with three sewage sludges. *Agric., Ecosyst. Environ.*, 50, pp. 151–163, 1994.

Klamberg, H., G. Matthess, and A. Pekdeger. Organo-Metal Complexes as Mobility-Determining Factors of Inorganic Toxic Elements in Porous Media, in *Inorganic Contaminants in the Vadose Zone*, B. Bar-Yosef, N.J. Barrow, and J. Goldshmid, Eds., Ecological Studies Series, Vol. 74, Springer-Verlag, Berlin, 1989, pp. 3–17.

Lindsay, W.L. *Chemical Equilibria in Soils*. John Wiley & Sons, New York, 1979, p. 222.

Lund, U. and A. Fobian. Pollution of two soils by arsenic, chromium and copper. *Geoderma*, 49, pp. 83–103, 1991.

Madrid, L. and E. Diaz-Barrientos. Influence of carbonate on the reaction of heavy metals in soils. *J. Soil Sci.*, 43, pp. 709–721, 1992.

Madrid, L. and E. Diaz-Barrientos. Retention of heavy metals by soils in the presence of a residue from the olive-oil industry. *Eur. J. Soil Sci.*, 45, pp. 71–77, 1994.

Madrid, L. and E. Diaz-Barrientos. Nature of the action of a compost from olive mill wastewater on Cu sorption by soils. *Toxicol. Environ. Chem.*, 54, pp. 93–98, 1996.

Martín-Olmedo, P., F. Cabrera, R. López, and J.M. Murillo. Successive applications of a composted olive oil mill sludge: Effect on some selected soil characteristics. *Fresenius Environ. Bull.*, 4, pp. 221–226, 1995.

Martínez-Nieto, L. and S.E. Garrido-Hoyos. El Alpechín, un Problema Medioambiental en Vias de Solución (I). *Química e Industria*, 17–28, November 1994.

McBride, M.B. Retention of Cu^{2+}, Ca^{2+}, Mg^{2+}, and Mn^{2+} by amorphous alumina. *Soil Sci. Society Am. J.*, 42, pp. 27–31, 1978.

McBride, M.B. Reactions controlling heavy metal solubility in soils. *Adv. Soil Sci.*, 10, pp. 1–56, 1989.

McBride, M.B. Toxic metal accumulation from agricultural use of sludge: Are USEPA regulations protective? *J. Environ. Qual.*, 24, pp. 5–18, 1994.

McBride, M.B. and D.R. Bouldin. Long-term reactions of copper(II) in a contaminated calcareous soil. *Soil Sci. Soc. Am. J.*, 48, pp. 56–59, 1984.

McGrath, S.P. and J. Cegarra. Chemical extractability of heavy metals during and after long-term applications of sewage sludge to soil. *J. Soil Sci.*, 43, pp. 313–321, 1992.

Neal, R.H. and G. Sposito. Effects of soluble organic matter and sewage sludge amendments on cadmium sorption by soils at low cadmium concentrations. *Soil Sci.*, 142, pp. 164–172, 1986.

Papadopoulos, P. and D.L. Rowell. The reactions of copper and zinc with calcium carbonate surfaces. *J. Soil Sci.*, 40, pp. 39–48, 1989.

Perdue, E.M. Measurements of Binding Site Concentrations in Humic Substances, in *Metal Speciation: Theory, Analysis and Application*, J.R. Kramer and H.E. Allen, Eds., Lewis Publishers, Boca Raton, FL, 1988, pp. 135–154.

Pérez, J.D. and F. Gallardo-Lara. Direct, delayed and residual effects of applied wastewater from olive processing on zinc and copper availability in the soil-plant system. *J. Environ. Sci. Health*, B28, pp. 305–324, 1993.

Pinheiro, J.P., A.M. Mota, and M.L. Simoes Gonçalves. Complexation study of humic acids with cadmium(II) and lead(II). *Analytica Chimica Acta*, 284, pp. 525–537, 1994.

Saiz-Jiménez, C., J.W. De Leeuw, and G. Gómez-Alarcón. Sludge from the waste water of the olive processing industry: A potential soil fertilizer? *Sci. Total Environ.*, 62, pp. 445–452, 1987.

Salomons, W. and U. Förstner. *Metals in the Hydrocycle*. Springer-Verlag, Berlin, 1984, pp. 176–179.

Saviozzi, A., R. Levi-Minzi, and R. Riffaldi. How organic matter sources affect cadmium movement in soil. *Biocycle*, pp. 29–31, May/June 1983.

Schubert, J. The use of ion exchangers for the determination of physical chemical properties of substances particularly radio tracers in solution. *J. Phys. Colloid Chem.*, 52, pp. 340–356, 1948.

Selim, H.M. Modeling the transport and retention of inorganics in soils. *Adv. Agron.*, 47, pp. 331–384, 1992.

Selim, H.M., M.C. Amacher, and I.K. Iskandar. *Modeling the Transport of Heavy Metals in Soils*. U.S. Army Corps of Engineers, CRREL Monograph 90-2, U.S. Government Printing Office, Washington, DC, 1990.

Senesi, N. Metal-Humic Substance Complexes in the Environment. Molecular and Mechanistic Aspects by Multiple Spectroscopic Approach, in *Biogeochemistry of Trace Metals*, D.C. Adriano, Ed., Springer-Verlag, New York, 1992, pp. 429–496.

Singh, B.R. and E. Steinnes. Soil and Water Contamination by Heavy Metals, in *Soil Processes and Water Quality*, R. Lal and B.A. Stewart, Eds., Advances in Soil Science Series, Lewis Publishers, Boca Raton, FL, 1994, pp. 233–271.

Sposito, G., L.J. Lund, and A.C. Chang. Trace metal chemistry in arid-zone field soils amended with sewage sludge: I. Fractionation of Ni, Cu, Zn, Cd, and Pb in solid phases. *Soil Sci. Soc. Am. J.*, 46, pp. 260–264, 1982.

Sterrit, R.M. and J.N. Lester. Comparison of methods for the determination of conditional stability constants of heavy metal-fulvic acid complexes. *Water Res.*, 18, pp. 1149–1153, 1984.

Stevenson, F.J. and Y. Chen. Stability constants of copper(II)-humate complexes determined by modified potentiometric titration. *Soil Sci. Soc. Am. J.*, 55, pp. 1586–1591, 1991.

Stevenson, F.J., A. Fitch, and M.S. Brar. Stability constants of Cu(II)-humate complexes: Comparison of select models. *Soil Sci.*, 155, pp. 77–91, 1993.

Tiller, K.G. Heavy metals in soils and their environmental significance. *Adv. Soil Sci.*, 9, pp. 113–142, 1989.

Ure, A.M., Ph. Quevauviller, H. Muntau, and B. Griepink. Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities. *Int. J. Environ. Anal. Chem.*, 51 (Special Issue), pp. 135–151, 1993.

Wenzel, W.W., M.A. Pollak, and W.E.H. Blum. Dynamics of heavy metals in soils of a reed bed system. *Int. J. Environ. Anal. Chem.*, 46, pp. 41–52, 1992.

Wilson, S.A., T.C. Huth, R.E. Arndt, and R.K. Skogerboe. Voltammetric methods for determination of metal binding by fulvic acid. *Anal. Chem.*, 52, pp. 1515–1518, 1980.

Xue, H.B., D. Kistler, and L. Sigg. Competition of copper and zinc for strong ligands in a eutrophic lake. *Limnol. Oceanogr.*, 40, pp. 1142–1152, 1995.

Zunino, H., G. Galindo, P. Peirano, and M. Aguilera. Use of the resin exchange method for the determination of stability constants of metal-soil organic matter complexes. *Soil Sci.*, 114, pp. 229–233, 1972a.

Zunino, H., P. Peirano, M. Aguilera, and I. Escobar. Determination of maximum complexing ability of water-soluble complexants. *Soil Sci.*, 114, pp. 414–416, 1972b.