3 Availability of Heavy Metals Applied to Soil through Sewage Sludge

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3.1 INTRODUCTION

Sewage sludge is the residue product of the treatment of municipal or industrial waste water. Usually, it only contains 10 to 30% solids. The disposal management options include disposal to landfill sites, application to land (as a soil amendment or on dedicated waste land), or incineration [1]. Sewage sludge contains high amounts of organic matter and significant quantities of macro- and micronutrients [2]. This makes it an efficient organic fertilizer because it is cheap and produced in great amounts all year. The fertilizer value of sludge is considerable, especially in warm or semiarid regions, where common agricultural practices (e.g., intense cultivation, plowing surface soil) tend to reduce the average soil organic carbon content. In addition, sewage sludge may improve soil physical properties because it promotes the development of good structure and macroporosity and prevents soil erosion [3].

However, sludge also contains various contaminants, such as inorganic potentially toxic elements, and persistent organic compounds. It is believed that sewage sludge is source as well as sink of heavy metals; however, because, along with the metals, it also provides adsorption sites in the humic phases, a great controversy still exists concerning the availability of heavy metals long after the sewage sludge application has ceased. A number of researchers claim that "all evidence available indicates that the specific metal adsorption capacity added with sludge will persist as long as the heavy metals of concern persist in the soil" (Chaney and Ryan [4], as quoted by McBride [5]). On the other hand, some concerns are that heavy metal availability to plants may increase over time.

The preceding exhibits the need to address and study the chemical behavior of heavy metals in relation to various organic phases carefully. The reason is that, although organic matter content as a whole will decrease over time, important fractions of it may increase, in absolute terms or in proportion to the total organic matter content. These fractions may lead to an increase in heavy metal availability over time. However, the chemistry and evolution of humic substances resulting from organic matter decomposition is not yet clear for a number of reasons.

One reason is that long-term experiments are scarce, so results are not always safe to extrapolate and generalize outside the particular conditions of specific experiments. A second reason may be that separation techniques are costly in time and money, and the protocols are not necessarily identical among the various university laboratories. This leads to production of a variety of results that are difficult to combine and interpret. For example, high molecular weight humic acids bind metals strongly enough to keep them away from available pools, and dissolved low molecular weight substances tend to chelate metals and to inhibit their adsorption from solid surfaces, thus increasing metal availability [6]. The substance that will dominate the organic phase of the soil–sludge mixtures will depend on a variety of reasons and conditions that are not always easy to recognize and predict.

In addition, inorganic phases in soil may also play an important role in the complexation reactions with heavy metals. The solubility and therefore the mobility of heavy metals will depend on adsorption, precipitation, and complexation mechanisms; these will, in turn, be affected by heavy metal concentration, pH, colloidal phase content, etc. Thus, it is of great importance to be able to assess heavy metal availability risks because metals may be taken up by plant roots or leached down the soil profile months or years after sewage sludge has been applied. The possible adverse environmental effects of sludge-borne heavy metals need to be understood and managed.

The objectives of this review are to discuss the chemical behavior and environmental fate of heavy metals after sewage sludge has been applied to soils. In the first section, the role of sludge- and soil-borne organic substances found or evolving in the soil matrix is considered. Also, the inorganic phase equilibria are discussed. The next section discusses the availability and environmental fate of heavy metals. The possible risks of heavy metals being introduced to the human food chain or leached down the soil profile, as well as how this behavior may change over time, are examined. In each section, results from various published data are discussed and assessed in the light of the authors' findings.

3.2 THE COMPOSITION OF SEWAGE SLUDGE

3.2.1 ORGANIC PHASE

3.2.1.1 Origination, Composition, and Metal-Chelating Properties

Sewage sludge contains a load of organic and inorganic phases. The organics will eventually be assimilated into the soil via the cycling of nutrients as N, P, and S, while metals will accumulate in the surface soil [7]. The more easily decomposable groups of sludge-borne organic matter (protein, cellulose, and hemicellulose) will be rapidly acted upon by soil microorganisms, once sludge is applied to soil, because they are utilized by them as a source of C and N. The resistant groups (lignin, waxes, and tanin) will remain "as is" for a long time and, along with newly formed substances, will define the humic substances of soil [8].

Sludge-borne organic matter will improve physical and chemical soil conditions. In physical terms, organic matter improves the stability of soil aggregates, thus resulting in better aeration, and increases water retention capacity of the soil. In chemical terms, soil solid phase per unit mass increases significantly, due to the large specific surface of the humic substances. Thus, it contributes to the increase of the adsorption sites, improves the nutrient retention of soil, and reduces the losses by leaching. Further decomposition of humic substances will produce low molecular weight organic substances (LMWOS) or dissolved organic carbon (DOC); these are highly active in the soil environment and bear significant binding abilities for heavy metals. These LMWOS comprise free amino acids, sugars, peptides, aliphatic acids, and their polymers, with molecular weights usually not exceeding 5000 to 10,000 g mol^{-1} [6].

Humic substances have pH-dependent behavior, according to the reaction:

$$\text{R–COO}^- + \text{H}^+ = \text{R–COOH} \tag{3.1}$$

where R is the carbon chain of organic matter.

The deprotonated form (R–COO^-) dominates at neutral to high pH, and the R–COOH form exists at acidic pHs. Spark et al. [9] reported that humic substances are insoluble in the soil solution at acidic pH. As the pH increases, humic phases dissolve in the solution and the deprotonation of the functional groups increases the repulsion forces among the organic molecules. This leads to a more open and linear form at neutral pH, compared to the "spherocolloidal" form at lower pH. On the other hand, water-soluble organic carbon (DOC) and fulvic acids have lower molecular weight, bear more active groups per unit mass than the humic acids, and are thus soluble to the whole range of pH values — from acidic to alkaline. Organic ligands on humic and fulvic acids behave as soft Lewis bases; metals are soft acids and thus they tend to form organometallic complexes. The complexation reaction follows the formula:

$$\text{R–}L^{1-} + M^{m+} = \text{R–}L\text{–}M^{m-1} \tag{3.2}$$

where L is the active group; M is the metal; and the valencies are represented as superscripts.

The main complexing functional groups are carboxyls, phenols, and alcohols. Bonding can be covalent, where the metal and counter-ion contribute one electron each, or coordinate, where the ligand provides both electrons. Theoretically, any organic molecule containing trivalent N or P or divalent O or S can act as a ligand [10].

Heavy metals added in soil with sewage sludge are greatly influenced by the presence of humic substances, of native soil and sludge borne. Heavy metal availability depends on the binding capacity of humus, especially for elements like Cu and Pb. Addition of humic substances with sewage sludge application increases the cation exchange capacity of the soil, thus enhancing the ability of soil to retain greater quantities of heavy metals. As stated, this ability is pH dependent. At pH 6 to 8, humic acids develop the greatest surface area as they become more linear; subsequently, heavy metal retention reaches a peak [9]. Spark et al [9] also concluded that humic acids have greater affinity for metals than inorganic-hydroxide forms and thus control metal solubility at this range of pH.

On the other hand, fulvic acids tend to behave in a different way than humic acids do because they can be taken up by plants directly, along with the metals that are bound onto them [11]. Dissolved organic carbon (DOC) is often reported to reduce metal adsorption soil solid constituents by competing more effectively for the free metal ion and forming organometallic complexes or by being preferentially adsorbed onto the solid phases [12]. This behavior is more effective at near

TABLE 3.1
Relative Affinity for Metals of Humic and Fulvic Acids

Material	Relative affinity	Ref.
FA (pH 5)	Cu > Pb > Zn	14
HA (pH 4.5)	Pb > Cu > Zn > Ni > Cd = Cr	15
HA (pH 6.5)	Pb > Cu = Zn > Cd > Ni > Cr	15
HA (pH 4–7)	Zn > Cu > Pb	14
HA (pH 4–8)	Cu > Pb >> Cd > Zn	14
HA (pH 3.5)	Cu > Ni > Co > Pb > Zn	16
HA (pH 5)	Ni > Co > Cu > Cu > Pb > Zn	16
HA (pH 4–7)	Hg = Pb = Cr > Zn >Ni = Zn	17
HA (pH 5.8)	Hg = Pb = Cr = Cu > Cd > Zn > Ni	17

neutral pH. This is probably because hydroxide, carbonate, and phosphate phases control heavy metal solubility at higher pHs, and, at acidic pHs, free metal ions are predominant. Metal–ligand complex stability generally decreases with a reduction in pH, reflecting the role of $R\text{–}COO^-$ in metal complexation [13].

However, not only do the organic phases bear different binding abilities for metals, but also different metals have different affinities for humic substances. Metals like Cd, Ni, and Zn are generally reported to be more mobile in the soil environment than Pb, Cu, and Co. Table 3.1 shows the relative affinities of different metals onto humic and fulvic acids at various pH values, as reported by various researchers [14–17].

In addition to this, various researchers have differentiated humic behavior in accordance with the hydrophobic (Ho) or hydrophilic (Hi) nature of humic substances. According to Han and Thompson [18], in the DOC of molecular weight (MW) < 3500 g mol^{-1}, 56% is Hi and 44% is Ho; the total concentration is 860 mg DOC kg^{-1} organic matter. A MW > 14,000 g mol^{-1} 83% is Hi and only 17% is Ho (with a total concentration of 580 mg DOC kg^{-1} organic matter).

Explaining the binding of metals by organic matter has two main approaches. The first one is the discrete ligand model (DLM) and the second is the continuous distribution model (CDM). The DLM approach suggests that only a few ligands on the humic substance are required to fit experimental data. Given the complexity of humic phases, these ligands (or ligand classes) must be less than the actual total number presented on these molecules. For an individual adsorption site, v_i, the following formula is valid:

$$v_i = \frac{K_i[M]}{1+K_i[M]} \tag{3.3}$$

where K_i is the stability constant of the binding of metal M onto the given ligand class v_i and in brackets are the metal concentrations.

Although the DLM represents metal binding quite successfully, the CDM approach allows a large number of sites to be involved in binding metals, and thus it represents real conditions more closely. In this model, no discrete *Ki* defined, but rather a continuum of *K* values. This model assumes an irregular frequency distribution of the functional groups. The formula describing the macroscopic free ligand concentration, $L_T{}^f$, is:

$$[L_T{}^f] = \int_0^\infty \frac{L(K)dK}{1+K[M]} \tag{3.4}$$

which is the analogue of Equation 3.3. Kaschl et al. [19] suggested that the CDM was rather valid, in their work with the binding abilities of organic fractions for Cd. They differentiated further the Hi and Ho fractions to acid (A), neutral (N), and basic (B) and calculated the relative and absolute complexing capacities of these hydrophilic and hydrophobic fractions, as given in Table 3.2.

3.2.1.2 Sludge-Borne and Soil-Organic Matter Properties after Sewage Sludge Is Applied to Soil

When sewage sludge is added to soil, its organic matter decomposes rapidly. However, not only the sludge-borne organic matter, but also soil organic matter exhibits an increased rate of decomposition, even if soil organic matter decomposition had reached equilibrium before sludge was

TABLE 3.2
Binding Capacities and pK Values of Hydrophobic (Ho) and Hydrophilic (Hi) Acids (A), Neutrals (N) and Black (B) for Cd in Dissolved Organic Carbon (DOC) Extracted from Municipal Solid Waste Compost

	% of DOC	Complexing capacity (c.c.) in μmol Cd g^{-1} DOC	% of total c.c. of DOC	pK of highest c.c. groups	pK of most abundant groups
HoA	22	1100	38	7.74	5.51
HoN	17	400	14	7.69	6.21
HoB	1 (total Ho = 40%)	—	— (total Ho = 40%)	—	—
HiA	26	800	26	7.02	5.43
HiN	21	600	21	6.93	5.35
HiB	13 (total Ho = 60%)	400	13 (total Ho = 60%)	8.11	5.73

Notes:

HoA = Hydrophobic acids, representing the "young" fulvic acids (FA), the most soluble part of DOC, comprising polyphenols, and humic-associated carbohydrates.

HoN = Hydrophobic neutrals, apolar, closely related to humic acids (HA), the least soluble DOC, comprising fats, waxes, oils, resins, amides, phosphate esters, chlorinated hydrocarbons, high molecular weight alcohols, esteres, ketones, and aldehydes.

HoB = Hydrophobic bases, the least significant and least extractable fraction in DOC, comprising complex polynuclear amides, nucleic acids, quinones, porphyrins, aromatic amines, and ethers.

HiA = Hydrophilic acids, comprising small, highly oxidized organic compounds, polyxydroxy phenols, and uronic acids high in inorganic salts.

HiN = Hydrophylic neutrals, comprising oligo- and polysaccharides, carbohydrates, polyfunctional alcohols, or phosphate salts.

HiB = Hydrophilic bases, comprising proteins, peptides and amino–sugar polymers, low molecular weight amines and pyridine.

Sources:

Data rearranged from Kaschl, A. et al., *J. Environ. Qual.*, 31, 1885–1892, 2002.

Information on hydrophilic and hydrophobic compounds obtained from Kaschl, A. et al., *J. Environ. Qual.*, 31, 1885–1892, 2002; Smith, S.R., *Agricultural Recycling of Sewage Sludge and the Environment*, CAB International, Wallingford, 1996; Han, N. and Thompson, M.L., *J. Environ. Qual.*, 28, 652–658, 1999; and Chefetz, B. et al. *Soil Sci. Soc. Am. J.*, 62, 326–332, 1998.

added [16]. Although decomposition is a complex phenomenon, it is usually described by a first-order kinetics equation, as follows:

$$C(t) = C_0 e^{-k(t-t_0)} \tag{3.5}$$

where $C(t)$ is the residual organic carbon remaining in the soil after time t; C_0 is the initial organic carbon content at time t_0; and k is the decomposition rate. The k factor rarely stays constant, although it is considered so in the preceding equation. Decomposition depends on a variety of factors, which fall into four main categories [3]:

- Sludge characteristics. Decomposition depends on the source, the stabilization processes, and the composition. Decomposition is generally higher when C/N ratio is low (especially below 10) and when the sludge is dry rather than liquid.
- Soil parameters. Soil properties such as texture and pH play a key role. Decomposition is generally higher in a sandy and slower in a clayey soil. pH values need to favor microbe activity; thus, acidic values will mean less activity and subsequently poor organic matter decomposition.
- Environmental conditions. Ambient temperature and moisture will dramatically affect decomposition rate. The higher the temperature is and the closer the moisture is to the field capacity, the faster the decomposition is.
- Application conditions. Decomposition depends on application rate and method. For the application method, it is agreed that mineralization is faster when sewage sludge is surface applied than when it is incorporated into the soil. For the application rate, the greater the quantity of sludge is per hectare, the faster the decomposition is [21]. However, there is a disagreement on that [7,22].

Although the preceding are related to the individual decomposition rates of a given sewage sludge in a given soil under certain ambient environmental conditions, it is evident that k reduces with time (Figure 3.1). It can be observed that k, irrespective of conditions, will be higher when sewage sludge is first applied to soil and will significantly reduce as time proceeds. However, as stated before, different groups of sludge-borne organic matter will behave differently. Hydrophobic

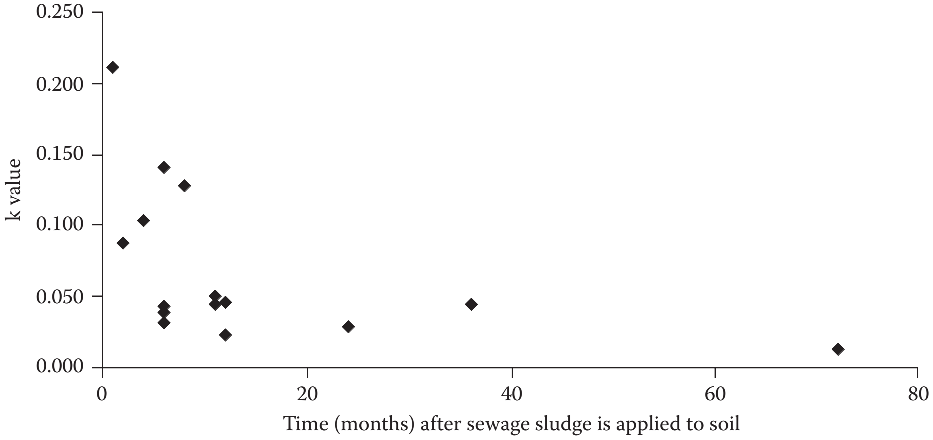

FIGURE 3.1 Mean k values (rate of organic matter decomposition) after sewage sludge is applied to soils. These k values represent a variety of experimental data. (Data modified from Metzger, L. and Yaron, B., *Adv. Soil Sci.*, 7, 141–162, 1987; and Antoniadis, V. and Alloway, B.J., *Water Air Soil Pollut.*, 132, 201–214, 2001.)

compounds increase remarkably in soil organic carbon after sewage sludge application and, as a result, they induce the formation of hydrophobic aggregates. Thus, Hi/Ho ratio will decrease as sewage sludge application rate increases [8].

Nevertheless, as sewage sludge application increases, DOC also increases in absolute as well as relative terms compared to the total organic carbon added to soil. Experimental data seem to agree on the fact that humic and fulvic acids in soil–sludge mixtures evolve, increasing their concentrations months after sewage sludge application. Heavy metals are preferentially associated with hydrophilic phases, so one could state that metal availability will tend to decrease with time after the termination of sludge application. However, this trend may be different if DOC increases more than the humic acids, and some evidence suggests that this may take place. Metzger and Yaron [3] reported that the ratio of humic over fulvic acids was reduced following sludge application, and Han and Thompson [18] found that, in the surface soil (0 to 5 cm), Hi/Ho ratio increased. These data point to the risk of heavy metals exhibiting enhanced availability even months after the termination of sewage sludge application.

3.2.2 INORGANIC PHASE

3.2.2.1 Fertilizer Value of Sewage Sludge

Sewage sludge is increasingly used as a fertilizer because land application is considered a more environmentally friendly disposal method and because of its great fertilizer value (Table 3.3). Nowadays, sewage sludge can be produced for agricultural use as dry granular, palletized, or fortified organic-based materials, which have more specialized uses in agriculture and horticulture compared with the conventional forms [23]. The technology for applying sludge is advanced and includes surface spreading and injection of the material into the soil, a practice that helps reduce odor problems and facilitates proper incorporation into the soil. The optimum dose of application is difficult to determine because of restrictions that depend on soil parameters, such as pH, clay content, and contaminant and nutrient content in sludge [24]. Usually, if no other restricting factors are present, the rate of application should not exceed 10 t ha^{-1} yr^{-1}, equivalent to 250 kg N ha^{-1} [25].

3.2.2.2 Heavy Metal Loadings in Sewage Sludge and in Soils where Sludge Is Added

Heavy metals occur in sewage sludge through domestic, run-off, and industrial inputs, with the industrial input contributing only a small percentage of the total in specific elements, such as Pb and Zn [1]. Nowadays, heavy metal loads in sewage sludge have been significantly reduced as a result of improved effluent control and the use of cleaner technologies from industries due to tighter state legislations. As a result, the metal loadings in sewage sludge and top soils are being reduced (e.g., reports by Chaudri et al. [26] for England and Wales concerning Cd; Barbarick et al. [27], reporting a period from 1982 to 1992; Sloan et al. [28]; and Berti and Jacobs [29]).

TABLE 3.3
Typical Concentrations of Nutrients and Organic Carbon in Sewage Sludges

	Organic carbon (%)	Total N (%)	NH_4–N (mg kg^{-1})	NO_3–N (mg kg^{-1})	Total P (%)	Total S (%)
Range	16–40	0.5–17.6	800–5600	79–160	0.5–14.3	0.6–1.5

Sources: Data obtained from O'Riordan, E.G. et al., *Irish J. Agri. Res.*, 25, 223–229; Gerba, C.P., in *Pollution Science*, Pepper, L., Gerba, C.P., and Brusseau, M.L., Eds., Academic Press, San Diego, 1996, 301–319; and Smith, S.R., *Agricultural Recycling of Sewage Sludge and the Environment*, CAB International, Wallingford, 1996.

Nevertheless, it is inevitable that sewage sludge application to soil will increase heavy metal concentrations well beyond their background concentrations. This is the reason that governments deal with this prospect, setting upper limits of heavy metals in soils and sludges to be added to soils. Heavy metal concentration limits in sewage sludge for the U.S. and the E.U. are shown in Table 3.4. Background metal concentrations in soils and maximum permissible loading rates are shown in Table 3.5. It is evident that metal-loading standards differ greatly between the U.S. and the E.U., and this stresses that sludge-induced metal contamination is still quite controversial and a matter not yet fully resolved [20].

TABLE 3.4
Concentrations of Heavy Metals in Sewage Sludges in the U.S. and the E.U.

	Permissible limits in the U.S. (mg kg^{-1})[a]	Cumulative pollutant loading rate limits in the U.S. (kg ha^{-1})[a]	Permissible limits in the E.U. (mg kg^{-1})[b]	Typical metal concentrations in sludges applied in agricultural land in 1991 (50 percentile)[c]
As	75	41	—	3.2
Cd	85	39	20–40	3.2
Cu	4300	1500	1000–1750	473
Pb	840	300	750–1200	217
Hg	57	17	16–25	3.2
Mo	75	—	—	1.0
Ni	420	420	300–400	37
Se	100	100	—	0.28
Zn	7500	2800	2500–4000	889

[a] Harrison, E.Z. et al., *Int. J. Environ. Pollut.*, 11, 1–36, 1999.
[b] Alloway, B.J., in *Heavy Metals in Soils*, Alloway, B.J., Ed., Blackie Academic and Professional, London, 1995, 38–57.
[c] Smith, S.R., *Agricultural Recycling of Sewage Sludge and the Environment*, CAB International, Wallingford, 1996.

TABLE 3.5
Typical and Upper Permissible Heavy Metal Concentrations in Soils

	Heavy metal concentrations in soils of England and Wales (National Soil Inventory)[a]	Heavy metal concentrations in agricultural soils in the U.K. in 1991[b]	U.K. regulation limits[b]	Annual pollutant loading rate (kg ha^{-1} yr^{-1})[c]
As	—	—	—	2
Cd	0.7	0.55	3	1.9
Cu	18.1	17	80	75
Pb	40.0	33	300	15
Hg	0.1	0.13	1	0.85
Mo	—	—	—	—
Ni	22.6	14	50	21
Se	—	—	—	5
Zn	82.0	57	200	140

[a] McGrath, S.P. and Loveland, P.J., *The Soil Geochemical Atlas of England and Wales*, Blackie Academic and Professional, London, 1992.
[b] Alloway, B.J., in *Heavy Metals in Soils*, Alloway, B.J., Ed., Blackie Academic and Professional, London, 1995, 38–57.
[c] Harrison, E.Z. et al., *Int. J. Environ. Pollut.*, 11, 1–36, 1999.

3.2.2.3 Heavy Metal Chemistry in Soils and Heavy Metal Properties after Termination of Sewage Sludge Application

After sewage sludge-borne heavy metals are introduced into the soil, a series of mechanisms tend to bind metals to the organic (soil and sludge-borne) and the inorganic constituents. A percentage of the metals will be reversibly adsorbed onto clay surfaces; some will precipitate out of the solution with other inorganic phases (carbonates, phosphates, etc.), especially at alkaline pH values. Some will be specifically adsorbed onto solid surfaces, and the organic colloids (fulvic and humic acids, as discussed earlier) compete for metal binding effectively. A small portion of the added metals will be soluble into the soil solution in pure ionic form and thus readily available for plant uptake or easily leached out of the root zone and probably into the groundwater.

These processes are usually pH dependent, with the metals bound more strongly onto the inorganic phases with an increase in pH value and heavy metals becoming more available in acidic pHs. In his early work, Harmsen [30] suggested two mechanisms to explain this metal behavior:

- Selective adsorption of metals on sites previously occupied by H^+ (M/H exchange, M = metal)
- Selective adsorption of hydrolysis products of metals onto sites previously occupied by H^+ (M(OH)/H exchange)

In a more recent review, Naidu et al. [31] agreed with the significance of the preceding mechanisms and they added that this process is related to the increase of the adsorption density of clay mineral margins. Evans [17] further explained that pH controls the two main retention mechanisms, i.e., adsorption and precipitation, because metal solubility depends on the solubility product of the solid phase (precipitate) containing the metal. The most important precipitation reaction, e.g., hydrolysis, can be described by the following reaction:

$$M(OH)_m + mH^+ = M^{m+} + mH_2O \tag{3.6}$$

The reaction constant (K) is then given by the equation:

$$K = \frac{(M^{m+})}{(H^+)^m} \rightarrow pM = mpH + pK \tag{3.7}$$

where M is the metal and m+ the positive valency that it bears.

The preceding equations indicate that, as pH increases, pM also increases and, subsequently, metal concentration decreases as a result of precipitation. This means that metal solubility depends on the solubility product of metal hydroxides. Specific adsorption of metal hydroxides increases with decreasing pK values. For elements with equal pK, the larger ionic radius plays a decisive role. The order of specific adsorption for the most common heavy metals given by Alloway [25] is as follows:

Cd (pK 10.1) < Ni (pK 9.9) < Co (pK 9.7) < Zn (pK 9.0) << Cu (pK 7.7)
< Pb (pK 7.7) (Cu has larger ionic radius than Pb) < Hg (pK 3.4)

At neutral pHs, the cation exchange (or retention) capacity of soils is also higher than that of acidic pHs, especially in soils with high content in variable charge constituents (such as Al and Fe hydroxides, 1:1 clays and clay edges, and humic substances); this explains the stronger binding capacity of soil for heavy metals when pH is high. In addition, metal diffusion into the inorganic lattice of phases such as Mn hydroxides and some 2:1 clays (illites) may also be possible. In that case, metals become almost irreversibly unavailable, with smaller ionic radius metals having greater affinity for such a process.

Many researchers have used the "sequential extraction" method to determine the relative affinity of heavy metals for the various organic and inorganic soil constituents (e.g., Mbila et al. [32]; Berti and Jacobs [33]; Sposito et al. [34]; Tsadilas et al. [35]; and Yong et al. [36]). It is agreed that organically bound forms are important in complexing metals and diminishing their environmental availability (mean values of the preceding works indicate contribution of metal retention by organic phases as follows: Cd 26%; Cu 55%; Pb 22%; Ni 17%; and Zn 24%). However, as explained earlier, organic phases are prone to intense mineralization and rapid alteration once sewage sludge has been introduced into the soil. With the humus decomposition, one significant part that contributes to metal retention approximately equal to the value mentioned earlier is ruled out. This means that, over time, the chemistry of metal retention will be altered. Whether soil will bear the same capacity to control heavy metal availability over time is a matter of great dispute within the scientific community. This will be discussed next.

3.3 AVAILABILITY OF HEAVY METALS AND THEIR FATE OVER TIME

3.3.1 FACTORS AFFECTING HEAVY METAL AVAILABILITY

In the complex soil environment in which heavy metals are introduced when sewage sludge is applied to agricultural land, their bioavailability to crop plants depends on various factors. These are well documented in papers reporting original experimental data and in review papers. A synopsis of these factors will be now discussed.

3.3.1.1 pH Value

Soil pH is probably the most widely recognized factor affecting heavy metal availability. With the exception of molybdenum, arsenic, and selenium, heavy metal retention increases with a pH increase and thus availability decreases. This is recorded in experiments measuring plant uptake or quantifying metal adsorption onto solid phases and metal extractability. In the first type of experiment, pH values of acidic soils increase with the effect of lime-stabilized sludge and are found to have depressed metal uptake by plants (e.g., Basta and Sloan [37]), or lime is applied to natural and metal-contaminated soils to improve soil pH and similar uptake effects are found (e.g., Oliver et al. [38]). In the second type of experiment, several solid phases, pure (oxides, clays, etc.) or natural soils, are used to evaluate the adsorption strength of heavy metals in a variety of pH values (e.g., Salam and Helmke [39]; Elliott et al. [14]; Yong and Phadungchewit [40]; Gray et al. [41]) (see also Figure 3.2).

These trends do not affect different heavy metals in a similar way. It is found that "mobile" elements such as Ni, Cd, and Zn are much more sensitive in changing their availability status with pH than other elements, such as Pb and Cu, which are more strongly retained by humus [1]. However, some data suggest that the positive pH effect on metal availability is not permanent, especially in high buffer capacity soils, because soils tend to return to initial pH over time. Ca^{2+} ions introduced to soil through liming may even compete with other metals for the limited adsorption sites, causing adverse effects [25]. Also, at certain periods of time, metal availability may have a dramatic peak, due to a temporary pH depression, even if pH values before and after that period are well controlled. Such periods may occur during early summer when the intense increase in soil microbial biomass may cause a rapid sludge-borne organic matter decomposition, which, in turn, tends to reduce soil pH due to the release of weak organic acids.

3.3.1.2 Organic Matter

This is a factor almost as important as pH. However, the role of different organic phases has been already discussed and will be stressed in subsequent chapters as well.

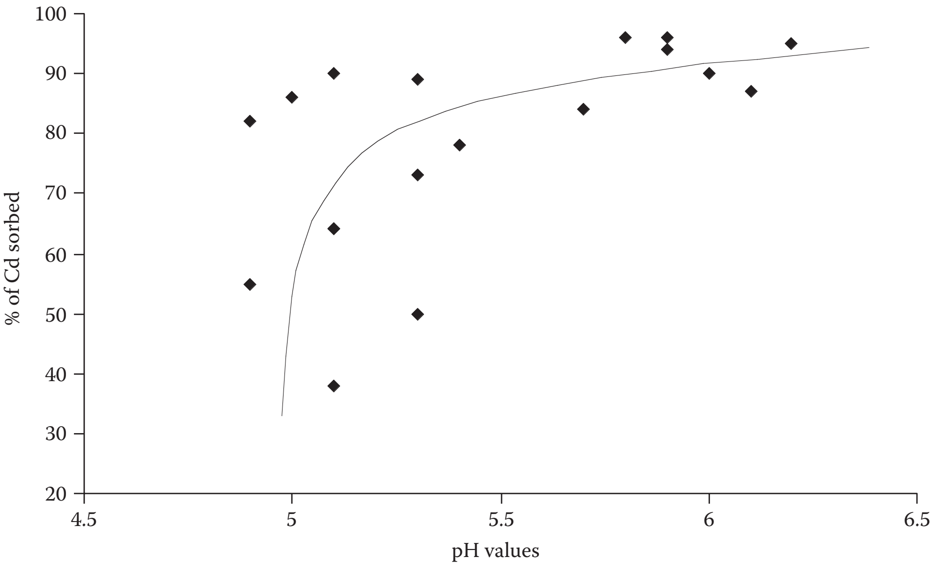

FIGURE 3.2 Effect of soil pH on percentage of Cd sorbed onto soils. Data concern five New Zealand soils that received 2 mg Cd kg^{-1} as $Cd(NO_3)_2$. (Data obtained from Gray, C.W. et al., *Austr. J. Soil Res.*, 36, 199–216, 1998.)

3.3.1.3 Redox Potential

Redox effects are particularly important in soils of aquic moisture regime (low lying soils in relief depressions, poorly drained, with water table normally into the root zone) and paddy soils intentionally flooded for cultivation reasons (rise fields). Generally, low redox values (reducing conditions) result in low metal availability, due to the formation of HS^- and the subsequent precipitation of sulfide–metal solids out of the solution [42]. However, in soils in which Fe and Mn hydrous oxides are predominant, this trend may be altered. Prolonged reducing conditions may cause total depletion of hydrous oxides. Even if oxic conditions prevail again, the contribution of these phases to the sorptive capacity of the soils is not recovered. It is found that, when cultivated, such soils (developing prolonged anoxic conditions) exhibit an impressive increase in heavy metal uptake by test plants compared to other soils with no history in waterlogged regimes [43].

3.3.1.4 Competition Effects among Metals

The competition or synergism between heavy metals and/or other ions present in the soil system has a very significant effect on metal mobility in the solution and in the root zone. An overview of antagonistic and synergistic behavior of the elements is given in Figure 3.3. A lot of research effort has been put into the investigation of the interactions between Cd and Zn and the findings appear to be contradictory. Works supporting synergism suggest a mechanism by which the two metals compete for the same adsorption sites, and thus the soil retention capacity of the soil is reduced for any given metal when the other increases in concentration in the solution. Thus, when both elements are present in the soil solution, they exhibit enhanced bioavailability and reduced retention [44].

On the other hand, when plant uptake is concerned, antagonism is the usual effect because it is found that plant roots favor the uptake of the metal found in higher relevant concentrations over the other (e.g., McLaughlin et al. [45]). A well recognized competition in plant uptake occurs between micronutrients (such as Ca, P, and S) and heavy metals. This is due to favorable plant selectivity for the nutrients over heavy metals and to precipitation of insoluble $Cd(PO_4)_2$, especially

Adjacent to roots

	Cu	Zn	Cd	Pb	As	Se	Cr	Mo	Mn	Fe	Co	Ni
Cu	■		γ					α	α			
Zn	α	■	β						α	α		
Cd		α	■									
Pb		δ	β	■								
As		δ			■				α			
Se	α	α	α			■						
Cr	δ						■		α	α		
Mo	α							■	α	α		
Mn	γ	α	γ		α	α	α	γ	■			
Fe	α	α	γ				α	α	α	■	α	
Co									α	α	■	
Ni	γ	γ	γ						δ			■

Plants

FIGURE 3.3 Interactions of heavy metals within plants and at the root surface. 'α: antagonism, β : synergism, γ: antagonism and/or synergism, δ: possible antagonism.' (Redrawn from Kabata–Pendias, A. and Pendias, H., *Trace Elements in Soils and Plants*, 2nd ed., CRC Press, Boca Raton, FL, 1992, 1–87; 131–141. With permission.)

at neutral to alkaline pH, that depletes Cd of the soil solution [46]. Also, Pb mimics the physiological behavior of Ca, and thus it may inhibit several enzymes in plants when Ca is not readily available and the plant takes up Pb rather than Ca [47].

3.3.1.5 The Effect of Carbonates

At high pH values, calcite ($CaCO_3$) sorbs Cd as $CdCO_3$ and reduces its availability. The same effect is evident for other metals too. This provides a further explanation as to why liming of acidic soils is effective for reducing metal availability to crop plants. Above pH 7.3, the order of carbonate solids precipitating is [17]:

$$\mathrm{Mg > Ba > Ca > Sr > Zn > Fe > Cd}$$

Papadopoulos and Powell [48] suggested for this sequence that the affinity of calcite for metals is related to their ionic radii. This is more evident for Cd^{2+}, which, at high pH, substitutes for Ca^{2+} by chemisorption because the Cd radius fits better for this process.

3.3.1.6 Chloride Ions

A factor especially important in arid soils is the effect of chloride ions, which are found to enhance heavy metal availability, particularly that of Cd [49]. Chloride complexes with Cd ($CdCl^-$, $CdCl_2^0$) may be very stable and inhibit Cd from being adsorbed onto soil solids [50]. Chloride ions can be found in soils because of environmental reasons (soil salinity due to high evapotranspiration), poor irrigation practices, or sewage sludge application to soils prone to salinity.

3.3.2 HEAVY METAL ACCUMULATION IN CROP PLANTS

All the preceding factors governing heavy metal availability may affect plant uptake of heavy metals. However, it should be stressed that other parameters related to plant physiology (such as plant genotype) are not studied here, but are of great importance as well. One of the greatest

TABLE 3.6
Soil–Plant Transfer Coefficients (TC) of Heavy Metals

Element	TC estimations[a]	Pot experiments[b]	Field experiments[c]
Cd	1–10	1	0.94
Cr	0.01–0.1	—	0.0005
Cu	0.1–10	0.25	0.21
Ni	0.1–1	1.29	0.06
Pb	0.01–0.1	0.09	0.02
Zn	1–10	0.88	1.05

[a] Obtained from Alloway, B.J., in *Heavy Metals in Soils*, Alloway, B.J., Ed., Blackie Academic and Professional, London, 1995, 38–57.

[b] Data from Antoniadis, V. and Alloway, B.J., *Water Air Soil Pollut.*, 132, 201–214, 2001; Antoniadis, V. and Alloway, B.J., *Environ. Pollut.*, 117, 515–521, 2002; Tsadilas, C.D. et al. *Commun. Soil Sci. Plant Anal.*, 26, 2603–2619, 1995; Hooda, P.S. and Alloway, B.J., *J. Soil Sci.*, 44, 97–110, 1993; and Jackson, A.P. and Alloway, B.J., *Plant Soil*, 132, 179–186, 1991.

[c] Data from Antoniadis, V. et al., in *Proc. 8th Conf. Hellenic Soil Sci. Soc.*, Kavala, 2000, 459–469; Berti, W.R. and Jacobs, L.W., *J. Environ. Qual.*, 25, 1025–1032, 1996; Bergkvist, P. et al., *Agri. Ecosyst. Environ.*, 97, 167–179, 2003; Brown, S.L. et al., *J. Environ. Qual.*, 127, 1071–1078, 1998; Chang et al., *J. Environ. Qual.*, 12, 391–397, 1983; and Schaecke, W., Tanneberg, H., and Schilling, G., *J. Plant Nutr. Soil Sci.*, 165, 609–617, 2002.

concerns is that after sewage sludge has been applied to soils, heavy metals borne in it may accumulate in plants and, subsequently, enter the human food chain or have toxic effects on plants and/or animals grazing on them. Heavy metal concentrations in plants depend on the concentrations (total and available) of the metals in the soil in which the plants are grown. The transfer coefficient (TC) between soil and plant gives a measure of metal mobility. Table 3.6 gives the TC of the main heavy metals as obtained by Alloway [25] and values of the same coefficient from several other works.

Although TCs are not supposed to be precise in predicting metal uptake by plants (because only orders of magnitude are indicated), it is evident that Cd, Ni, and Zn are among the most mobile elements and that the ones strongly sorbed onto humic substances (including Cr and Pb) are less available. From Table 3.6, it is evident that heavy metals exhibit behavior inside a greenhouse in pot studies different from that in field experiments; the latter usually gives smaller TC values. An explanation of this trend was given by De Vries and Tiller [51], who attributed the higher metal concentrations in pot experiments to the more favorable conditions (temperature, humidity, and light distribution) usually found inside a greenhouse.

Although McBride [5] agreed with that, he added that differences in plant rooting patterns are more critical. Most of the crops' rooting systems in the field go well beyond the sludge incorporation zone and thus heavy metal uptake is more conservative. In pot experiments, plant roots are "forced" to remain where sludge is thoroughly incorporated with the soil. Some researchers, however, have found no relationship between metal concentration in soil and in the plant. Kuo [52] and Del Castilho and Chardon [53] found no apparent relationship between DTPA-extractable Cd (probably the most widely used availability index) and plant Cd in five soils with a pH of 5 to 6. The same was also found by Barbarick and Workman [54] and O'Connor [55].

Although Cd and Pb are nonessential elements with no biological function within the plant, Ni and Zn are essential micronutrients for plant growth. However, Ni and Zn can cause toxicities when they are present in plants in excess. Zinc can be relatively easily translocated from roots to shoots in a plant and, in high concentrations, tends to accumulate in mature leaves although heavy metals accumulate mostly in roots. This is also shown in Figure 3.4. Other heavy metals, however,

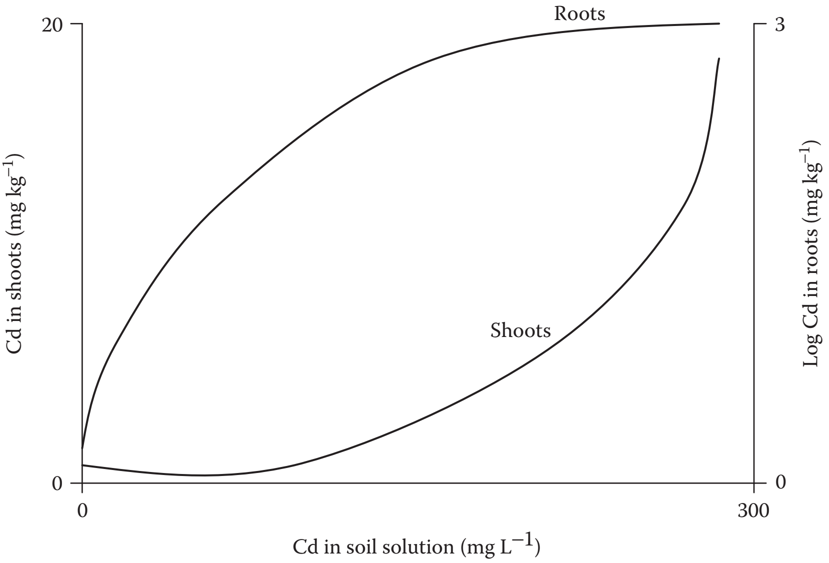

FIGURE 3.4 Cd in soil solution, roots, and shoots. (Redrawn from Kabata–Pendias, A. and Pendias, H., *Trace Elements in Soils and Plants*, 2nd ed., CRC Press, Boca Raton, FL, 1992, 1–87; 131–141. With permission.)

stay in the roots and move slowly upwards [56]. Kabata–Pendias and Pendias have summarized the several ways by which plants can tolerate high heavy metal concentrations [57]:

- Selective uptake of ions
- Decreased permeability through cell membranes
- Immobilization of ions in roots, foliage, or seeds
- Removal of ions from metabolism by deposition in insoluble forms
- Alteration in metabolic patterns: increased enzyme system that is inhibited, or increased antagonistic metabolite, or reduced metabolic pathway by-passing an inhibited site
- Adaptation to toxic metal replacement of a physiological metal in an enzyme
- Release of ions to plants by leaching from foliage and excretion from roots

However, it is evident that different plant species and different cultivars in the same species have different capabilities in tolerating heavy metals [58]. That is, different plants, grown in the same soil contaminated with heavy metals, may accumulate variable quantities of these metals. The response of some plant species to heavy metal exposure is shown in Table 3.7.

3.3.3 CONCERNS OF HEAVY METAL LEACHING OUT OF SOIL AND INTO GROUNDWATER

The movement of heavy metals down the soil profile is of a great importance because it involves the risk of groundwater contamination and deterioration of drinking water quality. The literature provides some extreme examples of cases of massive heavy metal movement up to 3 m depth [59]. After heavy metals have been introduced with sewage sludge application to land, downward movement will be a possibility when some, or any combination, of the following is evident:

- High sludge application rates
- Enhanced heavy metal load in sludge

TABLE 3.7
Relative Accumulation of Heavy Metals by Different Crops

High plant uptake	Low plant uptake
Lettuce	Potato
Spinach	Maize
Celery	Peas
Kale	Leek
Ryegrass	Onion
Sugar beet	Tomato
Turnip	Berry fruits

Sources: From Alloway, B.J., in *Heavy Metals in Soils*, Alloway, B.J., Ed., Blackie Academic and Professional, London, 1995, 38–57; and Kloke, A., Saurbeck, D.R., and Vetter, H., in *Changing Metal Cycles and Human Health*, Nriagu, J., Ed., Springer–Verlag, Berlin, 1994.

- Soils with low sorptive capacities (low organic matter and clay contents, acidic pH conditions)
- High rainfall or irrigation water rates

Many research efforts have been put into performing laboratory experiments with soil columns or monitoring metal behavior in soil profiles in areas with history in sludge application. As Camobreco et al. [60] pointed out, measuring metal movement in repacked soil columns is different from measuring it in the field under “real” conditions. The reason is that metal movement more often occurs through soil macropores or cracks. This leads to the preferential flow of the water and, subsequently, to the metals that it carries; this fragile soil structure is destroyed when soil is sampled and taken to the laboratory to be set up for a column experiment [61]. Thus, metal mobility in the profile is very often severely underestimated, and results seem very promising when conclusions rely only on laboratory trials. However, column experiments are useful because they provide a picture based on carefully controlled parameters.

Although it is often assumed that downward movement of heavy metals is not a significant process, there is a disagreement in the literature on that matter. For example, Davis et al. [62] applied 40 t ha^{-1} sludge and found heavy metal movement only down to 10 cm depth, after a residual time of 3 years. El-Hassanin et al. [63] found that Cd, Zn, and Pb only moved in the surface soil layer; similarly, Higgins [64] found that no heavy metal movement to the B horizon was evident. Chang et al. [65] reported that, 4 years after the termination of sewage sludge application, heavy metals were deposited only in the 0- to 15-cm upper soil layer, and Harmsen [30] found that Cd and Pb did not accumulate below 40 cm of the surface in a heavily contaminated Zn smelter area. Dowdy et al. [66] also reported that heavy metals did not move significantly below the incorporation zone (or plow layer). The same was concluded by Williams et al. [67], Emmerich et al. [68], and Miner et al. [69].

In contrast to this, data have also been published suggesting that metals can move below the incorporation zone, under certain conditions; such works many times concern long periods of sludge application. Works of this kind are very important and should be taken seriously under consideration before sludge utilization to agricultural soils is to be generalized. Antoniadis and Alloway [70] studied an area in central England where sewage sludge had been applied in a farm for decades at normal rates. They found that Ni was significantly higher than the control even at a depth of 80 cm; Zn had been moved to 60 cm and Cd to 40 cm. Lead was the only metal found higher than

TABLE 3.8

Heavy Metal Distribution in the Profile of a Soil Receiving Sewage Sludge for Many Decades at "Normal" Rates[a] and in a Nonsludged Control Soil

Soil depth (cm)	Cd		Ni		Pb		Zn	
	Farm	Control	Farm	Control	Farm	Control	Farm	Control
0–20	0.95	0.85	20.3	13.8	70.0	30.3	120.3	80.4
20–40	0.82	0.78	17.2	10.6	32.3	30.6	107.1	72.7
40–60	0.63	0.63	16.5	5.6	28.5	29.7	85.2	68.2
60–80	0.51	0.55	14.0	4.7	27.4	27.9	75.5	65.0
$LSD_{0.05}$	0.13		4.3		9.5		20.5	

[a] c. 3–5 t ha^{-1} at site S2.

Source: Data obtained from Antoniadis, V. and Alloway, B.J., *Commun. Soil Sci. Plant Anal.*, 34, 1225–1231, 2003.

the control only in the topsoil (see also Table 3.8). At a site where raw sewage wastewater had been applied for 5 decades, Schirado et al. [71] found a rather uniform distribution of Cd, Zn, and Ni in the soil profile up to a depth of 150 cm; this was attributed to the movement of the metals. Barbarick et al. [27] applied sewage sludge for 11 years at a rate of 27 t ha^{-1} yr^{-1}. Nine years after the commencement of their experiment, Zn had moved down to 125 cm depth, although other metals (Pb, Cd, and Ni) did not move significantly. Sloan et al. [72] found significant movement of all metals studied (Cd, Cr, Cu, Ni, Pb, and Zn), down to a depth of 30 cm, after 16 years of continuous sludge application.

The literature also offers examples of data exhibiting that it is not necessary to have many favorable factors for metal mobilization in order to measure significant movement. Using repacked columns of a neutral pH soil and single sludge application rates of 50 t ha^{-1} of a sludge relatively low in heavy metals (Cd 2.41; Ni 38.08; Pb 317; and Zn 645 mg kg^{-1}), Antoniadis and Alloway [73] found that Cd, Ni, and Zn moved to 8 cm depth below the incorporation zone. Also, some work that has been performed on sources of heavy metals different from sewage sludge reports significant metal movement through the soil profile. Li and Shuman [74] contaminated coarse soils with low sorptive capacities with flue dust and found movement of Zn down to a depth of 75 cm and of Cd and Pb to a depth of 30 cm. Similarly, Stevenson and Welch [75] found that Pb moved to a depth of 75 cm after inorganic Pb salt applications of 3.2 t ha^{-1} to soil.

In recent years, much work has concentrated on the effect of low molecular weight humic substances, often identified as dissolved organic carbon (DOC), in metal movement. As mentioned previously, DOC may preferentially sorb heavy metal, reducing metal adsorption onto solid phases enhancing and thus metal availability and mobility. Because DOC elution may be associated with the decomposition of sewage sludge-borne organic matter, several workers have hypothesized that DOC may facilitate heavy metal transport down the soil profile [76,77].

Sawhney et al. [78] mixed soil and compost containing heavy metals at rates of 0, 15, 50, and 100% compost, and they measured the leachate after applying 20 mm of water per day for 70 days. They found that all metals (Cd, Pb, Cr, Cu, and Zn) had moved into the leachate in the first half of their experiment. However, in the second half, the soluble pools (presumably these included DOC elution) were "exhausted." Bolton and Evans [79] measured sludge landfill leachates and applied a computer model to calculate the metal speciation; they found that metals were predominantly complexed with Cl^- ions and fulvic acids. Zhu and Alva [80] found a positive correlation between metals (Zn and Cu) and DOC in the leachates eluted in their leaching experiment.

From the preceding, it is evident that heavy metal leaching from sludge-treated soils is not always exhibited and that a clear and positive correlation between metal leaching and actual groundwater contamination has not been recorded. However, the existing evidence discussed should be considered seriously and certain soil parameters should be studied further before sewage sludge application is advised, in order to avoid any unnecessary future risks of groundwater contamination. For example, Antoniadis and Alloway [73] found small but significant concentrations of heavy metals in the leachates eluted from their soil columns, although metals in these columns had moved only slightly. Richards et al. [81] concluded that preferential flow and metal complexation with soluble organic phases may facilitate metal leaching that leaves no traces of metal subsurface readsorption, and the same was recognized by McBride et al. [82].

3.3.4 Approaches to the Time Factor or the Residual Effects of Sludge-Borne Heavy Metals

After sludge has been applied to soils, the heavy metals introduced to the soil environment interact with other soil components for a long time. Thus, it is widely recognized that long-term experiments should be used for assessing heavy metal bioavailability. Alloway and Jackson [83] stated that it is difficult to assess whether heavy metals remain highly available to plants many years after sewage sludge application has ceased. The literature provides many examples of research findings suggesting that metal availability decreased or did not change over time. Chang et al. [84] studied a residual period of 10 years and concluded that metal availability to plants tends to reach a plateau a few years after the last sludge application. Over a residual time of 10 years, Hyun et al. [7] assessed the hypothesis that organic matter decomposition may adversely affect metal availability of Cd; they found that, although the former decreased by 43% over that period of time, Cd availability did not significantly increase.

Similarly, Canet et al. [85] applied sewage sludge in equivalent doses of 400, 800, and 1200 kg N ha^{-1} (approximately 13, 26, and 39 t sludge ha^{-1}) and 7 years later found no significant increase in metal uptake by Swiss chard and lettuce. Krauss and Diez [86] found that test crops, such as ryegrass, barley, maize, and potato, remained unaffected 12 years after the cessation of a period of intense sludge application (40 mg Cd and 808 mg Pb kg^{-1} had been applied to soil). Moreover, Bidwell and Dowdy [87] reported a dramatic decrease in heavy metal availability after the termination of sewage sludge application. Chaney and Ryan [4] found that metal availability decreased after the termination of sewage sludge application and maintained that metal availability is more likely to be kept to a minimum in sludge-amended soils due to the enhanced specific adsorption capacity of soils after the addition of sludge-borne organic matter.

However, McBride [5] criticized this work by saying that soil organic matter will not possess the same ability to sorb heavy metal over time; this capacity is likely to decrease with maturing, probably due to organic matter decomposition. He also stated that research works tend to underestimate metal dynamics with sludge application; metal availability is measured by plant shoots' uptake, but "uptake may be suppressed by changes in the translocating efficiency of the plant" which may change over time. He also gave reasons as to why heavy metal availability should not be expected to increase after the sewage sludge application. First, the microbial biomass may be less effective in decomposing organic matter due to possible toxic effects on it and, second, sludge particles will reach an equilibrium with soil matrix after some time of sludge application. All these may lead to a delayed decomposition of organic matter and reduced heavy metal availability.

In a long-term experiment, Chang et al. [84] discussed two hypotheses likely to be valid after the termination of sewage sludge application. The first is the "plateau effect" or "sludge protection," in which heavy metal accumulation in plants reaches a maximum and will not substantially increase, even if heavy metal loadings in sludge increase. In the second, the "time bomb," heavy metal concentrations of plant tissues remain unchanged or rise slowly soon after the termination of sewage sludge; however, as organic matter is decomposed in the soil, the heavy metal concentrations of the plant tissue rise rapidly. They concluded that data point to the first hypothesis, but they admitted that this conclusion could not be definite and that more data would be needed.

On the same subject, Petruzzelli et al. [88] found that Zn and Cd concentrations in plants grown in sludge-treated soils were higher in concentration 4 years after the last sludge application. Sloan et al. [28] found that Cd was still highly recovered from the soil 15 years after sludge application, and McBride et al. [82] found that Cd and Zn were still more available to plants in sludge-treated plots in their field trial than the counterpart control plots. Moreover, in the field experiment of Heckman et al. [89], up to 112 t ha^{-1} of sludge was applied; after a period of 5 to 9 years, the concentrations of Cd and Zn in soybean were still significantly higher than those in controls. Gardiner et al. [90] applied sewage sludge for 5 years at a rate of 20 t ha^{-1} yr^{-1} and found an impressive sixfold increase in Cd concentration in Swiss chard. After that time, the increase was slower. However, apart from Cd other metals, including Zn, Cu, and Ni, did not increase as much.

Other research works that reported enhanced heavy metal availability to plants in soils treated with sewage sludge include Mulchi et al. [91], who found that, after nearly 10 years of continuous sludge application to soil, concentrations of Zn, Cd, Mn, Ni, and Cu correlated very strongly in tobacco with "total" metal concentrations in the soil (R^2 values of 0.65 to 0.95), and Chang et al. [92], who found that Cd concentrations in plant tissues (radish and Swiss chard) tended to increase yearly with each sludge application. Chaudri et al. [93] measured higher Cd concentrations in wheat grains in the treated plots than in the controls 31 years after a single sludge dose of 125 t ha^{-1}. Moreover, McGrath et al. [94] found that, after 23 years of the cessation of sewage sludge application, Cd and Zn extractability and availability at high sludge rates (which introduced 2158 kg Zn ha^{-1} and 70.2 kg Cd ha^{-1} into the soil) did not equal that of the control. Other experiments recording shorter periods also found that heavy metal availability to plants did not decrease to equal that of the control after the termination of sludge application (Obrador et al. [95] and Antoniadis et al. [96] reported a residual period of 1 year).

An important consideration to bear in mind concerning the residual effect of heavy metals is the matter of temperature. In areas of higher temperature regimes, organic matter decomposition is faster, and the protective role of humic substances over metal availability is less important than in temperate countries. Antoniadis and Alloway [97] tested the behavior of heavy metals in two different temperature regimes (namely 15 and 25°C) in a pot experiment for 2 years. They found that, over time, heavy metal availability to plants and extractability with 0.01 M $CaCl_2$ were higher at 25°C than at 15°C.

White et al. [98] applied sludge at a rate of 45 and 90 t ha^{-1} in a land with warm temperatures and measured the extractability of metals with DTPA over a period of 9 years. They found that DTPA-extractable Cd, Pb, and Zn increased significantly (Cd and Zn had nearly a tenfold increase) until the fourth year; then they subsequently decreased. However, metal concentrations were significantly higher at the end of the experiment than at the beginning. Although they failed to explain the reasons for the peaks in metal concentrations in the fourth year, their work provided evidence that heavy metal extractability may be significantly enhanced, especially in warm environments.

3.4 CONCLUSIONS: IS LAND APPLICATION OF SEWAGE SLUDGE SAFE?

From the preceding discussion, it becomes evident that the answer to the question of whether application of sludge to agricultural lands is a safe practice may not be a simple "yes" or "no." Heavy metal behavior and fate depend on their chemistry in soil inorganic and organic phases; their bioavailability depends on a variety of factors concerning the ambient environment, soil, and sludge. For some, the fact that the research evidence of the last three decades — even in cases of sludge application far exceeding regulation limits — does not clearly point to any major contamination risk for crops, animals, and humans is sufficient to assure that "high-quality biosolids may be used beneficially in sustainable agriculture" [99] if appropriate regulations are followed.

Others adopt a different perspective and consider that the lack of evidence of any significant contamination risk is not sufficient to render the matter settled. The fact that there is no clear evidence of absolute safety should lead to more caution and impose the need for more research. Otherwise, as McBride [5] put it, “the long-term consequences of the application of metal-laden sewage sludges…are still unknown.”

It is undisputable, however, that heavy metals deposited in the soils with sludge application will stay there for a long time. Evidence so far bears promising elements in support of the use of sludge because metals are strongly bound onto organic phases, especially when the sludge application follows the relevant regulations. However, this does not rule out any future risks because of serious predictions for changes in climatic conditions that will alter heavy metal chemistry due to possible alteration of organic matter decomposition patterns and heavy metal behavior when concentrations approach a crucial threshold, after which their mobility may be less beneficial for the environment [100]. Ongoing research efforts may provide a more substantial answer to the matter.

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