Section V

Risk Assessment

31 Risk Assessment, Pathways, and Trace Element Toxicity of Sewage Sludge-Amended Agroforestry and Soils

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CONTENTS

31.1 INTRODUCTION

Heavy metal accumulation in farming soil depends mainly on the heavy metal concentration in fertilizers or amendments and the application rate of each. Use of municipal sewage sludge as soil amendment is of current interest because of environmental and economic concerns. Application of sludges, as sources of plant nutrients, to soil at rates consistent with the nutrient requirements of a crop are believed to be most beneficial. It has been observed that sludge application reduces the surface runoff and gives some protection against soil erosion [1]. The composition of sewage sludge varies greatly depending on the source of sewage (domestic, industrial, etc.) [2]. The undesirable consequence of sludge application arises from the heavy metal content of the sludge, which may be taken up by the plants [3] and will have indirect impacts on animal health, human health, and/or the environment.

When considering the toxicity of heavy meals, the route by which the smallest amount of an element can cause harm is used as the limiting concentration. For most heavy trace elements, this limiting route of exposure falls into one of the three categories: plant growth, animal health, or human health [4,5]. When elements such as Cu and Zn are applied to soil in excess, they can accumulate in plant tissues and interfere with plant growth [4]; different soil types and soil pH will affect how plants react to these heavy trace elements in the soil. Additionally, many plants have different element uptake rates and heavy metal tolerances. All these factors will affect the potential crop effects of heavy trace elements in sewage sludge. Decrease in crop yield can occur and this could lead to crop loss if heavy trace elements are applied in excess to heavy metal-intolerant plants [4,6].

During the last decade, concern about the hazards of toxic trace elements for human health and the environment has increased worldwide. In many countries, legislative and administrative measures have been taken to reduce environmental contamination and to prevent adverse effects resulting from environmental exposure to metal pollutants [7,8]. Because the consensus is that trace elements in soil may be taken up by plants and thus enter the food chain, value limits for maximum tolerable metal concentration in agricultural soils were set in various countries [1,9]. Sewage sludge can be the most important localized source of heavy metal increase in agricultural soils, so the existing limits have been developed to regulate sludge application in agriculture [10,11] (Table 31.1).

In India, treated or untreated sludge is dumped indiscriminately on land or directly applied to agricultural land as manure. In drought-prone areas of India, it has been a common practice to cultivate food crops in sludge-amended soils. Land application of municipal sewage sludge is one of the most commercial alternative methods for solving the waste disposal problem and increasing the organic matter content of the soil in India. However, little work has been carried out on sludge-amended soils and the risks associated with them.

As a result of their nonbiodegradable nature, heavy trace elements present in soil accumulate by organisms and undergo biochemical cycles in the environment during which they are transformed with various chemical species [12]. Knowledge of the chemical state of trace metal in the biogeochemical cycle or biological fluids is important for undertaking their reactivity, transport, and toxicity [13,14]. The potential toxicity of various trace elements is controlled to a large extent by their physicochemical forms. Biochemical and toxicological investigations have shown that, for living organisms, the chemical form of a specific element or the oxidation state in which the element is introduced into the environment, as well as the quantities, is crucial [15,16].

To get information on the activity of specific elements in the environment — particularly for those in contact with living organisms — it is necessary to determine the total content of the element and to gain an indication of its individual chemical and physical forms [16]. Thus, the chemical form and species of the metal present in sludge-amended soils (SAS) in which vegetables are grown becomes an important parameter. In all the studies carried out on the application of sludge and its possible entry into food chain, the total metal concentration is reported, rather than the forms in

TABLE 31.1
Permissible Limits of Trace Elements in Biosolids

	King County biosolids for 2000		EPA standards	
Trace elements	**South (mg/kg)**	**West Point (mg/kg)**	**Exceptional quality (mg/kg)**	**Maximum limit (mg/kg)**
Arsenic	7.3	7.1	41	75
Cadmium	4.4	3.7	39	85
Chromium	36.5	45.3	1200	3000
Copper	642.1	529.1	1500	4300
Lead	51.0	141.3	300	840
Mercury	2.7	2.8	17	57
Molybdenum	14.6	11.1	Na	75
Nickel	21.9	35.0	420	420
Selenium	6.4	6.0	36	100
Zinc	714.9	803.8	2800	7500

which metals are present. This chapter reviews application of sludge as manure and health risks associated with the trace elements present in the sludge, as well as factors affecting metal mobility.

31.2 SEWAGE SLUDGE

Sewage sludge (often referred to as biosolids) is the mud-like material that remains after the treatment of household and industrial wastewater that flows into sewage treatment plants. This malodorous mess contains volatiles, organic solids, nutrients, disease-causing pathogenic organisms, heavy trace elements, etc. The chemical composition and physical characteristics of the sewage sludge depend upon the nature of the sewage water treated in the sewage plant and the treatment process used. The options for dealing with sewage sludge include its application to agricultural land, incineration, land reclamation, landfill, forestry, and sea disposal. The benefits of recycling biosolids onto agricultural land include providing essential nutrients for crop needs and organic matter for improving the tilth, water-holding capacity, soil aeration, and as an energy source for earthworms [17] and beneficial microorganisms [18].

Crop yield on land amendments with biosolids can be as great as or greater than that on land fertilized with only commercial synthetic fertilizers (Table 31.2) [19]. Organic nitrates constitute a significant fraction of the organic solids. When applied to the land for agricultural or horticultural purpose, nitrates are gradually mineralized through a biological decomposition process. They then became nutrients feeding plants. The inorganic fraction contains mineral salts; adding minerals to soil to improve plant growth has been recognized for centuries. Sludges contain most of the 13 mineral elements considered essential for plant growth that are often not economically viable with chemical fertilizers [20]. Many plant species respond to biosolids favorably because they release nitrogen and also contain phosphorus and potassium [21]. The crops use the organic nitrogen found in biosolids very efficiently; because it is released slowly throughout the growing seasons, the crop can take it up as it grows [22]. Biosolids may also correct crops' micronutrient deficiencies [23].

31.3 TRACE ELEMENT TOXICITY

Despite these positive results of soil amendment with biosolids, the dark side of the sludge is evident in the health risks. Sewage sludges also contain components considered to be harmful to the environment. Sewage sludge contains three constituents of environmental concern: (1) heavy metals; (2) organic pollution; (c) pathogenic organism [24]. Generally, sludges contain heavy trace elements such as Cu, As, Cd, Ni, Zn, and Pb in diverse concentration; these originate from a number of different sources, such as industry, commerce, business, domestic household waste, corroding pipes, and runoff from roads and roofs [5].

TABLE 31.2
Comparison of Main Nutrient Loads between Various Fertilizers Used

	Nutrient load in 1000 t		
	N	P	K
Manure	128	20.5	162
Mineral fertilizer	53	7.4	27
Sewage sludge	3.7	2.2	0.25
Compost	2.9	0.74	1.8
Other organic water	1.5	0.57	1.5
Total	189	31.4	192

Some heavy trace elements (Cu, Zn, etc.) are micronutrients essential for plant growth and therefore are beneficial to the crops; however, in excessive amounts they can reduce growth or can be toxic to plants [25]. Other heavy trace elements present in sewage sludges (As, Cd, Hg, Pb, and Se) are not essential for plants, but are toxic above certain defined levels [26–28]. Similarly, animals will have different tolerance levels for heavy trace elements, e.g., cattle are more susceptible to Se poisoning than sheep are [4]. Many trace elements present in sewage sludge form stable complexes, when applied to soil, with biomolecules and their presence in even small amounts can be detrimental to plants and animals [29,30].

In the soil environment, a heavy metal ion can undergo a number of processes and will be distributed among its different chemical forms and physical phases (water-soluble mobile phase, organic matter bound, oxide bound, etc.). It was found that trace elements that form stable complexes with ligands tend to be more toxic and remain in the soil for much smaller periods of time [15,31,32]; this can result in phytotoxicity and increased movement of trace elements into the food chain. Figure 31.1 illustrates the speciation of heavy trace elements in a soil–water system [33,34].

The processes that determine the speciation of trace elements in a soil environment are [33–35]:

- Precipitation and dissolution
- Sorption and desorption
- Complexation with organic compounds
- Complexation with inorganic compounds

Which of these processes occurs depends on the chemical characteristics of the trace elements and properties of the soil environment.

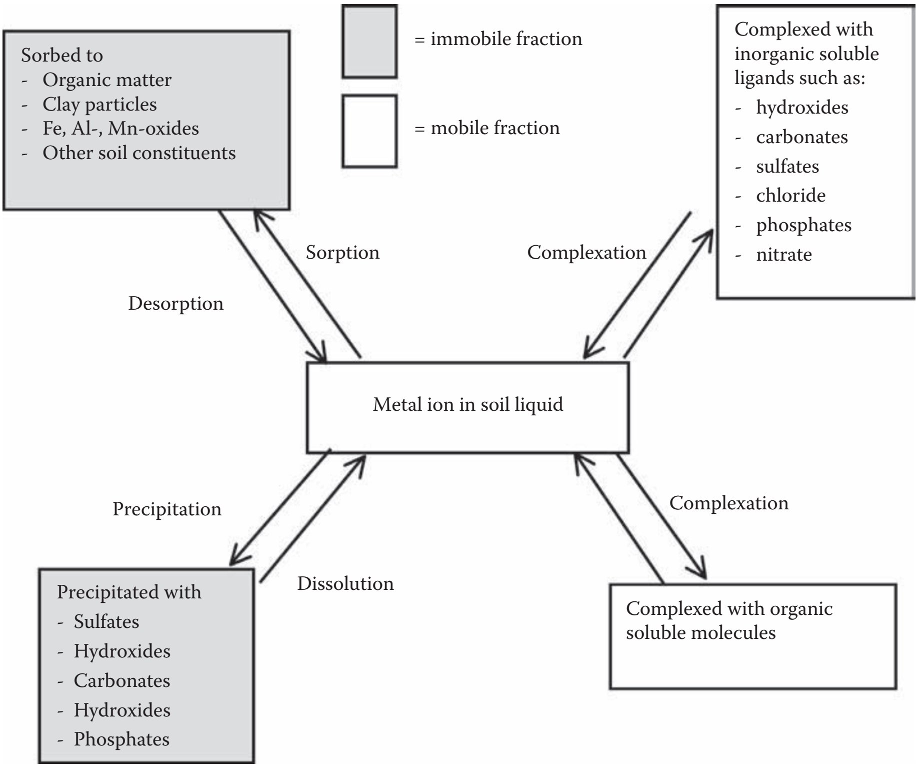

FIGURE 31.1 Fractionation of trace elements in soil–water system.

Depending on their nature, heavy trace elements are associated in a variable manner with different phases making up the sludge. The distribution of heavy trace elements in the different forms and phases in which they occur in soil and sludge can be determined using sequential extraction procedures [36,37]. These procedures provide information about the differentiation of the relative binding strength of the metal on various solid phases and about their potential reactivity under different physicochemical environmental conditions.

31.4 PROPERTIES AFFECTING TRACE ELEMENT MOBILITY

Once they have entered the soil, heavy trace elements can be removed from a given soil volume if they enter the soil solution because this is the mobile part of the topsoil system. The more metal that can be found in solution, the more of it is available. The soil properties determining the speciation of heavy trace elements are as follows:

- pH. Sorption of heavy trace elements depends strongly on pH; in general, sorption increases with increasing pH. That is, the lower the pH value is, the more metal can be found in solution and thus the more metal is mobilized. When pH falls to below 5, mobility is enhanced as a result of the increased proton concentration. At pH values above 7, some heavy trace elements tend to form hydroxyl complexes, which will increase the solubility of the metal in question [38,39]. A soil that has high pH and high cation exchange capacity will be able to immobilize the trace elements added to it via the sewage sludge. An alkaline soil may not always remain that way; thus, if the pH drops at a later stage (i.e., becomes acidic), the trace elements may get released [40].
- Organic matter. The organic matter makes trace elements soil most strongly onto the soil constituents [41,42]. The chemical composition of soil water determines which ligands are available for complexation, whether precipitation is likely to occur, and whether competitive sorption exists. For example, the presence of chloride ions in the soil solution has been shown to enhance the mobility of some heavy trace elements by the formation of more soluble complexes [43].
- Redox potential. The oxidation state of a given metal is determined by the redox potential. Different oxidation forms of a metal behave differently chemically. For example, chromium in the oxidation state (+6) is much more soluble and toxic than chromium in the oxidation state (+3) [43,44].
- Cation exchange capacity (CEC). The CEC of a soil is a measure of the negative charge density of a soil as function of the soil's ability to adsorb positively charged ions, cations. Thus, a high CEC reflects a soil with a high sorption capacity. Quebec researchers [45] suggest that the maximum heavy metal concentration in soils be based on the CEC of the soil, which is a measure of soil's ability to retain heavy metal ions. CEC increases with increasing clay content of the soil. Thus, they recommend maximum heavy metal concentration for fine textured soils, such as clay and clay loam, rather than for coarse textured soils, such as sand. Table 31.3 shows the recommended maximum concentration (ppm) of heavy trace elements in soils based on their cation exchange capacities [45].
- Soil texture. Texture reflects the particle size distribution of the soil and thus the content of fine particles like oxides and clay. These compounds are important adsorption media for heavy trace elements in soils.
- Temperature. Several chemical reactions are temperature dependent in the way that they proceed at a higher rate when temperature increases.

It is now well established that determination of the individual physicochemical forms and phase of metal are required for understanding the role of trace elements in the environment or human health [4,31,47]. One of the main interests has been the state of elements found in the soil and

TABLE 31.3
Recommended Maximum Concentrations (ppm) of Trace Elements in Soils Based on Cation Exchange Capacities (CEC)

CEC[a]	Cu	Co	Hg	Cd	Cr	Zn	Pb	Ni
CEC > 15	50	34	0.14	2.4	120	160	70	60
CEC < 15	25	>17	0.07	1.2	60	80	35	30

[a] Measured as milliequivalents (meq) per 100 g.

their effect on living organisms. Speciation in environmental, toxicological and biochemical aspects usually refer to very low concentrations; these may be even two orders of magnitude lower than the total concentration of the element, which is mostly in the range of extreme trace analysis [48–51].

In most soil environments, sorption is the dominating speciation process; thus, the largest fraction of heavy metal in a soil is associated with the solid phase of that soil [52]. Pollution problems arise when heavy trace elements are mobilized into the soil solution and taken up by plants or transported to the surface or ground waters. Therefore, the properties of the soil are very important in the attenuation of heavy trace elements in the environment. The U.S. Environmental Protection Agency (USEPA) has issued numeric standards for ten trace elements (As, Cd, Cr, Cu, Pb, Hg, Mo, Ni, Se, and Zn) [53]. However, the movement of trace elements from soils into ground water, surface water, plants, and wildlife — and of the hundreds of other toxins in sludge, which EPA chooses not to regulate — is poorly understood [54]. Their movement depends upon at least the following factors: plant species, soil type, soil moisture, soil acidity or alkalinity, sludge application rate, slope, drainage, and the specific chemistry of the toxins and of the sludge [6,55].

In creating its regulations, the EPA assumed that sludge-treated land would be under the perpetual care of a farmer who would lime the soil to keep it alkaline and prevent the trace elements from moving dangerously. For this reason, a build-up of toxic heavy trace elements in soils is often dismissed as irrelevant. However, in the real world, farmers go out of business while acid precipitation keeps soaking soils with dilute acid year after year [56]. Soil acidity seems to be the key factor in promoting or retarding movement of toxic trace elements into ground water, wildlife, and crops [50,57].

31.5 BIOAVAILABILITY OF TRACE ELEMENTS

The trace elements present in sewage sludge may be divided into three categories on the basis of their availability to plants (Figure 31.2) [58–60]:

- Unavailable forms, such as insoluble compounds (oxides or sulphides)
- Potentially available forms, such as insoluble complexes, trace elements linked to ligands, or forms attached to clay and organic matter
- Mobile and available forms, such as hydrated ions or soluble complexes

The fraction of the total metal content in a soil available for plant uptake, i.e., the bioavailable fraction, is usually considered to be the sum of water-soluble and exchangeable metal. Factors affecting transference of the trace elements to the plants are temperature, total metal contents of the soil, and time [3,61]. Temperature has been shown to have an effect on the resulting metal concentration in plants grown on sewage sludge-amended soils. When the temperature rises, the metal activity in the soil solution may increase and the plant roots may be more active and have

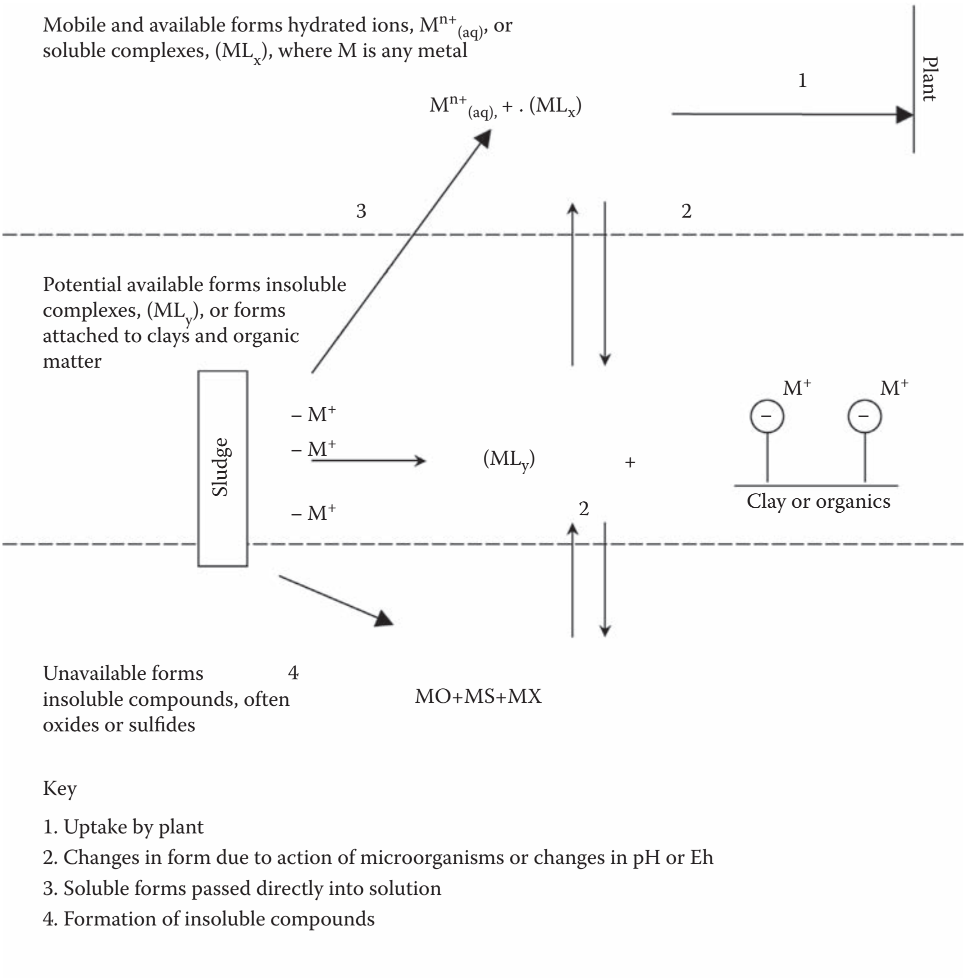

FIGURE 31.2 Availability of trace elements from sewage sludge. (From Ashwathanarayana, U., *Soil Resources and the Environment*, Oxford and IBH Publishers, New Delhi, 1999.)

faster absorption rates. Furthermore, the absorption rate of the roots may be increased as a result of higher evapotranspiration from the plant [3].

The concentration levels in plants also depend on the concentration levels in the soil. Several studies have established that metal concentrations in plants increase with increasing metal content of a specific soil [3,61–63]. Time after application of the sludge — the so-called residual time — may affect the mobility and thus the metal content in the plants grown on it [64]. When the organic matter applied with the sludge is decomposed, sorption sites are lost and the accompanying pH decrease also affects desorption of trace elements [65]. It has been shown that the metal content increased in successively harvested plants grown on a sewage sludge-amended soil. Thus, the availability of trace elements in the amended soil may change over time [43,66].

The large amount of organic matter in the sludge has been shown to present excessive plant uptake on a short term basis [43,67]. It has also been argued that a fraction of the organic matter resists degradation and will provide protection against plant uptake and leachability of the trace elements on a long-term basis. However, this depends on soil and sludge chemistry [67,68]. Repeated application of trace element-contaminated sewage sludge can result in an accumulation of toxic trace elements in the soil [69]. Once accumulated, trace elements are highly persistent in the topsoil [15,70,71] and can cause potential problems such as phytotoxicity [72], injury to soil microorganisms [73], or elevated transfer to the food chain [74–76].

Current debates on the bioavailability of sludge-borne trace elements center on two hypotheses. The first concerns how the bioavailability of trace elements is likely to change following the termination of sludge application. Some advocate the "sludge protection hypothesis," which states that sludge-borne trace elements are maintained in chemical forms of low bioavailability by inorganic components of the sludge and that the specific metal absorption capacity added in sludge will persist in the soil. According to this hypothesis, sludge-borne trace elements should become less bioavailable with time as surface adsorbed trace elements become occluded.

In contrast, others believe that sludge-derived organic matter contributes significantly to the metal adsorption capacity and that slow mineralization of this organic matter could release trace elements into more soluble, more phytoavailable forms. This is often termed the "sludge time bomb hypothesis." Because the decomposition of sludge organic matter is often associated with an acidification of soil, if this is uncorrected, further increase in the bioavailability/phytoavailability of the sludge-borne trace elements would be expected [31,77,78].

From an ecotoxicological point of view, any addition of trace elements will have some impact on organisms in the soil, vegetation, and food chain [79]. If a metal enrichment policy of environmental protection is followed, adopting the approach maintaining the metal balance in soils can diminish the potentially adverse effects of sewage sludge application to soil. If an accumulation of trace elements in sewage-treated soils is accepted, the maximum permissible metal concentrations in the soil depend upon the organisms that regulations are intended to protect, assuming that the cause–effect relationships are known [80].

Transfer coefficients (concentration of metal in the aerial portion of a plant relative to total concentration in the soil) are a convenient way of quantifying the relative differences in bioavailability of trace elements to plants. Alloway and Ayres [30] and Kloke et al. [76] have given generalized transfer coefficients for soils and plants (Table 31.4). However, soil pH, soil organic matter content, and plant genotype can have marked effects on metal uptake. The transfer coefficients are based on root uptake of trace elements, but plants can accumulate relatively large amounts of trace elements by foliar absorption of atmosphere deposits on plant leaves.

Table 31.4 shows that Cd, Tl, and Zn have the highest transfer coefficients — a reflection of their poor sorption in the soil [29]. In contrast, trace elements such as Cu, Co, Cr, and Pb have low coefficients because they are usually strongly bound to the soil colloids. The most toxic trace elements for high plants and several microorganisms are Hg, Cu, Ni, Pb, Co, Cd, and, possibly, Hg, Be, and Sn [81]. Although the occurrence and toxicity will depend on soil factors such as pH, plant genotype, and source of trace elements, a general indication of the toxic levels of some trace elements is given in Table 31.5 [82].

TABLE 31.4
Transfer Coefficient of Trace Elements in the Soil–Plant System

Element	Transfer coefficient	Element	Transfer coefficient
As	0.01–0.1	Ni	0.1–1
Be	0.01–0.1	Pb	0.01–0.1
Cd	1–10	Se	0.1–10
Co	0.01–0.1	Sn	0.01–0.1
Cr	0.01–0.1	Tl	1.0–10
Cu	0.01–0.1	Zn	1.0–10
Hg	0.1–1.0		

Source: From Kloke, A. et al., in *Health*, Springer–Verlag, Berlin, 1984. With permission.

TABLE 31.5
Normal and Phytotoxic Metal Concentrations Generally Found in Plant Leaves[a]

	Concentration in leaves (μg/g)	
Element	Normal range	Toxicity
Ag	0.01–0.8	1–4
As(III)	0.02–7	5–20
Cd	0.1–2.4	5–30
Cu	5–20	20–100
Cr	0.03–14	5–30
Hg	0.005–0.17	1–3
Ni	0.02–5	10–100
Pb	5–10	30–300
Sb	0.0001–2	1–2
V	0.001–1.5	5–10
Zn	1–400	100–400

[a] Alloway, B.J., in *Heavy Metals in Soils*, Alloway, B.J. (Ed.), Blackie and Sons, Glasgow, U.K. 1990; based largely on Bowen, H.J.M., *The Environmental Chemistry of the Elements*, Academic Press, London, 1979. With permission.

Usually, lime application reduces uptake of Zn and Ni more than Cd [83–85]; no decrease in availability is noticed in the case of Mo and Se [85]. Metal uptake in response to liming may also vary among plant species [86,87]. Liming decreased more Cd uptake by lettuce and carrot than by potatoes and peanuts [74]. Some evidence indicates that pH of about 6 is high enough to regulate metal uptake [88]. Increase of pH to 6.5, recommended for controlling trace elements in the food chain, does not seem to be necessary [89]. This finding is of practical importance because liming of acidic soils to pH 6.5 is often costly and can require a considerable amount of time.

The effect of other soil properties on element uptake by plants is less evident than that of pH, and the results are often conflicting. Hinesly et al. [91] conducted a study to determine the effect of CEC on Cd uptake by corn. The soil CEC inversely affected Cd uptake by corn when the metal was applied as a soluble salt, but not when Cd was supplied as a constituent of sewage sludge. These experiments were further confirmed in greenhouse studies conducted by Korcak and Fanning [92].

Some trace elements exhibit affinity for soil organic matter (OM), which has the CEC property and chelating ability. Therefore, addition of sewage sludge, peat, or plant residues can bind trace elements in soil. On the other hand, because of chelating ability, OM is viewed as a source of soluble complexing agents for trace elements. The binding ability of organic matter is not permanent; it is generally agreed that the OM level in soil must eventually return to a value not much greater than that of the original soil [38].

Trends in metal availability as a function of metal content in soils can be described by three models: (1) linear (constant partitioning model); (2) plateau (saturation model); and (3) the Langmuir sorption model (Figure 31.3) [10]. Usually, uptake of trace elements by plant tops does not occur in linear response to concentrations of the metal in soils, except at a low range of concentrations [10,38,92]. Uptake of trace elements by plants becomes less efficient at higher metal loading in soil, and the plateau relationship is used to describe this saturation effect [93]. Soils have a finite capacity to immobilize trace elements by adsorption or precipitation. When this protective potential is exceeded, a Langmuir type of relationship is expected (Figure 31.3). This relationship is found sometimes for trace elements added to soil in soluble salt forms [94]. Under more realistic field conditions, when trace elements are introduced to soil with sewage sludges or with industrial wastes,

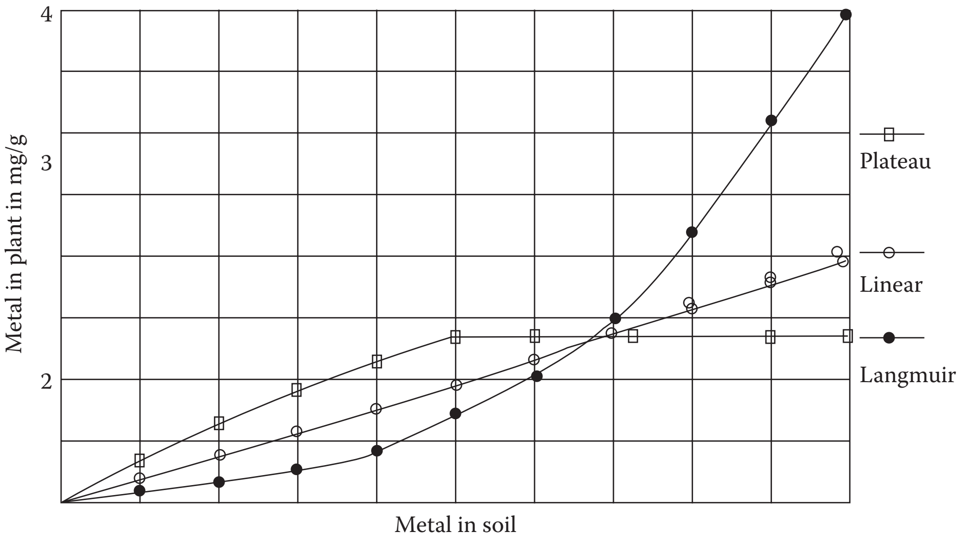

FIGURE 31.3 Metal availability as a function of metal content of soils. (From Dudka, S. and Miller, W.P., *J. Environ. Sci. Health B*, 34(4): 681–708, 1999.

the plateau model prevails because it best describes the plant response to increased metal concentrations in the soil [10].

The simple soil–plant relationship of plant element uptake is often modified by environmental, plant, and soil factors [95]. As a result, only a small proportion of elemental variability in plants can be explained by element concentrations in soils. Plants can accumulate trace elements, in their tissues due to their ability to adapt to various environmental conditions [96–98]. Plant uptake of elements from the soil solution requires positional availability to the plant root. The element must be moved to the root through diffusion or mass flow or the root must grow to the element [99]. This transfer requires that the element move through a solution phase. Therefore, water solubility and a variety of complexation, chelation, and other chemical reactions controlled by pH become important in regulating element availability [100].

Except for a few special cases, plant tissue concentrations do not positively correlate with total element content of untreated soils [101]. The element concentrations in plant tissues vary greatly, depending on species and cultivate, plant organ, age, and environmental conditions [102–107]. The extent of increase in trace element concentration above control for crops grown on metal-contaminated soils is strongly affected by crop species [108]. Studies conducted in England report [109] the response of many crop species grown in the same experiment on two soils contaminated with long-term sludge application. The relative crop uptake removes factors other than crop species (or cultivate). Leafy vegetables and, interestingly, wheat grains had the highest relative increased uptake of Cd [110,111].

31.6 ENVIRONMENTAL PATHWAYS AND HEALTH RISK ASSESSMENT

Trace elements' accumulation in soils and their entry into the food chain associated with land application of municipal sewage sludge has been reported [112]. Accumulation of trace elements in the tissue of edible vegetables grown on sludge-treated soils is well established [74,113]. Increased levels of Cd, Zn, and Ni were demonstrated in beets and chard grown on soils receiving sludge for many years [114,115]. Although these studies contain valuable information, they accept the site "as is," with little or no information on the amounts and characteristics of applied sludge, or soil changes that occurred after initiation of sludge application [116].

Other researchers investigated the extent of sludge-born metal accumulation in the edible tissues of seven vegetable crops [117]. According to these workers, metal accumulation was maximum in leaf tissue and the Zn and Cd content of edible fruits, tubes, and root tissues increased significantly; the Cu and Pb levels remain unchanged. Higher metal levels in vegetation against storage tissues for different vegetable species [118,119] has also been reported. Dowdy et al. also carried out extensive work on the growth and metal uptake of snap beans grown on sewage sludge-amended soil [121]; performance of goats and lambs fed on corn silage produced on sludge-amended soil [121]; and trace metal and mineral composition of milk and blood from goats fed silage produced on sludge-amended soil [122,123].

There is good reason to believe that livestock grazing on plants treated with sewage sludge will ingest the pollutants through the grazed plants or by eating sewage sludge along with the plants [124]. Sheep eating cabbage grown on sludge developed lesions of the liver and thyroid gland. Pigs grown on corn treated with sludge had elevated levels of cadmium in their tissues [125]. Cows, goats, and sheep are also likely to eat sludge directly. In grazing, these animals may pull up plants by the roots and thus ingest substantial quantities of soil [56]. A cow may ingest as much as 500 kg (1100 lb) of soil each year [126].

Small mammals have been shown to accumulate trace elements after sewage sludge was applied to forest lands. Shrews, shrew moles, and deer mice absorbed trace elements from sludge [127]. Insects in the soil absorb toxic trace elements, which then accumulate in birds [128]. It has been shown that sewage sludge applied to soils can increase the metal intake of humans eating beef (cow or buffalo milk) produced from those soils [129,130]. Studies have indicated that sludge application to soil increases the metal content in plants in this order [3,131]:

$$\mathrm{Zn} > \mathrm{Cd} > \mathrm{Ni} > \mathrm{Cu} > \mathrm{Pb} = \mathrm{Hg} = \mathrm{Cr}$$

The three basic methods for formulating limits to metal additions in soils receiving sewage sludges are: (1) analysis of pathways of metal transfers; (2) limits consistent with the no observed adverse effect level (NOAEL); and (3) metal balance approach [1,101]. The governing principle of the pathway approach [132] is that cumulative pollutant loading limits, which were derived from the analyses of various exposure pathways, will not be exceeded. To protect public health and the environment against the impact of high-metal sewage sludges, this regulation also defines maximum concentrations for metal present in the sewage sludge beyond which land application of the sludge is not permitted. The upper limit was calculated maximum concentration allowed according to the cumulative pollutant loading limits assuming sludge is applied at the annual rate of 10 tons per hectare for 100 years.

In adopting the environmental exposure pathway approach, one must select a target organism for each pathway. The process of selecting the contaminant-loading limit for each pathway is also based on the NOAEL. From the long-term perspective, it is very difficult to foresee whether the approach to setting limits for trace elements in soils allowing substantial increase in soil metal concentrations will be effective in protecting environment, food chain, and human health from adverse effects of potentially toxic trace elements. Limits consistent with the NOAEL are based on actual cases of effects due to trace elements, but not necessarily derived from studies that involved land application of sewage sludge.

The Commission of the European Communities (CEC) issued a directive to limit the inputs of potentially toxic trace elements to soil from sewage sludge so as to protect plant growth, crop quality, and human and animal health [133]. The directive has three types of metal limits:

- Concentrations allowed in sludges used for agriculture
- Maximum concentrations permitted in sludge-treated soils
- The 10-year average annual rate of addition of trace elements in sludge

The third category of defining rules for trace elements in soils, the metal balance approach, is concerned with the fact that, in industrial countries, the metal inputs to soil minus losses through crop removal, leaching, and erosion is positive for all trace elements studied [134,135]. These observations have led to a very cautious approach to the intentional addition of trace elements to soils. Quality standards and limits for pollutants in biosolids were developed from extensive environmental risk assessments conducted by USEPA and the U.S. Department of Agriculture.

The EPA used a rigorously reviewed methodology developed specifically for conducting the risk assessment [136,137]. The goal of the risk assessment was to protect a person, animal, or plant that is highly and continuously exposed to pollutants in biosolids. The rationale for this goal is that the general population would be protected if the regulations were developed to protect highly exposed individuals [19]. The risk assessment process was the most comprehensive analysis of its kind ever undertaken by the EPA. The approach has since been applied to other materials, such as municipal solid waste compost. The resultant part 503 rule was designed to provide "reasonable worst case," not absolute, protection to human health and the environment [19].

The initial task of the 10-year risk assessment process was to establish a range of concentrations for trace elements and organic compounds that had the greatest potential for harm based on known human, animal, and plant toxicities. Maximum safe accumulations for the chemical constituents in soil were established from the most limiting 14 pathways of exposure, which included risk posed to human health, plant toxicity and uptake, effects on livestock or wildlife, and water quality impacts [138]. The EPA screened a total of 200 chemical constituents and 50 of these were selected for further evaluation. The 503 rule was then limited to ten trace elements (arsenic, cadmium, chromium, copper, lead, mercury, molybdenum, nickel, selenium, and zinc). Chromium was subsequently dropped on a court challenge because the risk assessment had shown a very low risk level for this metal. The most limiting pathway for each of the nine regulated trace elements was used to develop pollutant concentration limits and a lifetime loading rate standard [139].

Under part 503, the cumulative loading limits established by EPA for eight trace elements would allow the concentrations of these elements to increase to levels 10 to 100 times the normal background concentrations in soil. The time for each of the eight elements to reach its cumulative loading limit when biosolid with typical trace element concentrations was applied annually at the rate of 5 dry tons per acre [19,140]. The cumulative loading limits were developed to ensure that the soil trace elements never reached harmful levels. Further applications of biosolids to the site would be prohibited if the cumulative loading limit for any of the eight trace elements was reached.

Although supporters of the 503 regulations believe that sludge-amended soils will maintain an ability to immobilize toxic trace elements in unavailable form, it is impossible to predict long-term consequences of high metal loading of soils. Predictions of no adverse effect on crops and food chain employ the sludge protection hypothesis, which states that the specific adsorption capacity added with sludge will persist in soil and will be effective in metal immobilization as long as trace elements are present in soils [92]. The experimental data, however, suggest that immobilization of trace elements in sludge-amended soils is due in some part to sludge organic matter. Therefore, the sludge time bomb hypothesis points out that slow mineralization of organic matter added with sludge could release trace elements into the more soluble forms, which eventually will adversely affect crop productivity and food chain quality [38].

In composts and sewage, as in wastes, trace elements are present in various chemical forms, which differ in respect to solubility in water, bioavailability, and stability [37]. The utilization of composts as fertilizers depends not only on the total content of trace elements but also on the chemical forms and phases in which they are present in compost and sewage [141]. The form in which a metal exists significantly affects its bioavailability, toxicity, and mobility in the soil to

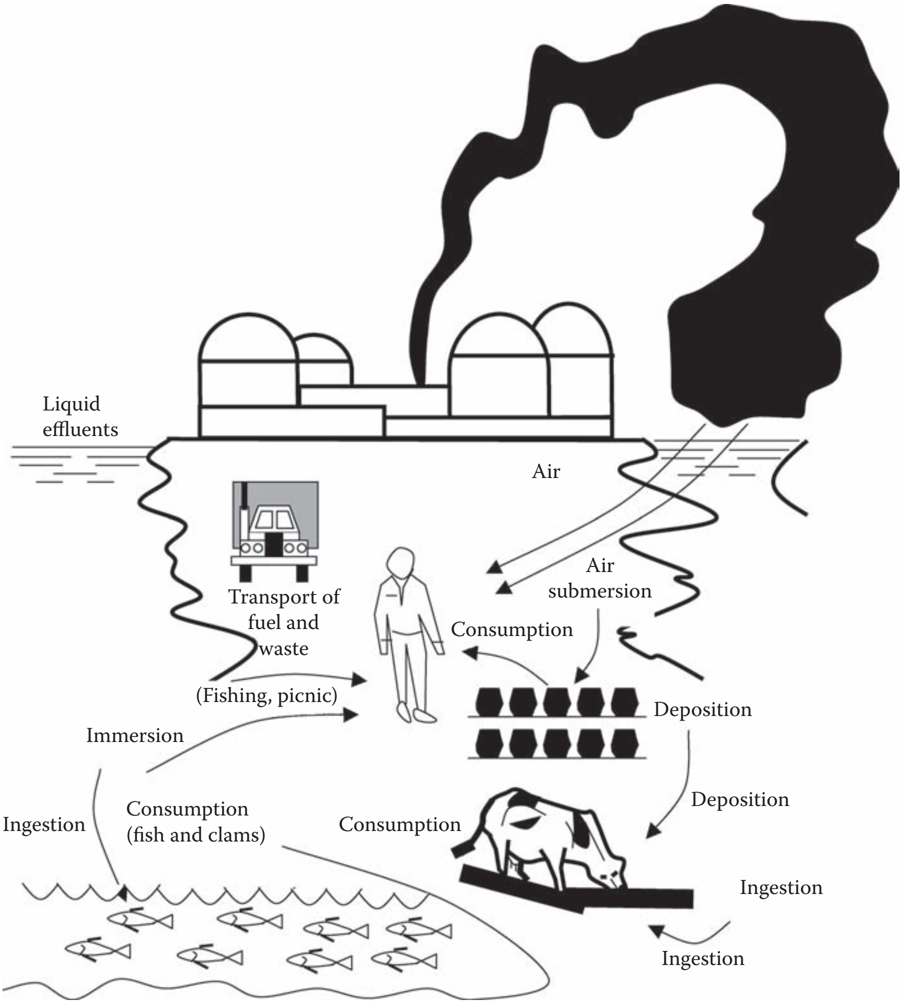

FIGURE 31.4 Pollutant transport and health risk associated with sludge-amended soils. (Modified and redrawn from USAEC, U.S. Atomic Energy Commission, WASH-1209, Washington, D.C., 1973.)

plant and, further, to human [142,143]. Possible distribution pathways of trace elements from sludge-amended soils are well illustrated in Figure 31.4 [144], which shows the movement of trace elements and the pathways that help determine whether individuals have been, are being, or will be exposed to trace elements contaminants.

Environmental pathways can be completed or potential. A completed pathway indicates that human exposure to contaminants has occurred, is occurring, or will occur. A potential exposure pathway indicates that human exposure to contaminants could have occurred, could be occurring, or could occur in the future. The movement, mobility, and transport of trace elements from soil to human can be well understand by the speciation analysis of trace elements [37,145]. Biological cycling includes the bioaccumulation, bioconcentration, bioavailability, and toxicity; geochemical cycling involves the transport, adsorption, and precipitation of the element in the water–soil system.

It is now well established that no meaningful interpretation of biological or geochemical cycling can be made without speciation information [146,147]. When the sewage sludge amendment of soils is judged by the potential health effects of trace elements, it should be emphasized that sewage sludge is not the only source of trace element contamination of soils. The knowledge of how trace elements are distributed in the environment and which processes affect the distribution can be used to evaluate the potential of sludge amendment of a certain soil with respect to trace element migration. Amending an acidic sandy soil with sewage sludge seems to be a bad idea. Such a soil may have no retaining capacity and, when the sludge starts to decompose, trace elements are susceptible to migrate at a high rate.

The movement, mobility, and transport of trace elements from soil to human can be well understood by the speciation of trace elements, which essentially include four main steps:

- Evaluation of the quantity of trace elements in the sewage sludge
- Evaluation of the levels of trace elements in the soil, water, vegetation, milk, etc.
- Identification of the exposure pathways and determination of ambient levels that result from the sources
- Identification of the population exposed to the trace element pollutants by carrying out epidemiological studies

31.7 INDIAN SCENARIO

Treated and untreated sewage and sewage sludge are extensively used for cultivation in the suburban areas of India and food crops and vegetables are grown in sludge-amended soils. Olaniya et al. [149] conducted a case study on trace element pollution in agricultural soil and vegetation due to the application of municipal solid waste in the Dhapa disposal site near Kolkata. At this site, fresh municipal solid waste results in accumulation of toxic trace elements in the soil; when edibles are grown on such soils, toxic trace elements enter into the food chain and pose risks to human health [149]. To determine the accumulation of trace elements, Srikanth et al. [150] conducted studies on forage grass (Guinea grass) cultivated in urban sewage sludge along the bank of River Musi, which receives sewage from the city of Hyderabad.

The same authors reported high concentrations of Pd, Cd, and Cr in various vegetables grown in urban sewage sludge, indicating possible health hazard for consumers [151]. The risk of toxic trace elements like Cd among the farmers working on sludge farms was reported by carrying out urine analysis on male sewage sludge farmers [152]. Ayyadurai et al. [153] studied the concentration of Pb and Cd in milk of cows and buffalos fed with fodder grown on wastewater sludge-irrigated soils. They reported that buffalo milk contained higher levels of Pb in comparison to that of cow milk in all the samples analyzed [153].

Much work has been carried out on the effects of trace elements on soil and vegetation, and their entry into human food chain [154]. Recently, a case study was conducted by the authors on the speciation and accumulation of trace elements in vegetation grown on SAS and their profound transfer to food chain. The results revealed that Ni, Cr, Pb, and Zn were associated often with the mobilizable fraction in the SAS; this was clearly indicated by the high concentration of these trace elements in the vegetables. The concentration factor (CF) for these trace elements in vegetables was calculated and it was found that Ni had maximum CF. The epidemiological studies showed that the trace element content — particularly, Ni, Pb, and Zn — was very high in people consuming these vegetables grown on SAS, indicating the metal transfer to food chain [156].

Forage grass grown on SAS was also analyzed for trace element content and Ni, Zn, and Pb concentrations were found to be high. Corresponding milk samples were collected from cows and buffalos fed on these forage grasses and high concentrations of Ni and Zn were found in milk compared to controls [156]. It is well known that the movement, mobility, and transport of trace elements from soil to human can be well understood by the speciation of the trace elements. Very little work has been carried out in India on these lines for assessing the mobility, phytoavailability, and transfer of trace elements to the human food chain.

31.8 INTERNATIONAL SCENARIO

31.8.1 SHORT-ROTATION FORESTRY USING SEWAGE SLUDGE AND BIOSOLIDS — IMPLICATIONS

Short-rotation forestry (SRF) is advocated as a means of phytoremediation and for disposing of sewage sludge [157]. Fast growing trees such as *Salix* (willow), *Populus* (poplar), *Alnus* (alder), and *Eucalyptus* (eucalypts) are ideal trees for SRF and have gained importance in mitigating CO_2, industrial effluents, and other air pollutants. Large quantities of fertilizer and water are required to sustain the intensive management of SRF. This demand prompted the application of sewage sludge, with the additional benefit of providing a viable alternative for the waste disposal [157–160].

SRF has been successful in Sweden for the production of biofuel for the past 20 years. SRF takes its name from the short rotation time typical of poplar and willows (4 to 6 years) compared to conifers (60 to 120 years) or broadleaved trees (35 to 50 years). Under optimum conditions (i.e., intensive management strategies), SRF can yield between 12,000 and 20,000 kg dry matter (DM) ha^{-1} yr^{-1}, although in general, lower yields of between 6000 and 9000 kg DM ha^{-1} yr^{-1} are more likely. If SRF is used for the generation of energy, approximately 4.5 MWh of energy can be produced from burning 1 ton of dry matter (50% moisture) [158].

A substantial body of data now indicates that biomass plantations are irrigated with sewage effluents; this helps in recycling effluents, biosolids, and other wastes. Current research on the use of sludge as a fertilizer for SRF indicates strongly that willow plantations may be able to perform the majority of the required cleanup steps well. SRF could be used as "vegetation filters" to utilize the nutrients in municipal sewage sludge, wastewater, leakage water, and bioash (wood ash), although dredged sediments containing organic chemicals and pathogenic bacteria have also been effectively "purified" following application onto biomass plantations [160, 161].

The tree species used in biomass forestry vary between areas in which they are grown. Many of the SRF species commonly used, especially *Populus* spp., have also shown considerable potential in the remediation of groundwater contaminated with inorganic chemicals — specifically, the *P. deltoides* × *nigra* and *P. trichocarpa* × *deltoides* clones. SRF fulfills important environmental and ecological factors: there is no net CO_2 contribution to the atmosphere compared to energy production using fossil fuel; in fact, there is a small net uptake. Pesticide use is lower than on conventional agricultural crops, and the growth of willows for SRF improves the condition of the soil as well as biodiversity

Primary requirements of SRF are a rich supply of nitrogen and water. The ability of fast growing trees to remove nutrients and water can also be applied to wastewater treatment; excessive concentrations of nutrient chemicals pose environmental problems when present in excess, such as eutrophication of streams and lakes, causing algal blooms, and a progressive reduction in potability. Standards usually monitor the biological oxygen demand (BOD), total N, ammonia N, and total P in water and often these strict regulatory limits cannot be met by conventional treatment methods alone.

The elimination of P from wastewater generally involves the use of large quantities of chemical agents, which are difficult to clean up once the process has been completed. Obarska–Pempkowiak [162] found that *Salix viminalis* and *S. arenaria* could significantly reduce the nitrogen concentration of municipal wastewater; in particular, *S. viminalis* reduced the total N concentration of wastewater from over 35 g m^{-2} to less than 5 g m^{-2} over a period of 270 days. Typical N and P contents of applied sludges are approximately 4.5 kg N t^{-1} and 2.8 kg P t^{-1} in the raw cake, of which 1.5 and 1.4 kg t^{-1} N and P respectively are available in the first cropping season. Willow and poplars irrigated with sewage sludge showed an increased yield and that the trees took up almost 95% of the N and P load of the effluent, simultaneously lowering the BOD of the effluent by an average of 96%.

Studies have emphasized that SRF can be used for "collecting" metals from the soil — in effect, using the trees as biological filters. Goransson and Philippot [163] found that almost all of the Cd applied during sludge application was taken up by *Betula pendula* and that, theoretically, the trees could remove 1.5 kg Cd ha^{-1} yr^{-1} when watered with sludge. Landberg and Greger [164] found that net transport of heavy metals to the shoots varied widely between 1 and 72%; therefore, certain clones were able to accumulate more metals than others, indicating the need for clone selection for resistant trees. The efficiency with which willows can remove metals from sewage sludge-fertilized soils has been demonstrated in several key studies.

Some evidence suggests that fast growing trees may be able to play a major role in reducing the concentration of organic chemicals in contaminated sludges, soils, and groundwater (see next section). Using land-farming techniques, Harmsen et al. used willows to remove PAHs from dredged harbor sediments and concluded that the high yield of biomass was instrumental to reducing the costs. Willows and poplar trees were also used in a multispecies wetland system to remove bacteria and other pathogens from municipal wastewater.

31.8.2 SLUDGE USAGE — INTERNATIONAL REGULATIONS

The residual product generated from sewage treatment is termed sludge. Sewage sludge contains heavy metals, organic compounds, and pathogens, in addition to substantial amounts of nutrients. Sludge may be disposed of by depositing, burning, or dumping into the sea or it may be used in forestry and agriculture. On the one hand, spreading sludge onto the land is desirable because the nutrients of sludge would participate in the biogeochemical cycle in ecosystems. However, due to the inherent nature of its composition, sludge involves the risk of harming the environment because the substances may be accumulated in the soil or damage the ecosystem. Thus, health considerations must be considered by environmental regulatory agencies with respect to the use of sludge because it contains pathogens in the form of bacteria, viruses, and parasite eggs. This content can be reduced by stabilization or disinfection of the sludge.

To ensure that the environment and man are fully safeguarded against the harmful effects arising from the uncontrolled use of sludge, it is necessary to regulate the agricultural use of sewage sludge. Therefore, most countries have legislation regulating the use of municipal sewage sludge in forestry and agriculture [165]. These regulations set maximum limits for the content of heavy metals in sludge (except in the U.K.). Limitations are set on the amount of sludge that can be spread on a given area, based on total amount of sludge (calculated as the amount of dry solids in the sludge), heavy metals, or nutrients added to the soil. It is especially with respect to this point that different national regulations vary [165]. In addition, there are restrictions in relation to certain crops and land uses, (it is normally not permissible to apply sludge to land to be used for growing vegetables). Germany prohibits spreading sludge on forest land, but Denmark and the U.K. permit this. Before application of sludge, chemical composition of the soil must be taken into account (pH, texture, and concentration of heavy metals).

Sludge producers are required to make analyses of the sludge. Typically, the frequency of the analysis is determined by the size of the treatment works and is intensified if the composition of the sludge is variable. The frequency varies from a daily sludge sampling to one analysis every second or fourth year; sometimes, with respect to certain substances, analysis is not required at all. Usually, sludge is analyzed for its content of heavy metals, nitrogen, and phosphorus, but identification of other substances may also be required. In Norway and the U.S., samples must also be taken for the control of pathogen content. Furthermore, in the U.S., it must be controlled whether the vector attraction reduction requirements of the sludge are met or not, so that the sludge exerts only a limited attraction to animals, which can transmit infection to other animals as well as to man. The frequency of the analyses and the substances for analysis vary among the different countries, so the use of sludge may be indirectly limited in some countries by the high cost of analysis.

For the purpose of controlling the legislation, the sludge producers must register the production and the agricultural use of their sludge. Therefore, the controls must be drawn up differently in the different countries. In all countries, except the U.K., maximum limits are set for the content of heavy metals in sludge. In addition, some countries have set value limits for arsenic, selenium, and molybdenum. Germany also limits the content of the following organic compounds: polychlorated biphenyles (PCB), polychlorated dibenzoefuranes and polychlorated dibenzoedioxines (PCBP, PCDF, PCDD), and organic halogens (AOX). The German value limits for the content of organic compounds in sludge are not set on the basis of qualified toxicological tests, but they are set out of prudence [165]. In Germany, the present content of PCB in sludge is unlikely to limit use of sludge, but the content of PCDD/PCDB may exceed the fixed limits. Furthermore, the analyses are complicated and costly [165].

In general, heavy metals and persistent organic compounds cause damage to the environment by accumulating, while the introduction of nutrients may harm the environment through the leaching of nutrients to the aquatic environment. The extent to which organic compounds are accumulated has not yet been clarified. The effects of heavy metals and organic compounds on the soil fauna have not been sufficiently investigated. One of the most important sources of pollution from persistent organic compounds is pesticides; the pollution caused by heavy metals arises from industrial deposition and fertilizers.

When comparing the regulations, remarkably large differences appear concerning the restrictions on heavy metals with respect to their concentrations in sludge and soil and to the quantities that may be spread. The general tendency appears to be that countries that permit the highest concentrations of heavy metals in sludge also permit the largest quantities of sludge to be spread annually and permit the highest concentrations of heavy metals in soil. Countries that have the most stringent requirements for the heavy metal content in sludge also have a tendency to have the lowest value limits for the permissible heavy metal content in soils.

The great variation between the countries with respect to the amount of heavy metals that can be applied to soils and the lesser variation with respect to the permitted heavy metal concentrations in soils where sludge can be applied give rise to very different time horizons for the use of sludge on individual areas. Therefore, the value limits for heavy metal concentrations in soils can be regarded as an "emergency brake" on the use of sludge. However, this emergency brake is only effective if the control of heavy metal concentrations in soils is effective in the countries that risk exceeding the value limits after a few years' use of sludge.

31.9 CONCLUSIONS

Biosolids can provide essential plant nutrients, improve soil structure and tilth, add organic matter, enhance moisture retention, and reduce soil erosion. Sewage sludge contains organic matter and plant nutrients beneficial to soil health and crop production. Applying sewage sludge to agricultural lands fits well with the current concepts of resource recycling and sustainable agriculture. However, because sewage sludge contains contaminants, such as trace elements, that may decrease the quality of agricultural soils, careful control of contaminant levels in soils receiving sludge is needed.

Contamination of soil by trace elements is a concern because they are persistent and may affect plant, animal, and human health. Application to agricultural soils is a beneficial method of managing sewage sludge, but adding contaminants to soil in this, and other, waste materials must be controlled. The trace element content of sewage sludge is the main factor that still restricts its agricultural use.

However, steps can be taken to decrease the availability of trace elements in sludge-amended soils. Trace element content in plants is strongly influenced by pH and sludge treatment. Increasing the pH of a sewage-amended soil or heat-treating it can reduce the plant metal uptake. Manipulating the soil pH is the most effective and rapid method of controlling the availability of trace elements in sludged soil. Liming the soil to a pH of 6.5 to 7 can reduce the mobile fraction of most of the trace elements in soil.

The trace elements in sludge are present in various chemical forms that differ in respect to solubility in water, bioavailability, and stability [166,167]. The utilization of sewage sludge as fertilizer depends not only on the total content of trace elements but also on the chemical forms in which they are present. The form in which a metal exists significantly affects its biological activity availability, toxicity, and mobility in the soil environment. It is well known that vegetation grown on sludge-amended soils poses a direct entry for trace elements into human food chain. India has no administration or legislative measures to control the continued application of sludge as a manure.

Most regulations in India concerning trace elements in food, occupational health, and environment are based on the total element contents and are frequently given as maximum limits or guideline levels. In contrast, few regulations pay attention to the molecular species (speciation) in which the elements are bound. There is a great need for the development of more species-specific analytical and toxicological data and modified regulations are necessary if India wants to enter the global market in the area of food, agriculture, and environment. Also, there is a need for creating a different speciation scheme to study the toxicity, mobility, and phytoavailability of these trace elements for the development of a model to predict the soil-to-cell movement of metal pollutants. The model representing the pathways of trace elements in the environment and prediction about the fate of these pollutants based on the speciation studies will help in reducing the risk due to the application of sewage sludge as manure.

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