Toxic metals in sewage sludge-amended soils: has promotion of beneficial use discounted the risks?

M.B. McBride*

Department of Crop and Soil Sciences, Cornell University, Ithaca, NY, USA

Abstract

Land application of contaminated waste products has been defended as beneficial use by some scientists and regulators, based on the premise that the behavior of any toxins accumulated in soils from this practice is reasonably well understood and will not have detrimental agronomic or environmental impacts into the foreseeable future. In this review, I use the case of toxic metals in sewage sludges applied to agricultural land to illustrate that metal behavior in soils and plant uptake is difficult to generalize because it is strongly dependent on the nature of the metal, sludge, soil properties and crop. Nevertheless, permitted agricultural loadings of toxic metals from sewage sludges are typically regulated using the sole criterion of total metal loading or concentrations in soils. Several critical generalizing assumptions about the behavior of sludge-borne metals in soil-crop systems, built into the US EPA risk assessment for metals, have tended to underestimate risks and are shown not to be well justified by published research. It is argued that, in the absence of a basic understanding of metal behavior in each specific situation, a more precautionary approach to toxic metal additions to soils is warranted.
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1. Introduction

There is an increasing tendency to favor land application over other means of disposal of industrial or commercial waste material that have characteristics potentially beneficial for agriculture (the 'beneficial use' philosophy) despite the fact these wastes may have other properties undesirable for agriculture or may contain significant concentrations of numerous contaminants. Because wastes such as sewage sludge are not designed for agricultural use, contain some level of industrial and commercial discharge, and are of variable and unpredictable composition, it would be fortuitous indeed if virtually none of them contained contaminants detrimental to soils or the environment in the short or

long term. The large number of potential toxic pollutants in municipal wastes such as sewage sludge renders thorough monitoring and regulation expensive and incomplete at best. Funding has not been sufficient to conduct the necessary research to examine the nature and behavior of all known toxic chemical contaminants in wastes and their potential long-term impact on soil productivity, as well as on human and ecosystem health. In the absence of this research, the 'beneficial use' philosophy presumes that the known and immediate economic benefits outweigh less certain foreseen (and unforeseen) negative impacts.

In the case of sewage sludge applied to farmland, research emphasis has been placed on a few heavy metals—those metals considered most likely to produce toxic effects on plants, animals and humans. In the United States, the US EPA conducted a detailed risk assessment and promulgated regulations in 1993 (Part

*Tel.: +1-607-255-1728; fax: +1-607-255-2644.
E-mail address:* mbm7@cornell.edu (M.B. McBride).

503 rule) that set limits on the loading of eight potentially toxic metals in sewage sludges (biosolids) applied to agricultural land. Certain features of the 503 rule, such as the lack of a cumulative soil loading limit for these metals if the concentration in the sewage sludge is less than the 'exceptional quality' (EQ) value, no consideration of individual soil (including initial soil metal concentrations) or sludge physico-chemical properties in setting metal loading limits, the calculation of loading limits on the basis of linear extrapolation of crop uptake coefficients (UCs), and the regulating of only a few of the toxic substances in sludges, rely upon certain assumptions about the behavior of sludge-borne chemicals in soil–crop systems based on limited evidence. These assumptions, articulated in publications (e.g. Chang et al., 1992; Chaney and Ryan, 1993; Logan et al., 1997) and used to develop the 503 limits for toxic pollutants (US EPA, 1992), have provided a rationale for allowing large increases in toxic metal concentrations in agricultural lands above present levels. A number of states in the USA have adopted these metal loadings essentially unchanged. Environmental agencies in other countries may be influenced by these limits in establishing new regulations. It is therefore important to re-evaluate carefully these key assumptions relating to metal behavior in soils and crops, and determine if they can be applied generally.

2. 'Clean sludge' concept

Hypothesis 1. Toxic metal solubility/bioavailability in a given soil/sludge system is more strongly determined by the metal concentration in the sludge than the cumulative metal loading in the soil.

In the United States, the 'clean sludge' concept led the EPA to coin the term 'exceptional quality' (EQ) to define sludges with metal concentrations at or below certain levels (e.g. 39, 17 and 300 mg/kg for Cd, Hg and Pb, respectively), but still much higher than concentrations in agricultural soils. The assumption is that, if the toxic metal concentration in a given sewage sludge is below this EQ value, long-term application would not increase the solubility or bioavailability of the metal to an unacceptable level because of the strongly adsorptive properties of the sludge matrix itself. The evidence supporting this assumption is sparse, as the most convincing test would require very long-term field experiments using marginally 'EQ' sludges at agronomic application rates. No such experiment has been conducted to the knowledge of the author. Nevertheless, some evidence relevant to the hypothesis is discussed here.

Logan et al. (1997) concluded that crop uptake of soil Cd would be less from soil treated with a sludge with low Cd compared to a high-Cd sludge, even when

actual Cd loadings were similar, citing the study of Jing and Logan (1992) as evidence. However, that study showed only a weak relationship between plant Cd uptake and total Cd concentration in sludge ($r^2 = 0.327$), but a much better relationship of plant uptake to Ca-extractable Cd ($r^2 = 0.909$). When the three sludges in this study that exceeded the 503 rule Cd concentration limit for land application (85 mg/kg) are excluded from the analysis, there is *no* significant relationship between plant uptake of Cd and total sludge Cd concentration. Thus, *total* Cd concentration in sludge was not a good measure of initially plant-available Cd, although, not surprisingly, easily extractable Cd was. It should also be noted that this study was carried out with a total soil Cd concentration of 2.5 mg/kg, representing a soil loading of approximately 5 kg/ha, much lower than the 503-allowed soil loading of 39 kg/ha. Inferences from studies such as this to situations where soil Cd loadings approach the 503 limit over long time periods would be based on uncertain extrapolation.

Other studies have also failed to indicate a consistent dependence of metal solubility or plant uptake on the *total* metal concentration in sludges. Thus, Rogers (1997), in contradiction of the 'clean sludge' hypothesis, found greater uptake of Cd into crops from a low-Cd than from a high-Cd sludge. In another study, bioavailability of Cd in soils amended with different sludges, as measured by uptake into wheat grain, was not predictable on the basis of total Cd, but was dependent on individual sludge properties (Zarcinas et al., 2001). Where Cd-contaminated sewage sludges and soluble Cd salts were applied at comparable total metal loadings on field plots, earthworms in the sludged plots bioconcentrated Cd to similar or higher concentrations compared to earthworms in the Cd salt plots (Beyer et al., 1982).

Longer-term field studies have demonstrated inconsistent evidence of the 'clean sludge' hypothesis. At similar soil pH and Cd loading, Brown et al. (1998) found that lettuce uptake of Cd was generally higher from plots treated with Cd-salt treatments than similar levels of sludge-Cd, even though the soil treatments had occurred 13–15 years earlier. This indicates a 'sludge protection' effect, which could be due to a number of constituents added to soil in sludge, such as residual organic matter, P, S and mineral residues. McBride (1995) reanalyzed the study of Mahler et al. (1987) on Cd uptake from soils with long histories of sludge application, and concluded that 'sludge protection' against Cd uptake into plants was not consistently observed and could be attributed largely to residual organic matter. In effect, crops grown in soils with low Cd/organic C ratios tended to be protected against excessive Cd uptake. In contrast, Whatmuff (1999) found that applying equal loadings of Cd to acid soils from low-Cd and high-Cd sludge did not, 8 years after

application, affect plant uptake of Cd. Furthermore, a gradual increase in Cd bioavailability over the 8-year period was noted, which may have been related to organic matter decomposition. Thus, no 'clean sludge' effect was measurable in strongly acid soils.

Chemical tests are no more convincing than bioassays in suggesting a reliable relationship between metal solubility in sludges and sludge quality (total metal concentration). DeVries (1983) found no relationship between total metal concentrations and the $CaCl_2$-extractable metals in sludges. Oliver et al. (2001) found no relationship between potentially available Cu and total Cu in sewage sludges. Richards et al. (1997) demonstrated that, for the same sludge material, the stabilization pre-treatment (dewatering, pelleting, composting, alkali stabilization) dramatically changed the leachability of several heavy metals.

Metal lability tests, measured using stable Cd and Zn isotope exchange with soil-bound metals, also fail to show clear evidence that metals added to soils from sludges have lower lability than other forms of metal additions. Thus, Knight et al. (1998) found that Cd added to a soil as $CdSO_4$ had much lower solubility and free Cd^{2+} activity (after 2 years of equilibration) than residual Cd in the same soil type amended with sewage sludge at least 36 years earlier. Almost all of the Cd in soils of a long-term sludge site was in the labile form, as measured by isotope exchange (Lloyd et al., 1981). A comparison of Cd lability by isotope exchange in soils containing approximately equal concentrations of Cd (22–34 mg/kg), and contaminated by either natural sources of Cd or by smelter emissions or sewage sludge, revealed a very similar degree of Cd lability (Ahnstrom and Parker, 2001). Labile Cd typically exceeds 50% of total soil Cd, regardless of the source of Cd contamination (sewage sludge, mining waste, atmospheric deposition, Cd salts) or length of equilibration time in the field (Broos et al., 2001). Young et al. (2001) demonstrated that isotopically exchangeable (labile) Zn in soils spiked with Zn nitrate, after less than 2 years of aging, declined to a similar fraction of total Zn (approx. 20–40%) to that measured in sludge-amended soils. Broos et al. (2001) also found labile Zn in soils from long-term sludge plots to be generally in the range 20–40%, not appreciably different from the labile fraction in soils contaminated by Zn salts, mining, or air pollution. Generally, however, the fraction of Zn in labile form was lower than that of Cd.

The often-suggested significance of oxides of Fe or Al in some sludges as strong adsorbents for metals such as Cd is probably overstated; for example, Soon (1981) found that Cd affinity for soils that had been amended with high-Al and high-Fe sludges was actually weaker than that of the control soil. Free metal ion activity values in acid soils appear to be under the control of

organic matter rather than Fe hydroxides in many cases (Weng et al., 2001).

These results make it clear that the physico-chemical form of metals in different sludge products exerts strong control over immediate or short-term solubility and extractability, and that total metals in sludges have limited predictive value for short-term crop uptake or leachability of toxic metals. Most sewage sludge regulations are solely based on the total concentration of toxic metals in sludges, regardless of chemical form or solubility. Although total metal concentrations are important for predicting long-term loadings on soils and low-metal sludges should always be favored over more contaminated sludges for use on agricultural land, short-term behavior of the metals is unlikely to be closely correlated to sludge 'quality' as defined by total metal concentration.

Overall, the evidence fails to show a consistently strong 'sludge protection' effect for several toxic metals of concern, particularly Zn and Cd at higher metal loadings. In fact, measurements in a large number of long-term contaminated soils have not revealed a marked difference between heavy metal solubility and bioavailability in sludge-amended and otherwise contaminated soils when the key soil factors of pH, organic matter and day content are taken into account (Jopony and Young, 1994; McBride, 1995, 2002; McBride et al., 1997a,b). When non-acid or alkaline-stabilized sludges are first applied to soils, increases in pH and organic matter can limit the bioavailability of several metals of concern (especially Zn and Cd) for some time. A substantial fraction of the organic matter applied in sludge may persist in the soil for decades in particular climates (McGrath and Cegarra, 1992; McBride, 1995). Ultimately, however, solubility and bioavailability are subject to control by climatic factors, and soil chemical and biological properties.

3. 'Soil–plant' barrier

Hypothesis 2. Low plant availability of toxic metals in soils provides protection for the human food chain.

Bonding of potentially toxic elements to sludge solids and soils can limit transfer to roots. Some metals, such as Cr and Pb, have very low solubility in soils and show a particularly strong barrier. Even if they accumulate at the root, they are not usually translocated significantly to the leaves, fruit or seed. However, for other elements, much of the protection against transfer to the edible part of the crop is under the physiological control of the plant. Based on evidence from many experiments, metals can be ranked on a relative scale of the strength of this barrier: Pb, Cr, Hg > Cu > Ni, Zn, Cd > Mo, Tl. The problem with generalizations about the efficacy of the barrier is that plant physiological

Table 1
Concentration factors (CFs) for thallium (Tl) and cadmium (Cd) in seedlings of several crops grown on an in situ contaminated soil containing approximately 3 and 4.7 mg/kg of total Tl and Cd, respectively (data from Lehn and Bopp, 1987)

Crop species	Concentration factor	
	Tl	Cd
Brassica napus L. *napus*	66	1.7
Sinapis alba L.	1.1	2.0
Hordeum vulgare L.	0.14	0.22
Zea mays L.	0.05	0.18
Triticum aestivum L.	0.05	0.18

CF is defined as the ratio of metal concentration in the seedling top to that in the soil.

processes vary remarkably by plant species. For example, red clover grown in sludge metal-contaminated soil has a 30-fold-higher UC for Mo and a five-fold-higher UC for Ni than does lettuce grown in the same soil (McBride, unpublished data). Conversely, lettuce is more efficient than clover in taking up Cd from the same soil. Table 1 compares plant concentration factors (CFs) for Cd and Tl taken up from contaminated soils into different crops, showing dramatic differences depending on plant species. Clearly, it is plant physiology and associated rhizosphere effects, not bulk soil chemical factors, that explain the species dependence of the effectiveness of this 'soil–plant barrier' for some toxic metals.

The species-specific effect on crop uptake of potentially toxic metals is often not allowed for in risk assessment of the potential agricultural impact of excess trace metals in waste materials. For example, the potential hazard to livestock farming from Mo uptake into forage legumes appears to have been underestimated (McBride et al., 2000b).

Crops that are harvested for their leaves often have the weakest barrier to metal uptake, whereas the barrier for root crops is usually greater. Metal concentrations are typically lower in the edible seed or fruit than in the leaves, stems or roots. However, even this barrier cannot be assumed to be effective for all metals or crops. For example, Mo is more concentrated in soybean seeds than in the leaves (McBride et al., 2000b) and Tl concentrations in rapeseed are higher than in the leaves (Tremel et al., 1997). For slightly–moderately Cd-contaminated soils, the transfer of Cd to the seed of linseed (flax), sunflower, corn and wheat can be sufficiently high to exceed health standards in some countries (Li et al., 1997; Garrett et al., 1998; Nan et al., 2002).

Biota that absorb metals by mechanisms different from those of plants may show an entirely different relationship of metal bioavailability to soil physicochemical factors. For example, Beyer et al. (1982)

found that, in soils contaminated by Cd from sludge application, plant uptake of Cd was very much reduced by liming the soil to raise pH, yet bioconcentration of Cd by earthworms was very marked (up to 50-fold) and only slightly affected by liming. Osté et al. (2001) also found little effect of liming contaminated soil on the accumulation of Cd by earthworms, even though liming reduced Cd solubility and plant uptake. This suggests that, even when a barrier exists for transfer of a particular metal to plants, it may not protect other organisms.

4. 'Uptake plateau' concept

Hypothesis 3. Bioavailability and crop uptake of toxic metals approaches a maximum, so that assuming a linear uptake as a function of metal loading overestimates risk, and therefore provides a 'hidden' margin of safety.

Risk assessments must frequently extrapolate to high soil metal loadings for which there are no field data. The US EPA 503 rule for toxic metals is based on a linear extrapolation for metal uptake and does not assume an uptake 'plateau'. Nevertheless, the presumed existence of a 'plateau' in metal uptake provided a rationale for not building a 'safety margin' into metal loading limits (Chaney and Ryan, 1993). Less efficient uptake of metals at higher metal loadings in soils would permit greater metal loadings without exceeding acceptable concentrations in the crop. This 'uptake plateau' is not always observed, however, and when it is, the reason is usually not known. Logan et al. (1997) observed that plant top concentrations of trace metals were, in some cases, not a linear function of trace element or sludge application rate, but approached a maximum, which they believed was not controlled by the physiology of the plant. Instead, they attributed the 'uptake plateau' effect to the adsorptive capacity of the sludge itself (Corey et al., 1987).

The addition of metal salts to soils typically results in a constant slope (constant partitioning behavior) or increasing slope of metal solubility as a function of metal loading to the soil (exponential or Langmuir behavior), whereas the addition of sludge-borne metals sometimes produces a decreasing slope (plateau behavior) at higher loadings (e.g. Kiekens et al., 1984). However, soil properties are clearly important in limiting metal solubility, and Kiekens et al. (1984) observed much lower metal solubility in a calcareous clay soil than a sand (pH 6) regardless of whether the metals were added as salt or sludge form. Generally, short-term crop uptake of bioavailable metals such as Ni, Cd and Zn tend to follow the same dependence on metal loading as solubility—metal salts produce increasing slope (exponential) functions, whereas sludge metals produce
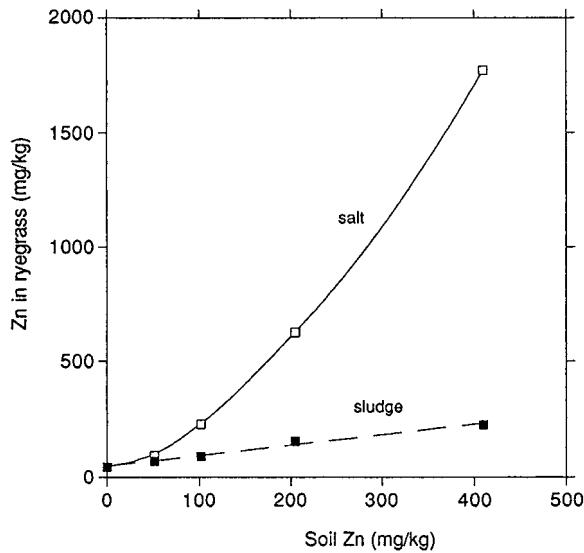
Fig. 1. Concentration of Zn in ryegrass as a function of total Zn added to a sandy (pH 6) soil in the form of metal salts or metal-contaminated sewage sludge (data from Kiekens et al., 1984).
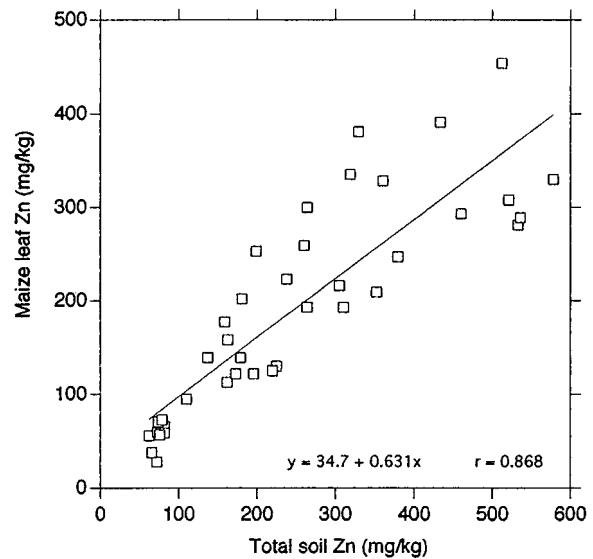

Fig. 3. The dependence of maize leaf tissue Zn concentration on total soil Zn in the multi-year 'continuous corn' field sludge experiment of Hinesly and Hansen (1983) and Hinesly et al. (1984).
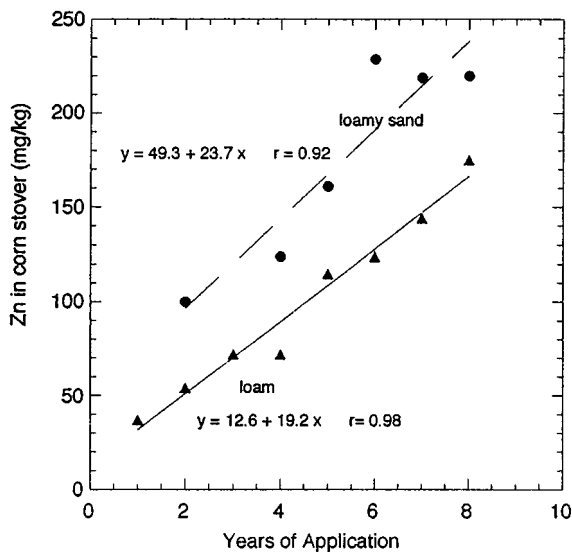

Fig. 2. Concentration of Zn in successive crops of corn stover as a function of years of metal-contaminated sewage sludge addition to a loamy sand and loam soil (both soils calcareous with pH > 7). Final cumulative Zn and Cd addition to these soils was 2890 and 19.0 kg/ha, respectively (data from Ontario Ministry of the Environment, Provincial Project No 78-012-11).

either a linear response or a plateau effect, as shown in Fig. 1 for Zn (Kiekens et al., 1984).

An important question, however, is whether the metal 'solubility plateau' sometimes observed in laboratory experiments is evident under field conditions over longer periods. As the less soluble forms of metals initially present in anaerobically digested sewage sludges (such as sulfides, organic complexes) decompose, more soluble forms may be released. Results from a number of long-term sludge application sites suggest that the 'solubility plateau' is not generally observed under field conditions. Instead, several metals, particularly Cd, Zn and Ni, typically show a near-linear relationship of soluble or easily extractable concentration to total metal concentration in the soil (Behel et al., 1983; Sloan et al., 1997; Hamon et al., 1999; McBride et al., 2000a; Chaudri et al., 2001).

Furthermore, the concentration of these metals in the plant tops is also frequently a linear function of total metal concentration in the soil. This is shown in Fig. 2 for Zn uptake by corn (maize) in a multi-year sewage sludge experiment on calcareous soils (Soon et al., 1980). Concentrations of both Zn and Cd (only Zn data shown) were essentially linear functions of cumulative Zn and Cd loading to the soil, with the more coarse-textured soil permitting greater metal uptake. A plateau in plant metal concentrations was not reached, and soil properties were important in controlling metal uptake throughout the experiment.
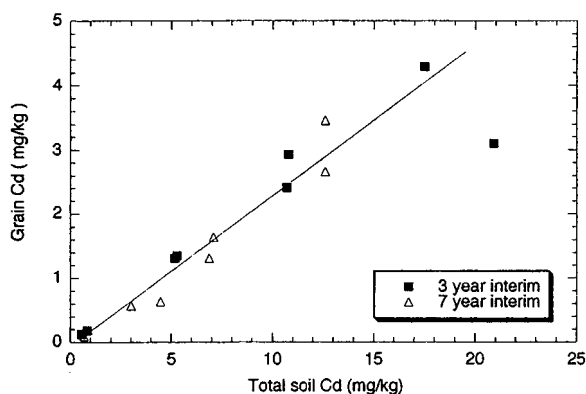
Fig. 4. The dependence of wheat grain Cd concentration on total soil Cd for wheat crops grown in 1979 and 1980, approximately 3 or 7 years after the last sewage sludge application. Soil pH range was 6.0–6.6 (data from Hinesly and Hansen, 1983; Hinesly et al., 1984).

The long-term (10 years) sludge application study of Hinesly and Hansen (1983) and Hinesly et al. (1984) revealed a near-linear dependency of maize leaf Zn and Cd concentration on total Zn or Cd added to the soil (Fig. 3 shows Zn data), despite large year-to-year variation in crop uptake coefficients, due in large part to pH fluctuations, arising from the acidifying effect of N and S mineralization countered by periodic lime additions. In fact, most of the variation in UCs of Cd and Zn was explained by two key soil variables: pH and total soil Cd (McBride, 2002). The large effect of these short-term soil pH changes prevent any clear conclusions being reached about longer-term trends in bioavailability of these metals during the 10 years of the maize trials. Nevertheless, when wheat was grown on these plots several years after completion of the maize trials, Cd uptake into the grain was essentially a linear function of total soil Cd, regardless of whether 3 or 7 years had passed since the last sludge application (Fig. 4).

Chang et al. (1997) found an approximately linear relationship between Cd in Swiss chard grown on long-term sludge-amended field plots, and concluded that if any uptake plateau was present, it would be reached at massive soil Cd concentrations (>300 mg/kg). In the longest experiment on residual metal bioavailability in sludge-amended soils (Woburn, UK), McGrath et al. (2000) showed that uptake of Cd and Zn by beets, carrots and barley remained a linear function of total soil Cd and Zn some 20 or more years after the last sludge application, with no indication of a plateau at the highest soil metal levels, which reached approximately 10–20 mg/kg Cd and 400–600 mg/kg Zn in the soil. If a plateau were to occur at even higher Cd and Zn loading, this would hardly be protective, as the crops grown on this site already had levels of Cd and Zn in their leaves and edible parts high enough to represent a health hazard or reduce yield.

Chaudri et al. (2000) found that dissolved and free Zn, as well as dissolved Cu, in soil solutions at the long-term sewage sludge field experiment at Gleadthorpe, UK, increased approximately linearly as a function of total soil Zn and Cu concentration. The concentration of Zn in pea seed grown at this site was essentially a linear function of total soil Zn concentration. Chaudri et al. (2001) reported essentially linear relationships between the concentration of Cd in wheat grain and Cd in soil porewater, when other important soil variables such as pH were held constant, on a long-term sewage sludge field experiment in the UK. The grain Cd concentration as a function of total soil Cd was slightly curvilinear, but there was no plateau up to the maximum soil concentration of 2.7 mg/kg. Despite near-neutral soil pH (in the range 6.3–7.4), grain Cd exceeded the German, Australian and New Zealand standard (0.1 mg/kg) at soil total Cd concentrations of 2–3 mg/kg. Nan et al. (2002) reported Cd and Zn concentrations in the grain and stems of wheat and corn (maize) grain crops to be in some cases exponential, and in other cases linear or curvilinear (quadratic) functions of total soil Cd and Zn concentration. Although the soils were calcareous, with Cd solubility expected to be low, concentrations of Cd in wheat and corn grain exceeded health standards by nearly three-fold when soils contained approximately 10 mg/kg Cd.

In greenhouse studies with large undisturbed columns of soils excavated from the field where heavy amendment with sewage sludge occurred approximately 17 years earlier, we have looked for an uptake plateau in lettuce and several other crops. Uptake functions for Cd and Zn (Zn data shown in Fig. 5) do not indicate a plateau. There may actually be an increasing slope (higher UC) at higher soil Zn, but this could be an artifact of phytotoxicity and stunted growth observed at the higher soil Zn levels.

Logan et al. (1997) presented multi-year uptake data for Cd, Zn, Cu and Ni in maize and lettuce after a single application of sewage sludge. Although there was evidence of an uptake plateau for Cd and Zn in maize in some years, lettuce showed evidence of increasing uptake coefficients at higher soil metal concentrations in some years, and no indication of an uptake plateau in any year, despite being grown in the same soil as the maize. This strongly suggests plant physiological (as hypothesized by Hamon et al., 1999), rather than soil chemical, control over metal uptake. Copper concentration in crops, particularly maize, was not closely related to total soil Cu; rather, Cu appeared to show a plateau effect. Similar results for Cu were observed in the long-term field sludge experiments of Hinesly and Hansen (1983), Hinesly et al. (1984) and Soon et al. (1980);
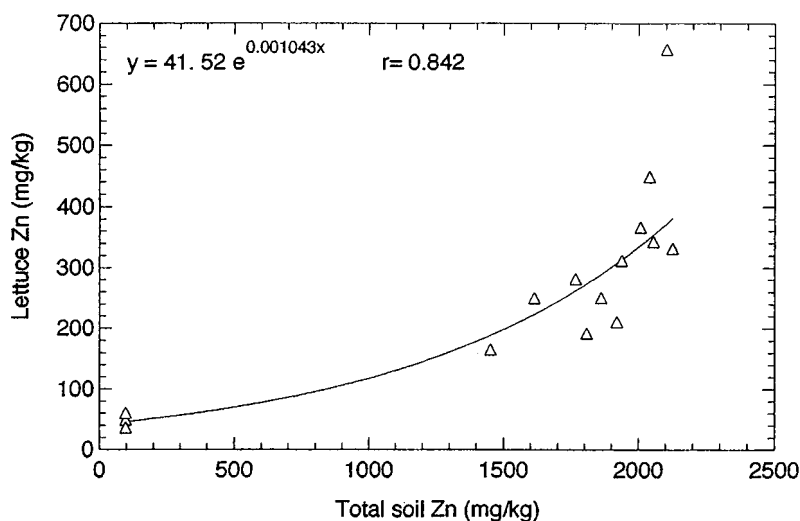
Fig. 5. The dependence of lettuce leaf tissue Zn on total soil Zn (determined by HF digestion of soils). Lettuce was grown in the greenhouse on soil columns (silty clay loam soil, pH 6.5) variably contaminated by heavy sludge application approximately 20 years earlier.

although Cu additions to soils substantially increased the Cu concentration in maize stover, the increase was not usually in proportion to total Cu loading. This can be attributed to both the strong sorption of Cu to sludge and soil organic matter, and the strong physiological control of Cu translocation (root barrier) by plants, even in severely contaminated soils (Poschenrieder et al., 2001).

Numerous long-term measurements of crop uptake, particularly of cadmium and zinc, have observed large, frequently two to three-fold, yearly variations in metals in the crop, with some studies indicating that wet years favor greater uptake than dry years (Kjellstrom et al., 1975; Chang et al., 1987; Guttormsen et al., 1995; Logan et al., 1997; Brown et al., 1998; McGrath et al., 2000). The fact that crop concentrations of Zn, Cd, Cu and other metals can fluctuate markedly from year to year in many experiments suggests that factors in addition to metal sorption and aging processes on sludge solids control year-to-year plant uptake. For example, cultural and climatic conditions affect rooting depth (maize roots deeper than lettuce) and the potential for contaminant metal uptake. Temporal–climatic, metal-specific and crop-specific factors sufficiently alter metal uptake functions on a year-to-year basis to raise doubt about the general existence of a solubility-controlled metal uptake plateau.

Where short-term sewage sludge application experiments show a 'plateau' effect in plant uptake of metals, the cause may be related to temporary increases in soil pH, growth dilution and ion competition effects due to excess application of macronutrients, or root toxicity effects that limit the crop's ability to take up trace metals. In longer-term studies, however, when a number of these effects have dissipated, there is less evidence for the plateau.

5. Single-metal abrupt toxicity threshold

Hypothesis 4. The potential for crop yield reduction from each phytotoxic metal in soil can be determined by comparing the above-ground plant concentration of that metal to the phytotoxicity threshold, the concentration at which 50% growth reduction occurs in young plants.

Quite different approaches have been used in different countries to establish loading limits for phytotoxic metals on agricultural soils (McGrath et al., 1994). These have ranged from the most cautious approach, preventing any additional net accumulation of toxic metals in topsoil, to the more effects-based method of limiting metal loading so that soil metal concentrations do not reach a level known to affect sensitive crops or soil biota. The method used by the US EPA to calculate 'acceptable' toxic metal loadings arrived at much higher values than those derived in European countries (McGrath et al., 1994). Schmidt (1997) and McBride (1995) have discussed some of the problems with the method, which involved calculating the risk of reaching an acute toxicity threshold (50% growth reduction in a short-term plant bioassay). Because this approach sets a very unacceptable endpoint (to growers at least) of 50% yield reduction from the phytotoxic effect of a

single metal, but evidently assumes that if a low probability of reaching this endpoint in the field is predicted, the probability of reaching a more tolerable endpoint (say 10% yield loss) is still low (although obviously higher than that estimated for 50% loss). The US EPA approach implicitly assumes that phytotoxic response in crop plants is not a gradual function of metal concentration in the plant tops, but is fairly abrupt and each phytotoxic metal exerts its effect independently. In Fig. 6, abrupt and gradual phytotoxicity responses for Zn are shown schematically to illustrate the point that, if the toxic response is gradual, a large safety margin would have to be introduced for Zn loading limits on soils to avoid small but economically significant losses in crop yield. Different plant species and cultivars are likely to show different toxic responses.

Numerous published data have measured 50% growth reduction in maize and other important crops at tissue concentrations well below the EPA calculated toxicity threshold of 1975 mg/kg. Fig. 7 shows that maize and several other monocots show 50% growth reduction with approximately 600–1000 mg/kg Zn in plant tops (Boawn and Rasmussen, 1971). MacNicol and Beckett (1985) reported that 10% yield reduction in maize occurs at approximately 100–200 mg/kg Zn. We have reconfirmed this Zn threshold of approximately 10% growth reduction at 120 mg/kg in a greenhouse pot study of maize seedlings grown in Zn-supplemented peat soils (unpublished data). Davis-Carter et al. (1991) found that peanuts first showed Zn toxicity at leaf Zn concentrations > 100 mg/kg; however, 50% probability of Zn toxicity was not reached until > 700 mg/kg in 6-
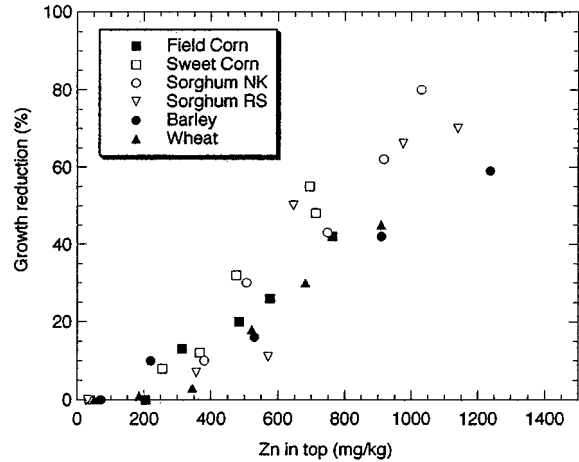

Fig. 7. Phytotoxic response to Zn in important graminaceous crops (data from Boawn and Rasmussen, 1971).

week-old plant leaves and > 300 mg/kg in 8–10-week-old plant leaves. That is, the occurrence and severity of Zn toxicity increased as the plants matured. Keisling et al. (1977) reported a critical toxic level of 220 mg/kg Zn in peanut shoots.

The sensitivity of the threshold tissue level of Zn toxicity to plant age (Davis-Carter et al., 1991), as well as to soil pH and the availability of essential trace elements such as Mn, argues against the simplistic US EPA approach of using short-term assays with young plants to determine a single critical tissue Zn concentra-
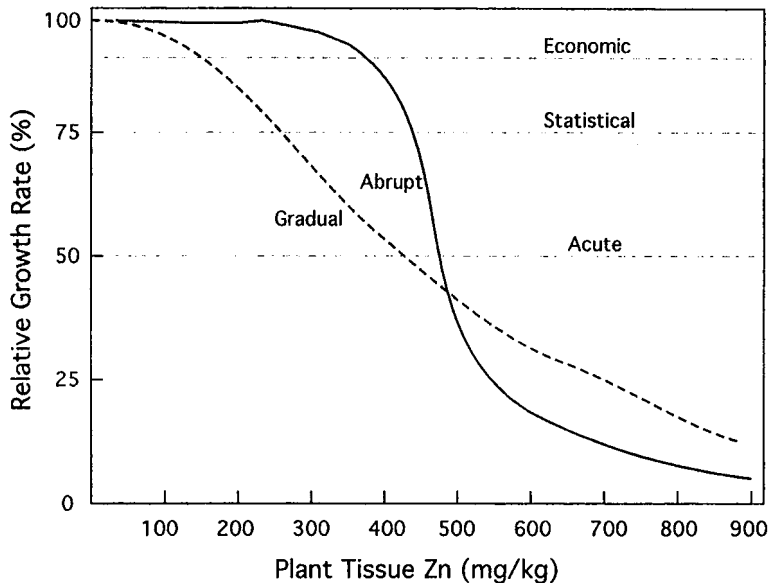

Fig. 6. Schematic diagram of gradual and abrupt phytotoxic responses in a crop.
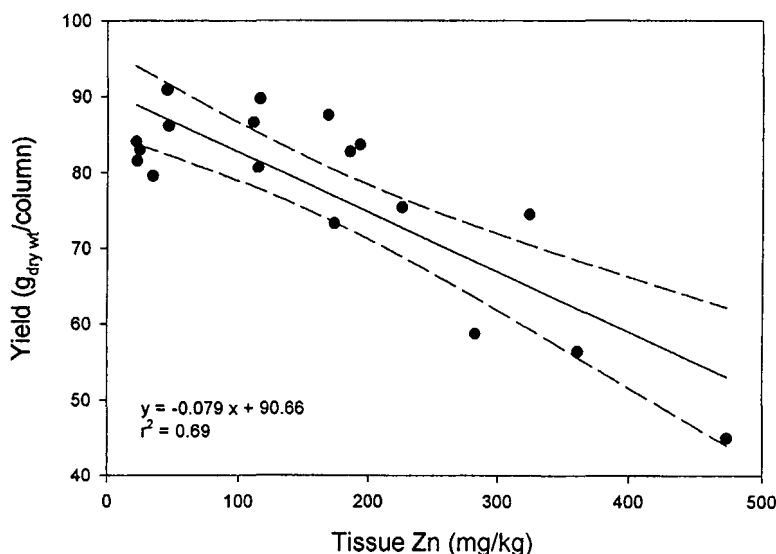
Fig. 8. Yield at maturity in lettuce as a function of leaf tissue Zn concentration. Crops were grown on the same soil columns described in Fig. 5. Broken lines define the 95% confidence limits on the best-fit equation (*solid line*).

tion that can be applied to field data for mature crops on all soils. As is well known for trace metal deficiencies (Bates, 1971), it is doubtful that single-value critical tissue metal concentrations determined in greenhouse and solution culture experiments will be generally satisfactory for predicting phytotoxic stress and yield decreases in the field.

A further problem is that the phytotoxic threshold concentration (PTC) should be, to protect soil productivity, the lowest observable growth reduction reliably (statistically) measurable, which, as shown in Fig. 7, is approximately 20%, and already corresponds to approximately 500 mg/kg Zn in the plant. Boawn and Rasmussen (1971) noted that, in order to achieve statistical significance (95% confidence level), yield reductions in the greenhouse usually had to exceed 20%, and sometimes 30%, because of experimental variability. That is, in order to be 95% certain that growth reduction has occurred, levels of Zn in the crop may have to reach concentrations that produce yield reductions averaging 20–30%. Such reductions are obviously unacceptable to growers. Clearly, *economically important* growth reductions can occur at Zn concentrations in the plant and soil well below that causing 50% growth reduction.

In Fig. 8, the relationship of lettuce yield to tissue Zn is shown, based on greenhouse studies. The 95% confidence intervals on the regression illustrate the point that a substantial yield loss is necessary before becoming statistically significant. A yield reduction of approximately 30% can be expected at tissue Zn levels near 400 mg/kg. With red clover, a similar experiment (data not shown) produced a yield reduction of 20–30% when

tissue Zn reached 150–200 mg/kg. It becomes clear that, in order to develop a risk analysis for phytotoxic metals in soils that is acceptable in agronomic terms, the standard statistical criterion of 95% certainty of yield loss as a tolerance threshold is unacceptable.

A more cautious and less simplistic approach to phytotoxicity could consider a range of estimated yield losses, and the probability of reaching these losses at different metal loadings. Table 2, from Chang et al. (1992), estimates the probabilities of 8, 10, 25 and 50% yield reduction in maize from Zn toxicity, based on field experimental data for sewage sludge. Although the US EPA used only the far right (50%) yield reduction column of Table 2 in establishing the Zn loading limit in the 503 rule, a more prudent approach could, for example, choose the lowest yield reduction (8%) as acceptable if it only had a 10% probability. This would limit field application to no more than 200–500 kg/ha of Zn in sludge, in contrast to the EPA 503 allowable loading of 2800 kg/ha. This is, however, a statistical approach that averages over highly variable field-observed Zn uptake for different soils and climates. In reality, the risk of Zn phytotoxicity is likely to be higher than average for a coarse-textured acid soil, and lower for a non-acid, clayey or calcareous soil.

In evaluating the risk of Cu phytotoxicity in soils, it must be recognized that Cu ions are strongly absorbed by plant roots (Minnich et al., 1987; Lexmond and van der Vorm, 1981), inhibiting fine root development and micronutrient (especially Fe) uptake, often without substantially increased uptake of Cu into shoots (Marschner, 1995). Thus, Cu concentration in the top growth of

Table 2
Probability of maize yield reduction for increasing zinc loadings to soils from sewage sludge (modified from Chang et al., 1992)

Zn loading (kg/ha)	Probability			
	Plant tissue Zn (mg/kg)/approximate yield reduction (%)			
	250/8%	500/10%	1000/25%	1975/50%
0–50	<0.0001	<0.0001	<0.0001	<0.0001
50–100	0.002	<0.0001	<0.0001	<0.0001
100–200	0.03	0.001	<0.0001	<0.0001
200–500	0.11	0.01	<0.0001	<0.0001
500–1000	0.26	0.05	0.003	<0.0001
1000–2500	0.28	0.021	0.010	0.001
2500–3500	0.35	0.04	0.001	<0.0001

maize is not a sensitive indicator of the threshold of toxicity (Dragun and Baker, 1982). Nevertheless, the US EPA risk assessment calculated an 'acceptable' Cu loading based on the observation that 40 mg/kg Cu in maize shoots did not decrease top growth in one cited hydroponic study, and identified this Cu tissue level as the PT50 for maize (Chang et al., 1992; US EPA, 1992). This decision led to a permitted soil loading of 1500 kg/ha total Cu.

Numerous older and recent studies have reported growth inhibition in maize shoots at 20–21 mg/kg Cu (Cottenie et al., 1976; MacNicol and Beckett, 1985; Mocquot et al., 1996; Borkert et al., 1998). Clearly, the US EPA chose an inappropriately high threshold toxicity value for Cu. The strong root–shoot barrier to Cu translocation (low UC) means that a very high soil Cu loading (and highly toxic soil Cu activity) is needed to force uptake to the level of 40 mg/kg in maize shoots. At this level, severe root damage has already occurred. In a recent maize bioassay with peat soils spiked with Cu, the lowest addition of Cu to the soil (200 mg/kg) increased shoot Cu to approximately 25 mg/kg and caused growth inhibition, but even 4000 mg/kg of added Cu failed to cause maize Cu to reach 40 mg/kg, although severe chlorosis and root damage were evident (McBride, 2001).

None of the above discussion considers the fact that several phytotoxic metals (e.g. Zn, Cu and Ni) are likely to be simultaneously present at appreciable concentrations in sewage sludges and other waste materials applied to soils. Combinations of phytotoxic toxic metals tend to further lower the threshold of toxicity in the soil (and in the plant tissue) for each metal (Smilde, 1981; Wallace and Wallace, 1994), although not necessarily in a simple or additive manner. In addition, marginal deficiencies in some trace metals can be exacerbated by excesses of others (e.g. Mn deficiency induced by Zn), so that phytotoxic thresholds for metals are sensitive to soil conditions such as pH. No attempt was made to model the combined effect of metals on toxicity thresholds in the US EPA risk assessment.

6. The 'aging' effect

Hypothesis 5. Toxic metals land-applied in sludges become less bioavailable with time because of permanent immobilization by soil or sludge solids, reducing the chance of a delayed 'time bomb' effect.

The bioavailability of trace metals is typically highest in the first 3–4 years following sludge application, followed by lower but generally sustained availability (Rundle et al., 1982; Hinesly and Hansen, 1983; Hinesly et al., 1984; Corey et al., 1987; McGrath and Cegarra, 1992; McGrath et al., 2000; McBride, 1995; Chang et al., 1997; Hyun et al., 1998). Nevertheless, there is concern that, following the cessation of application of organic wastes such as sewage sludges, bound metals could be released to soluble forms by processes such as organic matter decomposition, S oxidation and soil acidification (the 'time bomb' theory).

Although there are reports of cumulative loadings of Zn, Cu or Ni from sludges ultimately leading to phytotoxicity in crops, only a few studies suggest a 'rebound' of solubility or phytotoxicity years or decades following the termination of sewage sludge application (McBride, 1995). In contrast, greenhouse pot studies reveal a tendency for sludge-bound metals in soils to become more soluble and plant-available as the added organic matter decomposes (Beckett et al., 1979; Hooda and Alloway, 1993, 1994a,b; Sadovnikova et al., 1996; Basta and Sloan, 1999; Stacey et al., 2001). Metals solubilized by biological processes in field soils presumably do not accumulate because of leaching. Nevertheless, some metals, notably molybdenum (Mo), show a tendency to become more soluble and plant-available in soils for years after the application of sewage sludge (McBride et al., 2000b; Richards et al., 2000). This delayed effect could be due to release of Mo, initially bound in insoluble sulfides in anaerobically digested sludge, by oxidation of sulfur.

For most heavy metals and sludge types, the highest dissolved metal concentrations appear in leachates dur-

ing or shortly after the amendments (Richards et al., 2000). It has frequently been observed, however, that soils under long-term sewage sludge application become strongly acidified from mineralization reactions involving N and S, with pH values approaching 5 or lower. Without careful pH management at these sites, a delayed resurgence of heavy metal solubility and crop uptake can be expected. With typical management and the normal year-to-year variability in toxic metal uptake by crops, it may be difficult to identify and prove long-term gradual increases in phytotoxicity or plant-available toxic metals in the field. Any detrimental effects of phytotoxic metals on crops are likely to be severe before the cause is recognized.

7. Absence of evidence

Hypothesis 6. The ecological and human hazard of all *unregulated* toxic compounds in sewage sludges is assumed not to be significant, based on a lack of evidence indicating otherwise.

Most national regulations for contaminants in land-applied waste products such as sewage sludges put restrictions on approximately 10–12 metals at most, with some countries also regulating specific toxic organics such as dioxins and PCBs. This means that a number of toxic elements and organic compounds known to be present in waste products at concentrations much higher than in soils are being land-applied without regulation. For example, metal analyses for a number of cities in Canada revealed variable and sometimes very high concentrations of unregulated toxic metals (Webber and Nichols, 1995; Webber and Bedford, 1996). The ranges were undetectable to 131 mg/kg (median 16) for Tl, 7–394 mg/kg (median 33) for Sn, 24–117 mg/kg (median 64) for Sb and 5–81 mg/kg (median 43) for Ag.

Eight metals in sewage sludges have agricultural soil loading limits under the US EPA 503 rule. No loading limits for Mo and Cr are in place at present. Regulation of Cr has been problematic because of uncertainties about the potential for insoluble Cr^{3+} to be oxidized in soils to the much more soluble and toxic chromate, CrO_4^{2-}. It has generally been believed that, although Mn oxides in soils have been shown to oxidize Cr^{3+} to chromate, chromate should not form or persist in significant concentrations as long as the soil is high in reactive organic matter, as organic matter is known to reduce chromate chemically (Losi et al., 1994; James et al., 1997). Nevertheless, Milacic and Stupar (1995) reported that up to 1% of the Cr^{3+} from tannery wastes added to some soils was oxidized to chromate within 5 months, whereas sewage sludges (with much lower Cr concentrations than tannery waste) added to soils did not show evidence of chromate formation. Similarly,

James and Bartlett (1983) reported chromate formation in soils amended with tannery sewage sludge, evidence that high levels of organic matter in the sludge do not necessarily protect against oxidation to chromate. Although the potential for chromate formation is greatest in soils with high Mn oxide and low organic matter content (Kozuh et al., 2000), high levels of soluble chromate (0.7 mg/l) have been reported to persist in tannery waste-amended soils for more than 20 years despite high soil organic matter (Kamaludeen et al., 2001).

A long-term concern is that, once the more degradable organic matter in Cr-contaminated sludge-treated soils has decomposed, leaving soils with very high levels of Cr, there may be a potential for oxidation to chromate, particularly in high-pH soils. Chromate is the thermodynamically most stable form of Cr in non-acid aerated soils and water, and once added to soils as a pollutant or formed in soils by oxidation of added Cr^{3+}, can persist for decades (Bartlett, 1991; Szulczewski et al., 1997). Stable soil organic matter does not show much tendency to reduce chromate, particularly if the soil pH is near 7 or higher (Bartlett, 1991).

Based on the knowledge of Cr behavior in soils at present, it appears that, while no more than a very small fraction of total Cr in soil is likely to be oxidized to chromate, there are enough questions about the potential for chromate to form that a prudent approach would limit soil contamination by Cr. Even a small degree of Cr^{3+} oxidation to chromate in soils may be sufficient to contaminate groundwater (Chung et al., 2001).

Another common metal contaminant in sewage sludges is tin (Sn). Although inorganic Sn is relatively non-toxic, a significant fraction of Sn in sewage sludges is in the form of organo-Sn compounds, including tributyltin (TBT) and numerous other alkyltin species with each of the butyltin forms (MBT, DBT, TBT) in the range 0.3–2.0 mg/kg in municipal sewage sludges, and phenyltins at somewhat lower concentrations (Fent, 1996; Chau et al., 1997; Heninger et al., 1998). TBT is much more toxic than inorganic tin, and arguably the most toxic chemical ever deliberately released as a biocide into the environment (Chau et al., 1997).

Decomposition of organotin compounds in sediments appears to be slow, and studies of triphenyltin (TPT) found in soils from its use as a fungicide indicate slow decomposition of this organotin compound in aerobic soil environments (Kannan and Lee, 1996). Organotin compounds in land-applied sewage sludge may bioconcentrate in the terrestrial food web (Fent, 1996), but no studies of sludge tin on soil biota have been carried out to the knowledge of this author. The US EPA assessment of tin toxicity was based on studies of animals ingesting inorganic tin (US EPA, 1996), not an appropriate test for the more toxic forms of tin found in sewage sludge.

More attention to the potential impact of several other unregulated metals that occur at elevated concentrations in sewage sludges and mav be toxic to organisms, for example, Sb and Ag, may be justified.

8. Conclusions

This review has illustrated from the known behavior of trace and heavy metals that broad assumptions about the general behavior and bioavailabilitv of metal contaminants from different wastes and in different soils and cropping systems, such as those used to develop the US EPA rules for metals in sewage sludges, should be viewed with skepticism. Different metals can behave entirely differently in the same soil, as can a particular metal in different soils. The processes used to generate waste materials, such as sewage sludges, markedly alter the short-term solubility and mobility of metals in these materials. Ideally, situation-specific information would be the best guide to setting metal pollutant loading limits on agricultural land. Detailed knowledge of the soil at the application site, especially pH, CEC, buffering capacity, organic matter and clay content, is essential. Soils with little capacity to buffer pH and adsorb metals are poor candidates for metal-contaminated waste application. Obviously, knowledge of the crop to be grown at the site, and potential for transfer of metal contaminants into the harvested portion, should be known. As the crops to be grown at a site could change over time, predicting the future potential for metal uptake and exposure of animals and humans is problematic.

If site-specific data are unavailable and future land use uncertain, the most rational approach to land application of wastes containing toxic substances is precautionary, with metal loading limits restricted by a 'no net degradation' policy or a reasonable worst-case scenario. Restrictive policies have the benefit of driving metal contaminant levels in wastes to the lowest feasible. The argument for a precautionary policy regarding soil contamination by metals was stated by the Ministry of Agriculture and Food in the UK:

> ...it must be borne in mind that agricultural land is an asset held in trust for the future. Contamination of such land by metals should be regarded as irreversible and must be kept to the lowest practicable level. There is the possibility that further information on these metals may lead to the lowering of acceptable concentrations in soil and tolerable dietary intakes. (MAFF, 1993).

Acknowledgments

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