

TECHNICAL ARTICLES

LONG-TERM LEACHING OF TRACE ELEMENTS IN A HEAVILY SLUDGE-AMENDED SILTY CLAY LOAM SOIL

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Analysis by ICP-MS of shallow groundwater collected at a field site in New York that had been heavily loaded with sewage sludge more than 15 years earlier revealed elevated concentrations of Cu, Zn, Sr, Rb, Mo, Cd, As, Cr, Ni, Sb, W, Ag, Hg, and Sn compared with a nearby control site. Enhanced leaching of some elements from this near-neutral, fine-textured (silty clay loam) soil could be explained by exchange of soil-bound elements by components of the added sludge. For most of the heavy metals, however, increased leaching was a response to the high metal loadings in the soil, probably facilitated by higher dissolved organic matter in the leachate. Laboratory-determined distribution coefficients, K_D , for the metals in newly prepared sludge/soil mixtures were lower than K_D values of the field-aged sludge-treated soil, suggesting that metal mobility may have been substantially higher shortly after sludge application than many years later. Cumulative losses of certain trace elements from the topsoil have been estimated relative to Cr, a comparatively immobile element. These suggest that relative long-term losses range from 20 to 80%, with the order being: Sr, Mo, Sb > Ni, Cd, Cu > Zn, Ag. Generally, those elements with the smallest K_D values (most soluble) measured recently in the soil had the largest loss estimates. However, present leaching loss rates are too low to explain the estimated relative losses of several of these elements from the topsoil over the 15 or more years since sludge application. (Soil Science 1999;164:613-623)

Key words: Heavy metals, solubility, sewage sludge, distribution coefficient, mobility, facilitated transport, mercury, arsenic.

MASS balance calculations frequently show that substantial fractions of heavy metals applied to soils in sewage sludges cannot be accounted for in the topsoil or shallow subsoil (Richards et al. 1998; McBride et al. 1997; Dowdy et al. 1991; Williams et al. 1987; Bell et al. 1991; Chang et al. 1982, 1984; Hinesly et al.

1979). Nevertheless, leaching has usually been dismissed as a possible explanation for these losses because of the common observation that subsoil concentrations of the metals are not increased substantially and because repeated tillage spreads the metals laterally and could account for gradually lowered concentrations (McGrath and Lane 1989; Williams et al. 1987; Juste and Mench 1992). Tillage and erosion cannot readily explain losses of some heavy metals at relatively higher rates than others, as shown, for example, by McBride et al. (1997) and Mench et al. (1994).

Berti and Jacobs (1998) reported highly variable trace element recoveries (45-155%) from mass balance calculations on three long-term

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sewage-sludge treatment plots sampled in 1989 and 1990. In 1989, 16 of 18 estimates of recovery for six metals (Cd, Cr, Cu, Pb, Ni, Zn) on three sites were below 100%, and 12 were below 80%. Resampling in 1990 gave 11 of 18 estimates below 100% and seven below 80%. The high variability in these results points out the difficulty in estimating absolute metal losses. A re-analysis of these data (M. McBride, unpublished data), measuring loss of five analyzed metals relative to that of Pb, gave consistent deficits of Cd, Cr, Cu, Ni, and Zn relative to Pb in the 0- to 15-cm soil of all three treatment sites, averaging 56%, 30%, and 18% (for the five metals combined) on sites 1, 2, and 3, respectively. This relative method of measuring deficit is not prone to errors in mass balance calculations from sludge metal loading estimates, soil bulk density, tillage, and erosion, but still depends on a reasonably accurate analysis of the metal content of the sludge actually applied. This analysis suggests that movement of metals more soluble than Pb did occur between the time that sludge was applied (1977–1986) and sampling (1989).

Even in long-term sludge application sites where little or no tillage has occurred, such as those described by Brown et al. (1997), simple mass-balance calculations using the reported metal profile data and reasonable bulk density estimates indicate deficits of some heavy metals in soil profiles relative to the quantities of metal applied in sludge. Furthermore, investigations in the field (Lamy et al. 1993; Sidle and Kardos 1977) as well as in soil columns (Prakash et al. 1997; Frenkel et al. 1997) have documented rapid leaching of significant concentrations of several metals, including zinc, copper, chromium, and cadmium. Some elements in sewage-sludge, particularly the less metallic elements such as molybdenum, selenium, and arsenic, are often more soluble immediately (Sawhney et al. 1996; Logan et al. 1987; McBride 1998) so that substantial fractions of these could conceivably be lost from surface soils rather quickly. Preferential flow, combined with transport of metals as relatively nonadsorptive organic complexes, can lead to leaching without accumulation in the shallow subsoil (Camobreco et al. 1996; Richards et al. 1998). Soluble complexing ligands in sludge cause certain metals, particularly copper, to be more mobile than they would be in the absence of organics (Frenkel et al. 1997; Camobreco et al. 1996).

Correlations have been found between the level of dissolved organic matter (DOM) and the

concentrations of Hg, As, Cu, Cd, Zn and Cr in leachates (Kalbitz and Wennrich, 1998; McBride et al., 1997; Campbell and Beckett, 1988). Similarly, DOM from animal manure is able to dissolve and mobilize metals such as Cu and Cd (Japenga et al. 1992). If DOM is the vehicle for leaching of metals such as copper and nickel, then one could expect metal leaching to be highest immediately after sludge application or when biological activity is particularly high, with a gradual reduction over time as the most degradable organic matter is decomposed. Because organic matter tends to be more soluble at near-neutral or alkaline pH than at acid pH, the potential for leaching of metals with strong affinity for DOM (such as Cu) may be highest in soils recently amended with manure or sludge and maintained at high pH (Japenga et al. 1992). Recent studies show that substantial fractions of total Cu, Mo, and Ni in lime-stabilized sludges are soluble in water (McBride 1998), attributable to high DOM in leachates from these alkaline materials.

One of the main impediments to studies of effects of land application of sewage sludge on groundwater quality has been the need for an analytically sensitive method to measure the large number of trace elements that may be present in leachate from sludge-treated soils at low but non-negligible concentrations. Maximum contaminant limits (MCLs) for a number of trace metals in drinking water are in the part per billion ($\mu\text{g L}^{-1}$) range; neither flame atomic absorption nor older-generation inductively coupled plasma/optical emission spectrometry (ICP-OES) has the sensitivity to measure metals at these levels. Large positive matrix or spectral interferences in water or soil extracts, and especially soil digests, occur with ICP-OES because of the common occurrence of high concentrations of Al, Ca, and Mg in these types of samples (Ure 1990). More recent ICP-OES instrument designs have minimized these interferences. Differential pulse anodic stripping voltammetry (DPASV), graphite furnace atomic absorption spectrophotometry (GF-AAS), and ICP-mass spectrometry (ICP-MS) provide the sensitivity to detect metals in water at $\mu\text{g L}^{-1}$ concentrations or lower, levels that are typical for many trace elements in uncontaminated water. However, each method has unique sources of analytical error, with isobaric interferences being problematic for ICP-MS. It is advisable to use more than one analytical approach to confirm analyses at trace levels.

One objective of the present study was to apply highly sensitive techniques to measure the

dissolved (ICP-MS) and labile (DPASV) concentrations of trace elements in shallow groundwater at an old sludge site where earlier investigations had shown leaching of Zn, Cu, Cd, and several other elements (Richards et al. 1998). ICP-MS provides improved sensitivity, important for the most toxic trace elements with low MCLs, and allows analysis of a wider range of elements than was possible with the ICP-OES analyses reported earlier at this site. A second objective was to estimate metal losses from the topsoil at this site relative to that of a relatively immobile metal (Cr) to determine whether selective leaching has occurred over about 20 years. A final objective was to determine whether the measured distribution coefficients for trace elements at this site were correlated to estimated long-term elemental loss and whether present elemental solubilities can account for estimated losses.

MATERIALS AND METHODS

The study site is located at the Cornell orchard where a single heavy application of high-lime sewage sludge (pH near 7) was rototilled into the surface 20 cm in 1978 (for complete description of site, see Richards et al. 1998). The nominal loadings of Pb, Cd, and Zn were about 50% of the allowable cumulative loadings under USEPA Part 503 regulations, but in the center of the site, allowable loadings were exceeded. After a series of test crops had been grown on this site between 1979 and 1983, the soil was limed in 1985 and deep plowed. Dwarf apple trees were planted on both the sludged area and the control site in 1986, with grass cover maintained in the interrow areas. Soil water (percolate) was collected nine times in the period from 1994 to 1996 from wick samplers at a depth of 60 cm. The percolate samples represent a composite rather than single leaching events as percolate was allowed to accumulate before periodic collection. For comparison, percolates from an adjacent unsludged soil were collected by the same method. All percolate water samples, consisting of eight from the control and 15 from the sludged site, were stored at 4 °C in 0.5-L and 1-L plastic bottles until analyzed. These samples were then acidified with ultrapure HNO₃ (0.5 mL per 100 mL), vigorously agitated in their storage bottles, and analyzed by ICP-emission spectrophotometry (ICP-OES). In a further analysis, randomly selected percolate samples from the control (2 samples) and sludge-treated site (4 samples) were agitated and put through

0.45- μ m filters before acidification with ultrapure HNO₃, and re-analyzed by ICP-mass spectrometry (ICP-MS) for 35 elements at detection levels ranging from 0.01 to 0.001 μ g L⁻¹. Trace elements in the field-collected percolates and laboratory-created water extracts had previously been measured by ICP-OES for a limited number of elements at relatively low sensitivity on an older-generation instrument (McBride et al. 1997; Richards et al. 1998).

Randomly selected percolate samples were further analyzed by differential pulse anodic stripping voltametry (DPASV) using a PAR model 174A polarographic analyzer equipped with a model 303A hanging drop mercury electrode. Labile Zn, Cd, and Cu at pH 7–7.5 (the natural pH of the leachate), 5.5, and 4.0 were estimated by peak height measurement of the DPASV scan after adjustment of the pH with HNO₃. This measure of labile dissolved metals is considered to include free cations plus rapidly dissociable metal-ligand complexes.

The applied sewage sludge and the sludge-amended soil were both analyzed by ICP-OES in 1994 for strong acid-soluble metals (McBride et al. 1997). In the present study, distribution coefficients (K_d) were determined for the trace elements in these soils by agitating 10 g of soil with 20 mL distilled water for 1 day, centrifuging and filtering (0.2 μ m polycarbonate filters), and analyzing the filtrates for trace elements by ICP-emission spectrometry. Similarly, air-dried sludge archived from the 1978 sludge application experiment was combined in two different weight ratios (50% sludge and 20% sludge) with the untreated (control) orchard soil, in order to recreate a sludge/soil mixture representative of the freshly amended soil. The K_d values of trace elements of these mixtures were determined as before, using duplicate 10-g samples of the two soil/sludge mixtures in 20 mL of distilled water. All K_d values were calculated on the basis of total metals as estimated by 4 mol/L HNO₃ digestion so that any residual elements retained in acid-resistant minerals are not considered in the K_d measurement.

ICP-MS was used to measure total trace element composition of soils collected at the sludge application site, as well as the archived sample of the sludge applied at the site in 1978. The sludge and soils were digested by a standard HF method before ICP-MS analysis. These data are given in Table 1 and represent the average total trace element composition for soil samples collected in 1997 from the well mixed surface layer of 12 sludge-site soil columns and three control soil

columns previously excavated from the field orchard site and moved to the greenhouse. Heavy metals in these columns are essentially at constant concentration in the 0- to 25-cm depth, but they are not significantly higher than control concentrations less than 25 cm (Richards et al. 1998). Several crops had been grown on these columns in the greenhouse before soil sampling in 1997.

RESULTS

Concentrations of Trace Elements in Soil Water

Tables 1 and 2 indicate that large relative increases in several trace elements (notably Cu, Zn, Sr, Cd, Mo, and Ni) persist in the soil and percolates at the sludge site more than 15 years after sludge application. The analysis of a randomly selected subset of the percolate samples by ICP-MS gave close agreement with trace element analysis by ICP-OES of the entire set of samples, at least for those elements that occurred at concentrations well above the detection limits of ICP-OES

(Table 2). Several elements occurred at levels too low to be quantified by ICP-OES (Sb, Sn, Tl, Hg). The greater sensitivity of ICP-MS revealed that several other elements, including Cr, Sb, W, Ag, Hg and Sn, had increased solubility attributable to sludge application, (Table 2). However, the concentrations of Ag, Hg, and Sn in leachates are well below $1 \mu\text{g L}^{-1}$. The higher dissolved As at the sludge application site is interesting because the orchard soil where the sludge was applied had a high As content from historical use of lead arsenate; consequently, the sludge addition actually *reduced* the As concentration in the soil by dilution (McBride et al. 1997). However, the high phosphate levels in sludge-treated soil may have displaced adsorbed arsenate (Melamed et al. 1995; Darland and Inskeep 1997), and this competitive anion effect may be partly responsible for the elevated dissolved concentration of other elements known to occur as anions in soil, such as Mo, W, and Sb. Alternatively, since potentially anionic forms of Mo, Sb, and As are known to bond to humic substances (Pilarski et al. 1995; Bloomfield and Kelso 1973), the dissolved organic matter in percolates from the sludge-amended soil may have mobilized these elements. Nevertheless, because the control site had low soil As, it is not clear whether the elevated dissolved As at the sludge site was caused by the sludge addition or by the residual arsenate in the orchard soil.

Several of the alkali and alkaline earth metal concentrations were markedly higher in percolates from the sludged soil (data not shown), which can be attributed to the heavy application of the high-Ca sludge. Thus, dissolved Mg averaged 19.7 mg L^{-1} in the leachate compared with 5.5 mg L^{-1} for the control. Dissolved Ca averaged 79.6 mg L^{-1} in the percolate from the sludged soil, compared with 19.0 mg L^{-1} in the control. As shown in Table 2, Sr and Rb concentrations were also substantially higher in the soil water where sludge had been applied. Limestones tend to have Ca/Sr ratios of about 600 (Rankama and Sahama 1950), and the relatively high soluble Sr corresponds to a dissolved Ca/Sr ratio of about 300 compared with about 500 in the control soil, so the elevated Sr solubility seems to be explained by higher lime in the sludge-treated soil. Rubidium, in contrast, substitutes for K in K-bearing minerals, and the higher concentrations of this element in soil water may not have been caused directly by sludge application because sludges are low in K (and presumably, Rb) content. As shown in Table 1, the Rb concentration of the sludge (32 mg/kg) was

TABLE 1

Trace element concentrations (mg/kg) of sludge-treated and control soils from the Cornell Orchard Site, and of the sewage sludge applied at the site. All samples digested in HF, with elemental analysis by ICP-MS.

Element	Control (n = 3)	Sludge Site (n = 12)	Sludge (Archived sample)
Antimony	0.4±0.1	1.9±0.1	5.5
Arsenic	0.6±0.0	61.9±7.4	14
Barium	364±2	401±20	362
Beryllium	1.4±0.1	1.6±0.1	1.1
Bismuth	0.87±0.72	4.1±1.0	9.9
Boron	3.3±0.6	<1	<1
Cadmium	0.2±0.0	34.8±6.4	73.6
Chromium	47±1	490±71	514
Cobalt	11.8±0.3	11.9±1.0	6.2
Copper	20±2	321±49	542
Lead	36.7±0.6	392±24	576
Manganese	633±5	724±59	264
Molybdenum	1.1±0.3	3.34±0.50	12.4
Nickel	24.7±1.5	92.1±9.7	131
Rubidium	91.4±2.6	78.7±3.5	32.3
Selenium	<1.0	<1.0	2
Silver	0.3±0.0	11.0±2.3	12.5
Mercury	0.1-0.2*	0.64±0.04*	3-5
Strontium	71.7±1.5	142±11	280
Tellurium	<0.1	<0.1	<0.1
Tin	1.9±0.1	56.0±8.5	95.2
Uranium	2.2±0.0	2.8±0.1	3.8
Vanadium	72±2.6	44.5±8.2	24
Zinc	98.3±1.2	1660±240	2320

*Data from neutron activation analysis of duplicate samples, reported by McBride et al. (1997).

TABLE 2

Concentrations of trace elements in percolate samples collected from wick samplers at the sludge site and an adjacent control site (60 cm depth), measured by ICP-MS and ICP-OES (number of samples indicated by n). Standard deviations are indicated in parentheses. Measurements below detection are indicated as nd.

Element	Sludge Site ($\mu\text{g/L}$)		Control Site ($\mu\text{g/L}$)	
	ICP-OES (n = 15)	ICP-MS (n = 4)	ICP-OES (n = 8)	ICP-MS (n = 2)
Cu	157 (49)	174 (35)	14.8 (6.1)	10.3 (3.9)
Zn	259 (139)	261 (71)	15 (11)	14.9 (1.7)
Sr	285 (106)	292 (62)	28 (13)	38.2 (9.1)
Mo	4.3 (2.1)	7.6 (3.2)	<1	0.12 (0.03)
Rb		3.9 (3.6)		0.70 (0.50)
Cd	5.4 (1.6)	5.3 (0.6)	0.4 (0.3)	0.23 (0.08)
As	43 (33)	47.1 (33.9)	2 (2)	1.5 (0.7)
Ni	106 (33)	91.1 (18.5)	4.6 (1.4)	4.2 (0.5)
Cr	4 (6)	16.0 (1.6)	<1	1.3 (0.71)
Sb	<3	2.3 (0.4)	<3	0.44 (0.14)
W		3.98 (2.43)		0.04 (0.04)
Ag		0.17 (0.06)		nd
V	5 (0.8)	2.1 (0.7)	2 (0.5)	nd
Hg	<1	0.13 (0.11)	<1	nd
Sn	<1	0.09 (0.07)	<1	nd
Tl	<1	0.012 (0.006)	<1	≤ 0.005
Ba	40 (27)	44.2 (31.0)	26 (7)	20.8 (4.6)

lower than that of the soil, although it is possible that the Rb in the sludge is more soluble than that in soils. It seems most likely that the Rb is of natural origin in the soil, and the high Ca and Mg content of the sludge could be displacing Rb in solution by ion exchange.

Some of the elements detected in the percolates collected from the wick samples were not found to be at significantly different concentrations where the sewage sludge had been applied compared with a nearby site where no sludge had been applied. These elements were Li (0.20–0.90 $\mu\text{g L}^{-1}$), Be ($\leq 0.040 \mu\text{g L}^{-1}$), Sc (1.4–2.8 $\mu\text{g L}^{-1}$), Mn (3.3–7.9 $\mu\text{g L}^{-1}$), Fe (114–204 $\mu\text{g L}^{-1}$), Co (0.36–1.1 $\mu\text{g L}^{-1}$), Y (0.74–3.3 $\mu\text{g L}^{-1}$), Zr (0.09–0.22 $\mu\text{g L}^{-1}$), Nb ($< 0.002 \mu\text{g L}^{-1}$), Cs ($< 0.01 \mu\text{g L}^{-1}$), Ba (17.5–88.8 $\mu\text{g L}^{-1}$), La (0.11–0.80 $\mu\text{g L}^{-1}$), Hf ($\leq 0.01 \mu\text{g L}^{-1}$), Ta ($\leq 0.003 \mu\text{g L}^{-1}$), Au ($\leq 0.03 \mu\text{g L}^{-1}$), Pb (0.11–3.3 $\mu\text{g L}^{-1}$), and Th (0.003–0.014 $\mu\text{g L}^{-1}$).

Evidence That Mobile Metals Are in Complexed Form

Some metals, including Cu, Zn, Ni, and Cd have continued a gradual process of leaching out of the contaminated topsoil and through the shallow subsoil since the sludge application in 1978. Despite this, no significant accumulation of these metals has occurred to depths of 1.5 m in the subsoil (Richards et al. 1998). Since it is generally accepted that free metal cations could not migrate

far in a fine-textured soil at near-neutral pH without readsorption, the pattern of movement implies that the metals are being mobilized as complexes and move through preferential flow paths. This implication was confirmed earlier for Cu using the ion-selective electrode (ISE) to demonstrate that virtually all of the dissolved Cu in the percolate at this site is complexed (McBride et al. 1997). In the present study, DPASV analysis of the percolates from the sludge-amended soil shows that a large fraction of the dissolved Zn (70%), Cd (82%), and Cu (90%) is not DPASV-labile, and, therefore, not in the form of free cations or low molecular weight easily dissociated complexes. Furthermore, the labile Cd and Zn concentrations increased by two-fold or more upon adjusting the percolate pH (7.0–7.5) with HNO_3 to 5.5, whereas this degree of acidification increased labile Cu only slightly. Further acidification to pH 4.0 markedly increased labile Cd and Cu, but not Zn (data not shown). These results indicate that the mobile metals are largely in complexed form, probably with dissolved organic matter.

Although Cd^{2+} and Zn^{2+} have been assumed in the past to complex weakly with soluble organics on the basis of speciation calculations, recent evidence suggests that a substantial fraction of the dissolved Cd in sludge-treated soils can be complexed (Helmke and Salbu 1997; Hamon et al. 1995). Speciation models have generally predicted that most Cd and Zn in soil solutions will

be in the free cation form, but these models use unrealistically low association constants for metal-organic complexes, which are based on measurements at high metal loadings on the complexing sites of organic matter. Trace metals, in fact, occupy different and more selective bonding sites at low metal levels (John et al. 1988; Xia et al. 1997). That raising soil pH can increase the dissolved concentration of Cd and other metals in contaminated soils (Bruemmer et al. 1986; Evans et al. 1995) suggests that soluble metal-organic complexes form under conditions favorable to organic matter dissolution.

Predicted Metal Mobilities Based on K_D Values

In Table 3, the distribution coefficients, K_D , of elements in soil freshly mixed with samples of the archived sewage sludge applied at the field site are reported. These were determined at two different sludge/soil ratios, and are compared with the K_D values determined by the same procedure for the sludge-amended soil collected recently at the field site (McBride et al. 1997). It is notable that, for most of the elements, the K_D in the aged, sludge-treated soil (collected from the field more than 15 years after sludge application) is larger than the K_D measured in the fresh sludge/soil mixtures. This difference is particularly marked for Cd and Zn, where the K_D is about 15 to 20 times greater for the field-aged, sludge-amended soil than the freshly prepared soil/sludge mixture. The difference implies that relative Cd and Zn solubility and mobility may have been much higher at the time the sludge was field-applied than it is at present, as would be

expected because of high dissolved organic matter levels initially. Measured concentrations of metals such as Cu, Zn, and Ni in the percolates collected at 60 cm depth in the field site confirm that recent rates of leaching are low relative to the total metals present in the topsoil, on the order of 0.003 to 0.40% annually depending on the metal (Richards et al. 1998). These are comparable to reported annual losses by leaching from old sludge sites in Europe, ranging from 0.04 to 0.2% for Cd and from 0.05 to 0.4% for Zn (Holm et al. 1998). Nevertheless, the estimated cumulative losses of metals from many of these field sludge sites are on the order of 40 to 60% of total metals applied, based on mass balance calculations (McBride et al. 1997; Richards et al. 1998). Crop uptake is generally a small contributor to the measured metal deficits. If these metal deficits in the soil profile are largely attributable to leaching, large fluxes must have occurred within the first few years of application, subsiding substantially after several years. Dissolved and colloidal organic matter, which have been observed in percolates collected shortly after sludge application, are likely agents of mobilization.

It is noteworthy that for several elements, the K_D value is relatively unaffected by the degree of dilution of sewage sludge (and the element) by soil (see Table 3), as would be expected for adsorption behavior that follows a linear isotherm. For some elements, however, most notably Ca and P, the K_D increases with higher sludge content (that is higher Ca and P concentrations in the solids). This behavior is consistent with control of solubility by precipitation reactions.

TABLE 3

K_D values calculated from the measured water solubilities of selected elements in sludge/soil mixtures prepared with 20% and 50% (by wt.) sludge (standard deviations reported). The measured K_D values for soils collected at the orchard sludge site (McBride et al. 1997) are tabulated for comparison

Element	K_D (L/kg)*		
	20% sludge	50% sludge	Orchard sludge site
K	69±4	63±8	250
Na	5.3±0.3	6.3±0.8	15
Ca	5.6±0.4	11.8±1.3	120
Mg	35.8±1.5	36.4±1.7	450
P	1500±0	2310±80	1,900
Mn	90±15	85±20	1,300
Cu	221±15	208±10	360
Ni	102±13	65±3	240
Zn	293±75	283±39	4,800
Cr	1240±14	1590±120	7,500
Pb	>22,000	>15,000	>13,000
Cd	139±8	161±7	2,500

* K_D calculated using 4M HNO₃-digestible metals content of the orchard soils and sludge.

Estimated Metal Losses from Surface Soil

A previous analysis of the acid-extractable trace element contents of the surface soil at this orchard sludge application site indicated that selective losses of a number of elements had occurred relative to Cr (McBride et al. 1997). This analysis determined the soil concentration ratio of each element in question to Cr, based on the slope obtained when the concentration of the element was plotted against that of Cr for a number of soil samples collected at the site. The range of Cr concentrations in the individual samples is attributed to spatial variability in actual sludge content of the soils. By comparing this ratio with that in sludge applied at the site, an estimate of loss of the element relative to that of Cr was made. Chromium was chosen as the reference element because of its high K_D (see Table 3) and because sludge was the only significant contamination source of Cr at the site. However, it is possible that other trace elements at the site, particularly lead, were less mobile than chromium.

In the present study, a similar analysis using total metals by HF digestion was repeated on the 12 soil columns excavated at the site in 1993 and used in the greenhouse for repeated cropping experiments (Richards et al. 1998). One soil sample was taken from the surface layer of each soil column in 1997 and analyzed for total metals by ICP-MS analysis of HF digests. The resulting regressions between total concentrations of several of the elements known to be present in the sludge at elevated levels and Cr are shown in Table 4, and three of these regression lines are shown in Fig. 1 as examples. Since the slopes of these regressions quantify the increment in soil concentration for each element per unit incre-

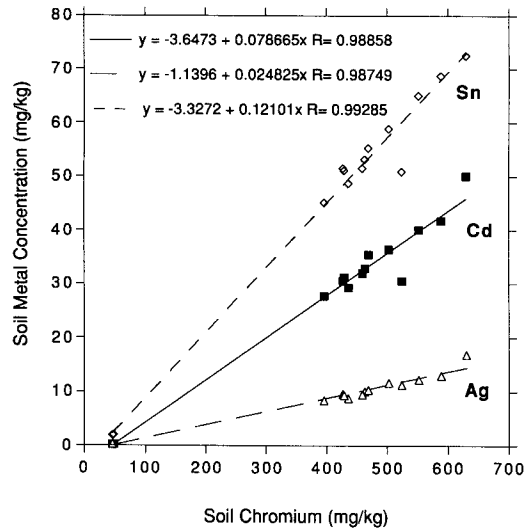


Fig. 1. Linear correlations of total HF-digestible Sn, Cd, and Ag to total Cr in soils of the old sludge application site. The linear regression lines are forced through points near the origin that correspond to the elemental composition of the control soils.

ment in Cr, the slopes would equal the concentration ratio of each element to Cr in the sewage sludge applied at the site if no selective losses of elements from the surface soil occurred since the sludge was applied (about 20 years earlier). However, subsequent loss from the soil of any element, if it occurred to a degree different from that of Cr, would change this slope. In Table 5, the slopes from the linear regressions are compared with the respective elemental ratios in the sludge, showing that for these elements, the concentration increase in the soil relative to Cr is less than would be expected based on the composition of the sludge applied. Based on the differ-

TABLE 4

Linear correlations between concentrations of several elements (C_M) and chromium (C_{Cr}) in soil samples from the old sludge site. All elements are in units of mg/kg. The regression line has been forced to originate at the value for C_{Cr} and C_M of the control soil at this site

Linear Regression	r value
$C_{Cd} = -3.65 + 0.0787 C_{Cr}$	0.989
$C_{Ni} = 19.0 + 0.149 C_{Cr}$	0.986
$C_{Sn} = -3.33 + 0.121 C_{Cr}$	0.993
$C_{Mo} = 0.798 + 0.00521 C_{Cr}$	0.967
$C_{Ag} = -1.14 + 0.0248 C_{Cr}$	0.988
$C_{Cu} = -10.9 + 0.678 C_{Cr}$	0.994
$C_{Zn} = -46.8 + 3.47 C_{Cr}$	0.991
$C_{Sr} = 65.5 + 0.155 C_{Cr}$	0.988
$C_{Sb} = 0.286 + 0.00327 C_{Cr}$	0.975
$C_U = 2.17 + 0.00126 C_{Cr}$	0.933

TABLE 5

Comparison of best-fit linear regression slopes from Table 4 to elemental ratios in the sludge, and elemental losses relative to chromium estimated from these

	Sludge ratio	Regression slope	Relative loss (%)
Cd/Cr	0.143	0.0787	45%
Ni/Cr	0.253	0.149	41%
Sn/Cr	0.180	0.121	33%
Mo/Cr	0.025	0.00521	79%
Ag/Cr	0.031	0.0248	20%
Cu/Cr	1.09	0.678	38%
Zn/Cr	4.50	3.47	23%
Sb/Cr	0.0107	0.00327	69%
Sr/Cr	0.551	0.155	72%

ence between the slopes and the sludge elemental ratios, the loss of each element relative to Cr was calculated (Table 5). Those trace elements listed in Table 5 seemed to show some degree of loss relative to Cr, with Sr, Sb, and Mo having the highest loss (70–80%). Losses of Cd, Ni, Sn, Cu and Zn were lower, ranging from about 20% to 45% of total. Losses of several of these elements had previously been estimated based on an analysis of the same soils for metals by nitric-perchloric acid digestion, giving similar loss estimates for Cu (43%) and Sr (73%) but a higher estimate for Zn (38%) and lower for Cd (23%) (McBride et al. 1997) compared with the estimates in this study (Table 5). Loss of Pb could not be estimated at the site because of the contamination of the soil by Pb arsenate as well as Pb from sewage sludge.

The greatest uncertainty in this analysis is whether the composition of the archived sludge (see Table 1) accurately represents the composition when it was actually applied. Details on other analytical data for this sludge are reported by McBride et al. (1997), indicating that losses of several trace elements occurred during field storage of the sludge prior to collection of the archived sample. Nevertheless, metal loss estimates on a relative basis are notably altered for only two metals, Zn and Cd, by using these other reported analyses for the sludge rather than that of the archived sample.

Field-estimated operational K_D values for these metals, obtained by dividing the average total metal concentrations in the soil (Table 1) by the soluble concentrations measured in the percolates (Table 2), represent the potential for these elements to leach. Percolates are lower in trace metal concentration than laboratory-extracted soil solutions from the topsoil by a factor of about 2 to 3 in most cases, probably because of some re-adsorption of metals in the subsoil before the percolate reaches the 60-cm sampling depth. The logarithm (base 10) of the field operational K_D values estimated in this way are plotted against estimated metal loss in Fig. 2, showing a general relationship of estimated long-term loss to K_D . However, Sn deviates from the general tendency of high K_D to correspond with lower loss. This could indicate that losses of Sn from the soil may occur by processes other than leaching or that Sn had been lost from the leachate samples during collection or the prolonged storage prior to ICP-MS analysis. Sn may form volatile organotin compounds in soil and water (Hirner et al. 1994), so that this could have lowered the Sn

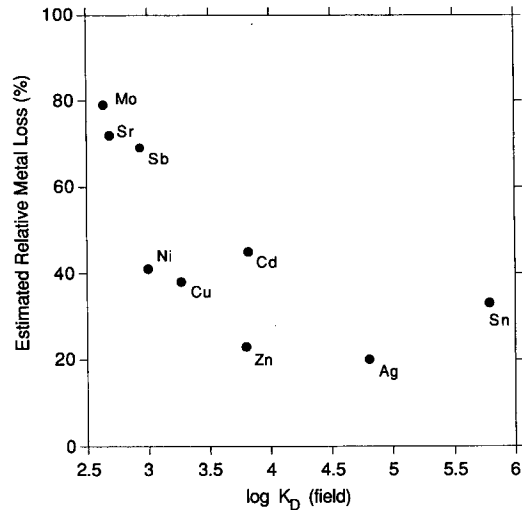


Fig. 2. Correlation of the operational (field) $\log K_D$ (distribution coefficient) of several elements to their estimated loss from the topsoil. Loss is measured as the percentage reduction of total (HF-digestible) elemental concentration relative to total soil chromium concentration.

concentration in stored water samples or accelerated loss from soil compared with other metals that do not form volatile compounds. However, Keijzer and Loch (1995) reported that Sn did not remain soluble in stored soil water solutions during prolonged storage, evidently precipitating as tin oxide. Other elements, including Sb, Hg and As, are also known to form volatile compounds, which could lead to losses by processes other than leaching.

DISCUSSION

Dissolved concentrations of several EPA-regulated and unregulated elements were much higher in percolates where sludge had been heavily applied in the orchard than at an adjacent control site. Some of these elements are known to have effects on biota at quite low dissolved concentrations, and thus, ecological effects could be of concern. For example, Hg in shallow groundwater from the control site was below detection by ICP-MS ($<0.010 \mu\text{g/L}$), but averaged $0.13 \mu\text{g/L}$ at the sludge site. Since the total Hg in the sludged soil (0–12") averaged $0.64 \pm 0.04 \text{ mg/kg}$, compared with 0.29 ± 0.07 in the control (orchard) soil (McBride et al. 1997), it is apparent that a large relative increase in dissolved Hg at 60 cm depth resulted from an approximate doubling of total soil Hg. This can be attributed

to the increased dissolved organic matter in leachate from the sludge-treated soil (compared with the control), known to have a strong correlation to dissolved Hg in natural waters (Gaudet et al. 1995), as well as to the evidence that some Hg has migrated to at least 60 cm depth in the sludge-treated soil (McBride et al. 1997). The control orchard soil is somewhat higher in Hg than normal, exceeding the average Hg concentration in agricultural soils (<0.10 mg/kg), yet this smaller contamination, possibly from use of Hg as a fungicide has not resulted in detectable Hg in leachate.

This result has implications for Hg loading in agricultural soils that are permitted by present EPA rules on sludge application. Permitted Hg loading under the 503 regulation is 17 kg ha^{-1} , roughly equivalent to 8 mg kg^{-1} Hg in the topsoil. Inasmuch as the sludge applied at this site contained between 3 and 5 mg/kg of Hg (Furr et al. 1981; Heffron et al. 1980), no loading limit would apply under the EPA 503 rule. That significant Hg is measured in percolate at a soil concentration $< 1 \text{ mg/kg}$ total Hg suggests that the much higher EPA-permitted loading could eventually result in dissolved Hg concentrations in percolates that exceed ecological and drinking water standards. Water quality guidelines in Canada have been set at $0.1 \mu\text{g L}^{-1}$ for Hg to protect aquatic life (Gaudet et al. 1995). Whether Hg in shallow groundwater reaches aquatic ecosystems or wells depends critically on subsoil depth and characteristics so that a particular Hg loading acceptable at one site may cause groundwater contamination at another.

The percolate concentrations of As, Cd, and Ni are close to the maximum contaminant level (MCL) values of 50, 5, and $100 \mu\text{g/L}$, respectively, set by EPA under the Safe Drinking Water Act. It is likely that the high As is a result of lead arsenate residual effects at this orchard site, but it cannot be determined if the sludge addition had a mobilizing effect on As since the soil at the control site had low total As (Table 1). Conversely, Cr, Cu, and Pb are below their respective MCL values. Since the soil at this site is fine-textured and near neutral pH, and below the EPA cumulative pollutant loading (CPLR) values for several elements exceeding the groundwater standard, the CPLR values may not protect shallow (such as agricultural tile drain) groundwater quality in a soil type having a high capacity to retain metal contaminants. Attenuation and dilution of contaminants in these percolates as they move to deeper groundwater is likely to occur, but the ex-

tent of this depends on subsoil characteristics and the degree of re-adsorption of metals.

The tendency of estimated metal loss from the surface soil to be related to the K_D values (Fig. 2) implies that, as expected, more soluble metals are lost from the surface soils in substantial amounts over a period of decades. For those metals that dissolve largely in the form of metal-organic complexes, release of the metal with dissolved organics may be by a very different mechanism (possibly biological) than subsequent readsorption (Guggenberger et al. 1998). This complex mobilization/immobilization process cannot be readily modelled using the convective-dispersive equation, which relies on the assumption of local equilibrium to predict metal movement through the profile. Thus, metal complexes released from surface soils, where biological activity is high, may leach into subsoils and be less strongly retained by mineral surfaces there (Bourg and Darmendrail 1992; Christensen et al. 1996). This lack of retention explains the low subsoil concentrations of heavy metals at the site described in this paper (Richards et al. 1998).

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