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Bioavailability and crop uptake of trace elements in soil columns amended with sewage sludge products

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Abstract

In order to assess the potential impact of long-term sewage sludge application on soil health, the equivalent of about 25 years of agronomic applications of low-metal ('EQ') sewage sludge products were made to greenhouse soil columns. After a 6-year period of 'equilibration', during which time successive crops were grown with irrigation by simulated acid rain, the plant-available quantities of trace elements were estimated in the soils by extraction with 0.01 M $CaCl_2$ at 90 °C, and measured directly by uptake into a crop of red clover (*Trifolium pratense* L.). Soil pH had a strong influence on the level of extractable and plant-available metals, and because the tested sludge products affected soil pH differently, pH was directly factored into the comparison of different sludge treatments with controls. $CaCl_2$-extractable levels of several metals (Cu, Zn, Mo), sulfur and phosphorus were found to be higher in the soils amended with organic-rich sludge products than in the control soils. However, extractable Cd and Ni were not significantly elevated by the sludge amendments, presumably because of the low total loading of these metals. Copper, Zn and Mo applied in the form of sludge ash had low soil extractability, suggesting that these trace metals were trapped in high-temperature mineral phases formed during sludge incineration, and resisted subsequent weathering in the soil environment. Extractable soil metals in the alkaline-stabilized sludge treatment were also generally low. Phytotoxicity from the sludge metal loadings (Zn $\leq$ 125, Cu $\leq$ 135 kg/ha), was not clearly indicated as long as soil pH was maintained in the 6–7 range by lime amendment. Nevertheless, unexplained depressions in yield were noted with some of the sludge products applied, particularly the dewatered and composted materials. On limed soil columns, the most consistent effect of sludge product amendment on red clover composition was a marked increase in plant Mo.

Introduction

Sewage sludges (biosolids) typically contain much higher concentrations of metals such as Cu, Zn, Ni, Mo, Cd and Pb than the soils to which they are applied. The initial solubility and leaching potential of these sludge-borne metals in soils is strongly influenced by the type of sewage sludge processing employed to 'stabilize' the sludge product prior to land application as well as the soil characteristics at the site (McBride,1998; Richards et al.,1997, 2000). Less is known about the long-term bioavailability or leachability of these metals in soils of different types, although experience from long-term sludge application sites suggests that soil physical-chemical properties, especially pH, CEC, and organic matter and clay content, are likely to assume greater importance than sludge characteristics in determining metal behavior over the long term (Chaudri et al., 2000; McBride et al., 2000a; Smith,1994). Regulations in many countries do not presently consider either the type of sludge applied, or the soil properties at the application site, in setting limits for heavy metal loadings.

Despite the common view that heavy metals are strongly immobilized in soils, numerous studies have shown that a substantial fraction of heavy metals ap-

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plied to soils, whether as salts or in sludge products, can be lost from the topsoil over years or decades of exposure to natural climatic conditions (Baveye et al., 1999; Richards et al., 1998; Gunkel et al., 2002; Mbila et al., 2001; McBride et al., 1997,1999). Although leaching of metals out of the topsoil is detectable following sewage sludge application (Gove et al., 2001; Keller et al., 2002), there remains some question whether the measured losses in the surface soils can be fully explained by leaching processes. Nevertheless, the high dissolved organic matter (DOM) and acidic pH generated in soils by sludge application may promote dissolution and facilitate transport of metals (Antoniadis and Alloway, 2002; Richards et al., 2000).

Total metal concentration in soils is not a very useful predictor of bioavailability or soluble concentration of the metal (Chaudri et al., 2000; Knight et al., 1998). Conversely, the $CaCl_2$-extracted metal fraction predicts metal solubility and crop uptake (Houba et al., 1986,1990; Sanders et al., 1987) and, presumably, the potential for metal leaching. Our objective in the present study was to determine the readily extractable (by 0.01 M $CaCl_2$ at 90 °C) fraction of trace metals, particularly Cu, Zn, Ni, Cd and Mo, after soils had been heavily loaded with different sludge products and subsequently cropped repeatedly. We also wanted to determine if the 0.01 M $CaCl_2$-extractable trace metal concentrations in the amended soils correlated to metal content in a test crop, red clover (*Trifolium pratense* L.). To accomplish this, we sampled and analyzed all soils and plant tissues for one particular crop, red clover, grown on intact soil columns that had been excavated from the field and amended several years earlier with various sewage sludge products. These amended columns have been continuously cropped for about 6 years under irrigation, with monitoring of column leachates for trace metals (Richards et al., 2000). Generally, the differently processed sludge products led to different concentrations of metals in leachates. Leaching of metals such as Cu and Zn tended to peak shortly after the sludge products were applied and incorporated. However, the cumulative metal losses in leachate after several years of irrigating the columns were small relative to the total applied metal loadings.

Our overall goal was to measure the long-term effects of sludge and soil characteristics on trace metal behavior and fate in soils and cropping systems. Also, because both phosphorus (P) and sulfur (S) are typically field-applied in excess of agronomic requirements when sludge products are used as nitrogen fertilizers, we investigated the long-term impact of the various sludge products on levels of easily-extractable soil P and S in amended soils.

Materials and methods

Greenhouse study

The on-going greenhouse experiment involved sequential cropping of 51 undisturbed Hudson silt loam and 39 Arkport fine sandy loam soil columns (28 cm in diameter by 35 cm deep), using irrigation with simulated acid rain (pH 4.1) typical for the region. The soil columns were excavated in 1993 from the Cornell Orchard and nearby pasture (Ithaca, NY), respectively, and are are classified as: fine, illitic, mesic, Glossaquic Hapludalf (Hudson series) and coarse, loamy, mixed, active, mesic Lamellic Hapludalf (Arkport series). Details of growing conditions and the multi-year cropping sequence for this experiment have been described elsewhere (Richards et al., 2000). In brief, columns of the Hudson and Arkport soils received different soil amendments at the beginning of the experiment (dewatered sewage sludge, pelletized sludge, incinerated sludge (ash), composted sludge, alkali-treated sludge), or received no amendment (control). All of these amendments were derived from the same anaerobically-digested sewage sludge stock material, and were applied and mixed into the top 10 cm of the soil columns at rates that approximately equalized heavy metal loadings from the different products. The sludge products were applied in 4 increments over 3 years in sufficient quantities to reach Cu and Zn loadings in the range recommended as cumulative limits in some European countries and Canada.

The trace metal concentrations in the sludge products are given in Table 1, and the estimated cumulative sludge product and metal loadings for the different treatments are given in Table 2. Although the total sludge loadings were very high, representing about 25 years of agronomic applications, the heavy metal loadings for all treatments were under 10% of the EPA-permitted cumulative pollutant loadings (USEPA, 1993).

Additionally, one set of 12 Hudson soil columns had been excavated from a field site (McBride et al., 1997, 1999; Richards et al.,1998) that had received a heavy application of metal-contaminated sludge some 20 years earlier (referred to as the Hudson 'old site'). These 'old site' columns were more metal-contaminated than the recently amended columns,

Table 1. Trace metal concentrations (mg/kg dry weight) in the sludge products applied to the Hudson and Arkport soil columns in the greenhouse

Metal	Dewatered	Pellets	Compost	Alkali-treated	Ash
		mg/kg (dry wt. basis)			
Cd	5.6	6.4	4.2	1.6	3.6
Cu	587	606	469	119	1220
Mo	50	55	33	9.8	95
Ni	36	38	33	13	75
Pb	132	137	109	NA[a]	145
Zn	545	567	458	115	959

[a]Could not be determined because of matrix interference from high Ca in digested sludge

Table 2. Estimated metal loadings applied to the Hudson and Arkport soil columns in the greenhouse

Metal	Dewatered	Pellets	Composted	Alkali-treated	Ash
		($kg\ ha^{-1}$)			
Cd	1.2	1.1	1.4	1.1	0.35
Cu	124	117	134	79	119
Mo	6.1	4.7	7.1	3.8	5.4
Ni	7.6	8.1	8.4	8.4	7.3
Pb	28	27	30	30	14
Zn	116	114	125	76	94
Cumulative sludge[a]	212	221	249	663	98

[a]Loading in units of metric tons/hectare

particularly with Zn and Cd. They were not further amended with sewage sludges, but were used to evaluate the impact of high soil metal concentrations on phytotoxicity in red clover.

Within each of the replicated sludge treatments, the soil pH was either (a) maintained near 6–7 (by initial and subsequent $CaCO_3$ addition), or (b) was initially adjusted to pH 5 (by H_2SO_4 addition) and received no subsequent pH management. Each pH treatment was triply replicated. Additionally, a set of 'natural' controls from each soil received no pH management and had unadjusted initial pH levels of $\sim$ 6.5 for Hudson and $\sim$ 5.0 for Arkport. Therefore, there were 9 Arkport and 9 Hudson control columns, divided into 3 different pH treatments. The pH in the columns, particularly those treated with dewatered sludge, tended to decrease over time because of the acidifying effect of the mineralization of organic N and S and the acid rain leaching. These pH treatments and additional acidifying processes produced a wide range of pH (from above 8 to below 4), with Arkport soils reaching the lowest pH values.

Soil extraction

Samples of the surface soil from each column were collected after the 12th cropping cycle (Romaine lettuce) was harvested, and were archived for subsequent pH measurement and extraction of trace elements by the hot 0.01 M $CaCl_2$ test. This soil test is similar to the technique described by Houba et al. (2000), but extracts somewhat larger quantities of most elements from soils than the same extractant at room temperature. The test has been demonstrated to estimate plant-available trace elements in soils at least as well as some more commonly used soil tests (McBride et al., 2003). Ten g of air-dry soil suspended in 25 mL of 0.01 M $CaCl_2$ were heated at 90 °C for 30 min. The resulting supernatants were filtered hot through #42 Whatman filter paper, and 2 drops of trace metal grade 1 M HNO_3 were added to prevent metal precipitation and to inhibit microbial growth. The filtered solutions were analyzed by axial-view ICP, at the Cornell Department of Agriculture ICP Laboratory, Ithaca, NY.

The pH of the soils were measured by glass electrode after 30 min of stirring equal parts soil and distilled water (by volume).

Crop analysis for metal uptake

During and following the 3 years of sewage sludge amendment, the columns were cropped alternately with oats and lettuce, typically 2 crops annually. The oat crop was later replaced by red clover (*Trifolium pratense* L.), and 3 crops of red clover were grown alternately with lettuce prior to the clover crop grown and sampled for this study. In summary, six years of cropping with irrigation followed the sludge amendments before this red clover crop, which is the 13th crop in the overall experiment.

The columns were fertilized with the equivalent of 39 kg/ha of P and 49 kg/ha of K at planting (using KH_2PO_4) in an attempt to equalize soil fertility across treatments. The crop was irrigated with simulated acid rain water (pH 4.1, ionic composition given in Richards et al., 2000) at a rate designed to promote soil column leaching. Over the complete cropping sequence spanning about 8 years, the equivalent of about 10 years acid rain deposition (for central New York state) was applied in the greenhouse.

The red clover was harvested at flowering stage by cutting the tops a few cm above soil level. The plant tissues were dried at 70 °C and ground in a stainless steel Wiley mill before storing in sealed plastic bags. The clover tissues were digested by a standard nitric-perchloric acid dry-ashing procedure, and the digests were analysed for total trace metals by axial-view ICP spectrometry. Standard QA/QC procedures were followed as described by McBride et al. (2000b).

Results and discussion

The impact of the different soil amendments (dewatered sewage sludge, alkali-treated sludge, composted sludge, pelletized sludge, sludge ash, control) on trace metal, P and S solubility and potential bioavailability in the soil columns was measured by 0.01 M $CaCl_2$-extractable elements. This soil extraction has been shown to predict the availability of trace elements for crop uptake (McBride et al., 2003). The results are reported below for Zn, Cu, Mo, Cd, Ni, P and S. Both Cr and Pb had low extractability in the amended columns (data not shown). The data for extractable metal concentrations in the Arkport and Hudson soils are combined because no clear difference could be discerned in extractable metal concentrations between the two soil series – type of sludge product applied and soil pH at time of sampling had the greatest impact on extractable metals.

Extractable soil Zn

Figure 1 displays the readily-extractable Zn (by 0.01 M $CaCl_2$) measured in the Hudson and Arkport soils (all soil column data shown) as a function of pH about 6 years after the sludge product amendments and repeated cropping and leaching. The figure reveals that, at any specific soil pH, extractable Zn remains elevated by the sludge amendments above that in the control soils, an increase essentially unaffected by the form of the sludge incorporated into the soil. The exception is sludge ash, a treatment which added almost as much Zn to the soil columns as the dewatered sludge, compost and pellets, but did not increase extractable Zn above the level in the unamended (control) soil columns. This result suggests that the Zn in the incinerated ash was entrained in high-temperature minerals that have subsequently resisted weathering in the soil environment, despite acidifying conditions. The alkaline-treated sludge also produced low Zn extractability, but this is consistent with the high soil pH (near 8) resulting from this treatment, and does not necessarily indicate the Zn to be irreversibly bound in the soil.

Although the increase in $CaCl_2$-extractable soil Zn was measurable from the 100–125 kg/ha Zn loading (Table 2), it was small relative to the extractable Zn in the 'old site' columns. Data for the 'old site' columns stand out in Figure 1 at much higher extractable Zn, an indication of the higher Zn present in these soils ($>$ 1000 mg/kg) compared to the recently sludge-amended columns ($\leq$ 200 mg/kg). Thus, despite the long time since sludge application ($>$ 20 years), Zn remains sufficiently available in the 'old site' to cause severe phytotoxicity in the crops (red clover, lettuce) grown on the columns (see next section).

Extractable soil Cu

As shown in Figure 2, $CaCl_2$-extractable Cu was generally increased (relative to the controls) by all sludge products applied with the exception of the sludge ash. Thus, as with Zn, the ash apparently contained Cu in a form that was not readily solubilized in the soil, even 6 years after incorporation. The 'old site' columns had substantially higher extractable

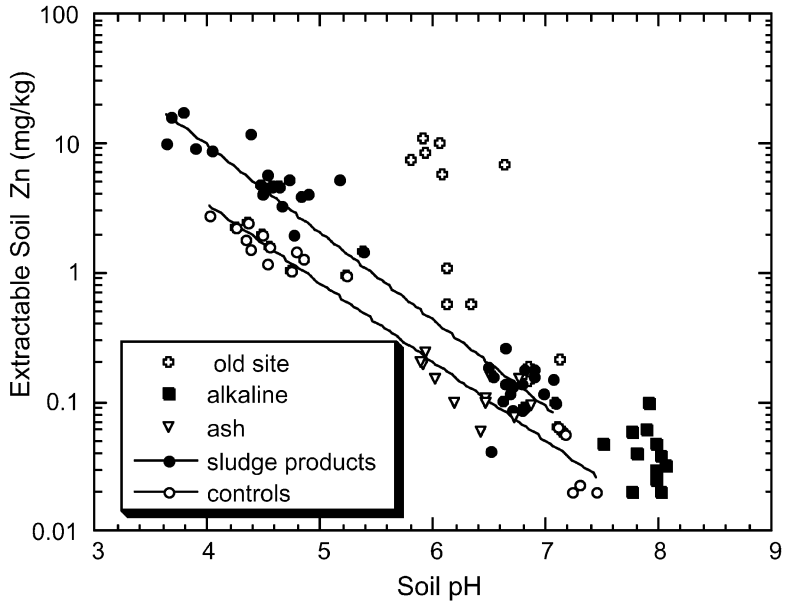

Figure 1. Concentration of 0.01 M $CaCl_2$-extractable Zn (mg/kg) in the topsoils of Hudson and Arkport soil columns 6 years after incorporation of sludge products. Data for the dewatered, composted and pelletized sludge products are combined as 'sludge products' because they showed similar magnitudes of Zn and other metal extractability. Best fit lines are drawn for the unamended (control) columns and the dewatered sludge-amended columns. The Hudson 'old site' soil columns, included for comparison, were excavated from a field where a heavy application of high-metal sludge had occurred in 1978.

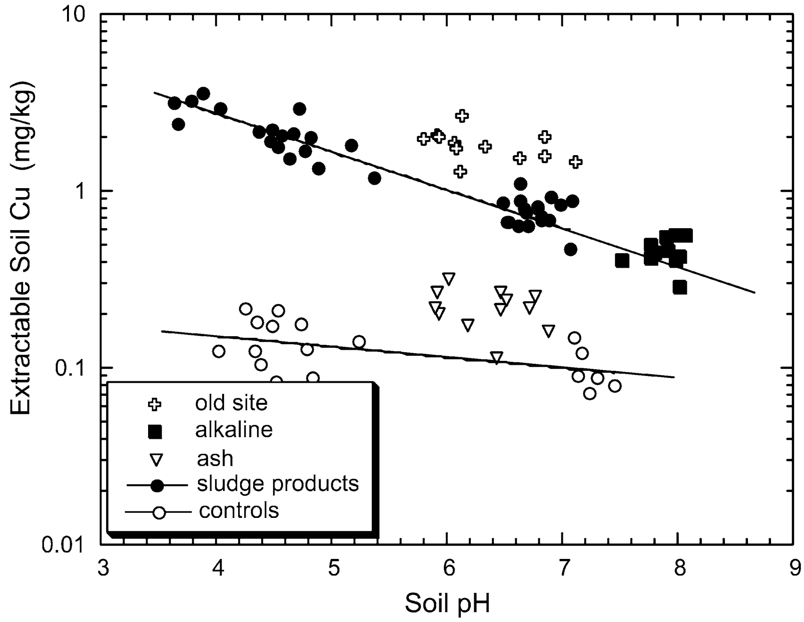

Figure 2. Concentration of 0.01 M $CaCl_2$-extractable Cu (mg/kg) in the topsoils of Hudson and Arkport soil columns 6 years after incorporation of sludge products. See Figure 1 legend for further explanation of treatments.

Cu than the sludge product-amended columns. This difference is explained by the higher total soil Cu (300–450 mg/kg) at the 'old site' than in the product-amended columns (< 170 mg/kg). For all sewage sludge amendments (except the ash), the most significant factor in determining the readily extractable quantity of Cu was soil pH (Figure 2). All sludge-amended soils (dewatered, composted, pelletized and alkali-treated) could be described by a single Cu solubility relationship to soil pH, with results from both soil series (Hudson and Arkport) pooled together.

The fact that high soil pH did not produce a higher level of easily extractable Cu is contrary to previous observations of enhanced dissolution of Cu by release of organic matter into soil solution at higher pH (McBride, 1998; McBride et al., 2000b). In the soil columns, however, several years of accelerated leaching by acid rain may have removed more soluble forms of Cu from the topsoil prior to this experiment. Earlier analyses of leachates from these same soil columns showed that Cu leached as readily from the alkaline sludge-amended Hudson and Arkport soils at near-neutral pH as at low pH, evidence for soluble organic-enhanced mobilization (McBride, 1998; Richards et al., 2000).

Extractable soil Mo

Sludge products generally increased $CaCl_2$-extractable soil Mo (relative to controls) if the soil pH was 6 or higher as a result of the alkaline reaction of the sludge product itself (e.g., alkaline-stabilized sludge), or if the soil was limed to control pH (see Figure 3) . Low soil pH, regardless of sludge product applied, prevented measurable increases in extractable Mo. The exception to this general pattern is, as before, the sludge ash, which did not appear to release significant Mo into extractable form, despite the pH of the ash-amended soils being in the 6–7 range (Figure 3).

Unlike the other metals, higher soil pH increased readily extractable Mo in the soil columns. It should be noted that the sludge products used in this study had Mo concentrations ranging from 9.8 mg/kg (alkaline sludge) to 95 mg/kg (sludge ash) (Table 1) , with cumulative loadings of 3.8 to 7.1 kg/ha on the soil columns. The fact that the most alkaline amendment (alkaline-treated sludge) did not produce the highest level of easily extractable Mo is contrary to expected dissolution and weak sorption of Mo at higher pH (Goldberg and Forster, 1998; McBride, 1998; McBride et al., 2000b). This may indicate that substantial leaching of soluble forms of Mo had already occurred before the soils were sampled for analysis, as earlier leachate analyses had shown that the greatest migration of Mo out of the topsoil had occurred from the columns amended with the alkaline sludge (Richards et al., 2000).

Extractable soil Cd and Ni

As shown in Figure 4, the various sludge products had little discernable long-term effect in increasing $CaCl_2$-extractable Cd in the soil columns over that in the controls, with soil pH having the most important controlling influence. Thus, those amendments that acidified the soil caused extractable (and bioavailable) Cd to increase. The sludge ash treatment added a smaller Cd loading to the columns than the other sludge products (Table 2), probably because the incineration process caused volatilization losses of sludge Cd (Abanades et al., 2002).

The 'old site' columns had much higher $CaCl_2$-extractable Cd than the sludge product-amended columns (Figure 4). This difference is explained by the much higher total soil Cd (25–50 mg/kg) at the 'old site' than in the sludge product-amended columns (< 1.5 mg/kg).

A very similar pattern to Cd was observed for extractable Ni as a function of soil pH for the different sludge treatments (data not shown). Again, the sludge products had little discernable long-term effect in increasing $CaCl_2$-extractable Ni in the soil columns over that in the controls. However, treatments that lowered soil pH increased extractable Ni. In contrast, the old-site columns had higher extractable Ni, consistent with higher total soil Ni (80–100 mg/kg) compared to the sludge product-amended columns (25–30 mg/kg).

Since Cd and Ni loadings from sludge products were less than 1.5 and 10 kg/ha, respectively, the results suggest that Cd and Ni applications of this magnitude from low-metal sludge products are not likely to have significant long-term effects on soil Cd or Ni status. Nevertheless, increased leaching of Cd and Ni was detected following the sludge applications on the Arkport soil columns (Richard et al., 2000). In fact, Ni leached as readily from sludge-amended soils at near-neutral pH as at low pH, evidence for alkali-enhanced mobilization (McBride, 1998). As with Cu, then, the lack of evidence for higher extractable Ni in the treatments at higher pH may simply indicate loss of most of the soluble metal fraction by leaching during the years of column irrigation prior to this study.

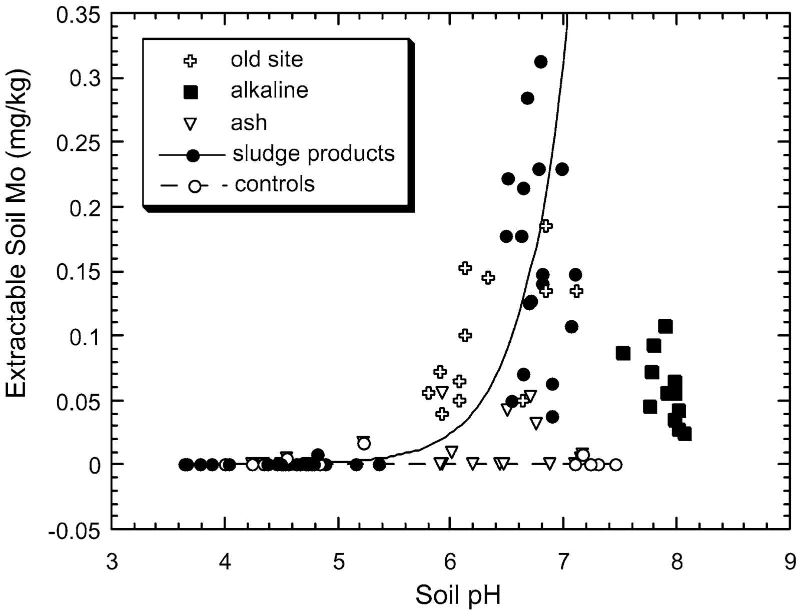

Figure 3. Concentration of 0.01 M $CaCl_2$-extractable Mo (mg/kg) in the topsoils of Hudson and Arkport soil columns 6 years after incorporation of sludge products. See Figure 1 legend for further explanation of treatments.

Extractable soil P and S

Figures 5 and 6 summarize, for the Hudson soil columns (data for the Arkport columns are very similar, and therefore not shown) , the long-term (residual) effect of the different sludge product amendments on $CaCl_2$-extractable S and P. In general, organic-rich sludge products (dewatered, pelletized, composted) increased soil extractable S and P, consistent with the relatively high concentration of these two elements in the anaerobically-digested sewage sludge. The incinerated sludge (ash) amendment increased extractable soil P, but not S. This can be explained by the fact that incineration retains P but results in loss of S upon combustion of organic matter and oxidation to SO_2. The alkaline-sludge amendment did not increase extractable soil S, and significantly decreased extractable soil P. Because sulfate is retained more strongly in soils at low pH, substantial earlier losses of S by leaching from the more alkaline treatments (Richards et al., 2000) could have diminished easily-extractable S in the near-neutral soils.

It is evident from Figures 5 and 6 that easily extractable S and P are highest in the most acid sludge product-amended soils. This result is not explained by the expected sorption behavior of sulfate and phosphate, which are bonded most strongly at acid pH on variable-charge mineral surfaces such as Fe oxides. Phosphate solubility in these soils may be controlled by Ca phosphate, which is most soluble at low pH. The fact that the alkaline sludge product produced the lowest extractable P value supports this interpretation, as this product favours Ca phosphate formation by supplying a large excess of $Ca(OH)_2$. However, the higher extractable S in the acid soil columns is partly the result of H_2SO_4 additions to adjust the pH, as can be seen by comparing extractable S in the acid (H_2SO_4-amended) and near-neutral control columns.

A comparison of the levels of extractable P and S in Figures 5 and 6 reveals that much larger quantities of S than P are $CaCl_2$-extractable. The higher extractability of S compared to P is reflected in leachate composition, with S in leachates from sludge product-amended columns exceeding 200 mg/L shortly after amendment, and persisting at concentrations well above the control levels for several years (Richards et al., 2000). Leachate P concentrations, in contrast, never exceeded 2 mg/L of P, regardless of the type of sludge amendment (Richards et al., 2000).

Uptake of trace metals by red clover

The average trace metal concentrations in the red clover (*Trifolium pratense* L.) grown on the sludge-product amended Hudson and Arkport columns are summarized in Tables 3 and 4, respectively. Because

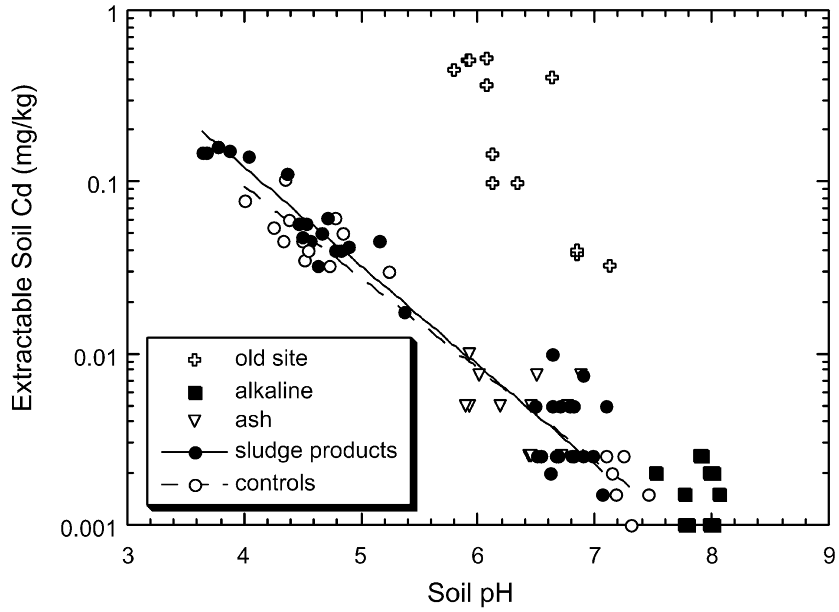

Figure 4. Concentration of 0.01 M $CaCl_2$-extractable Cd (mg/kg) in the topsoils of Hudson and Arkport soil columns 6 years after incorporation of sludge products. See Figure 1 legend for further explanation of treatments.

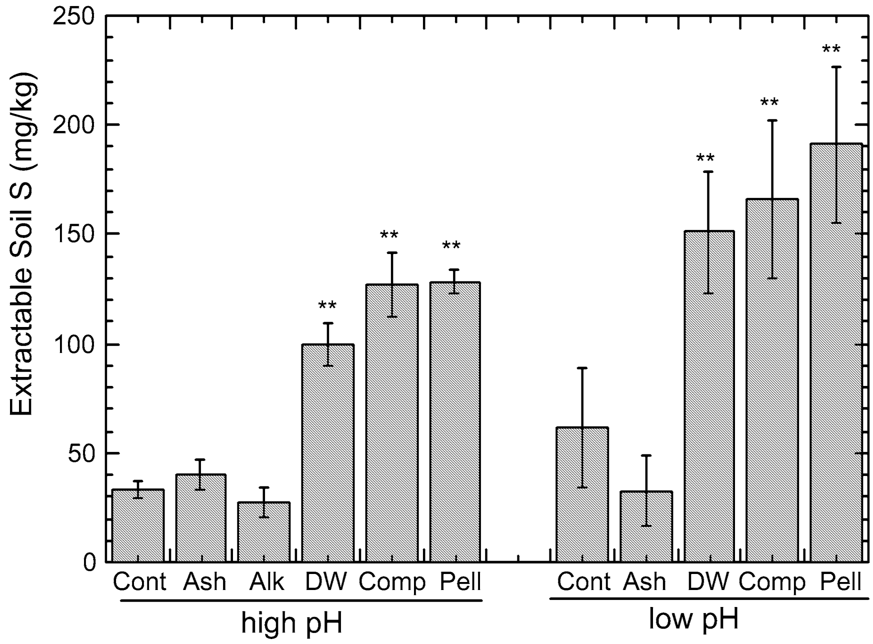

Figure 5. Concentrations of 0.01 M $CaCl_2$-extractable S (mg/kg) in the topsoils of Hudson soil columns 6 years after incorporation of sludge products. Treatments are labeled 'high pH' and 'low pH' depending on whether lime was applied to maintain soil pH. Treatments are labeled Cont (control), Ash (incinerated sludge), Alk (alkaline-stabilized sludge), DW (dewatered sludge), Comp (composted sludge) and Pell (pelletized sludge). Error bars denote±one standard deviation.

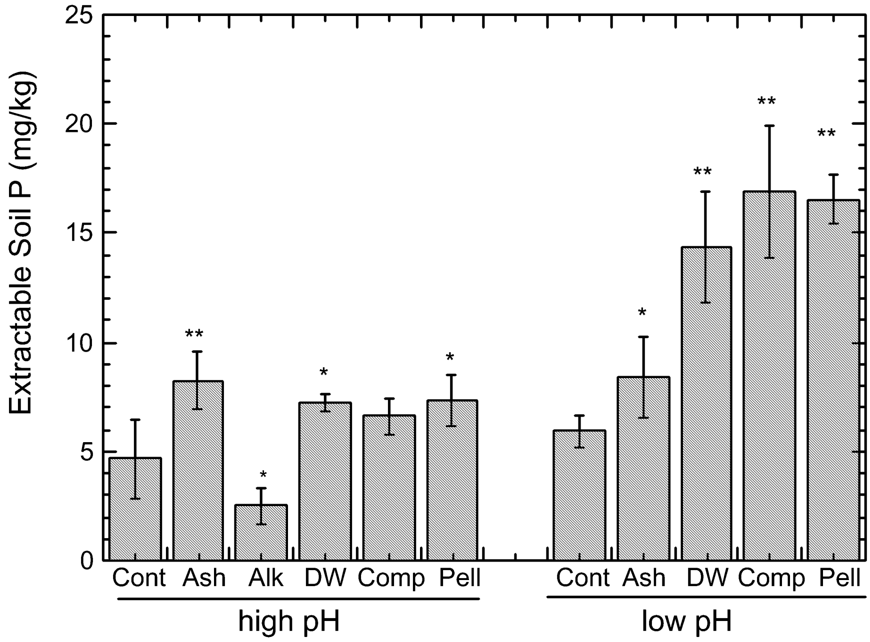

Figure 6. Concentrations of 0.01 M $CaCl_2$-extractable P (mg/kg) in the topsoils of Hudson soil columns 6 years after incorporation of sludge products. See Figure 5 legend for explanation of treatments.

of the large impact of soil pH on these trace metal levels in clover, the treatments are separated into the acid (either intentionally acidified or allowed to acidify by acid rain irrigation and mineralization of organic N and S) and limed (managed to maintain pH or amended with alkaline sludge products). It is clear from these Tables that Zn, Cd, Ni and Mn concentrations are higher in clover grown on the more acid soil columns. Soil pH did not have a consistent effect on Cu levels in clover, whereas higher pH treatments invariably resulted in greater Mo concentrations in clover.

Manganese concentrations in clover grown on a number of the soil columns were very high and presumably phytotoxic. This result was due in large part to depressed soil pH; those soil treatments which produced strongly acidified soils typically produced very high clover Mn concentrations, sometimes exceeding 1000 mg/kg. In contrast, the alkaline sludge and sludge ash amendments produced generally much lower clover Mn ($<$ 200 mg/kg), as these treatments strongly limited soil acidification.

The Mo, Zn, Cd and Ni concentrations extractable by 0.01 M $CaCl_2$ from the soils were found to predict reasonably well the tissue concentrations of harvested red clover, even when both soil series (Arkport, Hudson) and all sludge treatments were included in the analysis. The best-fit regression functions relating clover trace metal concentration to soil extractable metals are listed in Table 5. The relationship is weakest for Cu, with the low slope of the equation revealing a strong soil-plant barrier to Cu uptake that is not present for the other metals listed in Table 5.

Phytotoxic effects of sewage sludge amendments

The most severe clover yield depressions relative to controls are observed on the Hudson sludge ‘old site’ columns. Figure 7 shows the significant relationship between clover yield and $CaCl_2$-extractable Zn in the Hudson ‘old site’ soil columns, suggesting that the severe yield depressions are attributable to Zn toxicity. However, because other heavy metals are also present at high concentrations in soils of this site, Zn may not be the only metal causing toxicity. Plant tissue analyses confirmed that levels of Zn in the red clover grown on these soil columns often approached or exceeded concentrations (250–350 mg/kg) likely to cause serious phytotoxicity, and that the yield depression is significantly correlated to tissue Zn concentration (see Table 3). Concentrations of tissue Mn were also very high in some of the more acid ‘old site’ soil columns, and Mn toxicity could have contributed to yield reductions.

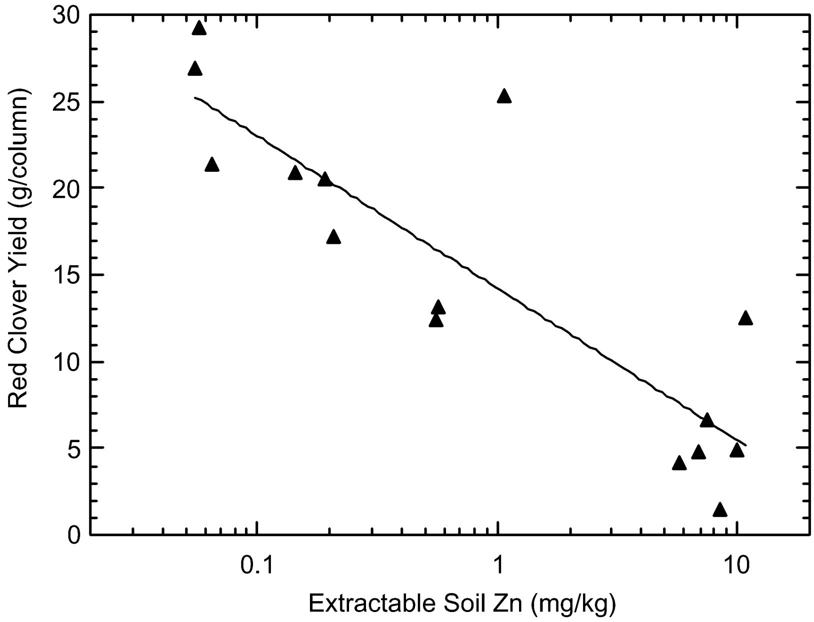

Figure 7. Red clover yields on the 'old-site' metal-contaminated Hudson soil columns as a function of 0.01 M $CaCl_2$-extractable Zn in the soil.

The changes in soil pH resulting from the acid rainwater and various sewage sludge treatments were a dominant factor in determining red clover yield, with strong yield depressions resulting on the unlimed control and sludge-amended columns, particularly for the acid weakly buffered Arkport soils. Much of these yield depressions can be attributed to the high Zn and Mn concentrations in the clover (see Table 4).

Some of the soil column treatments were too strongly acidified by the heavy organic sludge amendments and acid rain irrigation to realistically represent a managed agronomic field situation. For that reason, only the sludge-amended soil columns maintained at near-neutral pH have been compared in Figure 8 to determine if the sludge products had any impact on yield when acidification was countered by liming. With the limed Hudson columns, only the dewatered sludge appeared to decrease yield, whereas only the sludge compost decreased yield on the limed Arkport columns. These yield effects are difficult to attribute to specific metal toxicities; liming suppressed Zn and Mn availabilities to levels that did not produce obviously phytotoxic metal concentrations in the clover. The cumulative loading of 100–125 kg/ha Zn from the sludge products (Table 2) produced a significant increase in Zn concentrations in red clover grown on limed columns (Tables 3 and 4). However, these Zn concentrations, generally less than 100 mg/kg, may not be high enough to produce measurable yield depressions.

The Arkport columns showed a positive yield response to the alkaline products (sludge ash, alkaline-stabilized sludge), probably because of the initially acidic nature, low CEC and low Ca status of the Arkport soil. Red clover prefers near-neutral, high Ca soils.

When all the soil columns are considered together, clover yield is found to be more strongly correlated to clover tissue Zn concentration than to soil pH. When the clover yields from the Hudson and Arkport columns are analyzed separately, the relationship to tissue Zn persists:

Hudson :

$$\text{Clover yield (g)} = 27.5 - 0.0673[\text{Clover Zn (mg/kg)}]$$

$$r = 0.699$$

Arkport :

$$\text{Clover yield (g)} = 14.9 - 0.0454[\text{Clover Zn (mg/kg)}]$$

$$r = 0.598$$

Based upon the old-site yield depressions (Figure 7), it can be deduced that $CaCl_2$-extractable Zn > 2.5 mg/kg is likely to produce yield depression in red clover. As Figure 1 shows, this Zn threshold is exceeded in the sludge product-amended columns only when soil pH is less than 5.5. The control soil columns (without sludge amendments), because

Table 3. Trace metal concentrations in red clover grown on sludge product-amended Hudson soil columns under acid (A) and non-acid (B) soil condition

Treatment	*n*	Soil pH	Zn	Cd	Cu	Ni	Mo	Mn
Acid treatments								
Dewatered	3	3.9	211 ± 29	0.69 ± 0.12	14.5 ± 2.2	10.6 ± 2.0	1.04 ± 0.05	1810 ± 2070
Compost	3	4.9	125 ± 27	0.22 ± 0.02	11.4 ± 0.56	6.0 ± 1.6	3.75 ± 0.37	161 ± 15
Pellets	3	4.7	163 ± 9.7	0.34 ± 0.06	10.7 ± 1.3	7.9 ± 0.63	5.03 ± 1.83	1390 ± 1030
Ash	3	5.9	36.5 ± 4.7	0.06 ± 0.03	9.8 ± 1.8	2.1 ± 0.24	7.07 ± 1.29	86 ± 29
Old site	6	6.1	312 ± 42	3.5 ± 0.5	10.9 ± 1.1	19.5 ± 3.5	12.8 ± 5.0	435 ± 77
Control	5	4.6	60.6 ± 15.9	0.17 ± 0.03	11.4 ± 1.2	6.5 ± 1.7	0.92 ± 0.34	531 ± 451
Limed treatments								
Dewatered	3	6.6	42.5 ± 5.2	0.08 ± 0.01	11.3 ± 1.1	3.4 ± 0.28	26.2 ± 2.9	99.7 ± 9.2
Compost	3	6.9	33.9 ± 1.3	0.07 ± 0.03	11.9 ± 0.49	1.7 ± 0.19	13.2 ± 2.1	334 ± 260
Pellets	3	6.8	38.7 ± 3.7	0.06 ± 0.01	12.2 ± 0.46	3.1 ± 0.4	18.1 ± 3.9	301 ± 373
Alkaline	6	7.8	22.1 ± 7.0	0.06 ± 0.03	13.2 ± 2.0	4.2 ± 6.2	15.0 ± 3.5	190 ± 176
Ash	3	6.7	29.3 ± 0.98	0.05 ± 0.00	10.2 ± 0.99	2.4 ± 0.22	7.26 ± 0.41	367 ± 258
Old site	6	6.6	146 ± 43	1.60 ± 0.05	10.2 ± 0.77	10.3 ± 2.9	17.0 ± 5.0	278 ± 22
Control	3	7.1	27.1 ± 4.3	0.06 ± 0.03	9.73 ± 0.57	2.1 ± 0.16	1.69 ± 1.36	68.3 ± 12.4

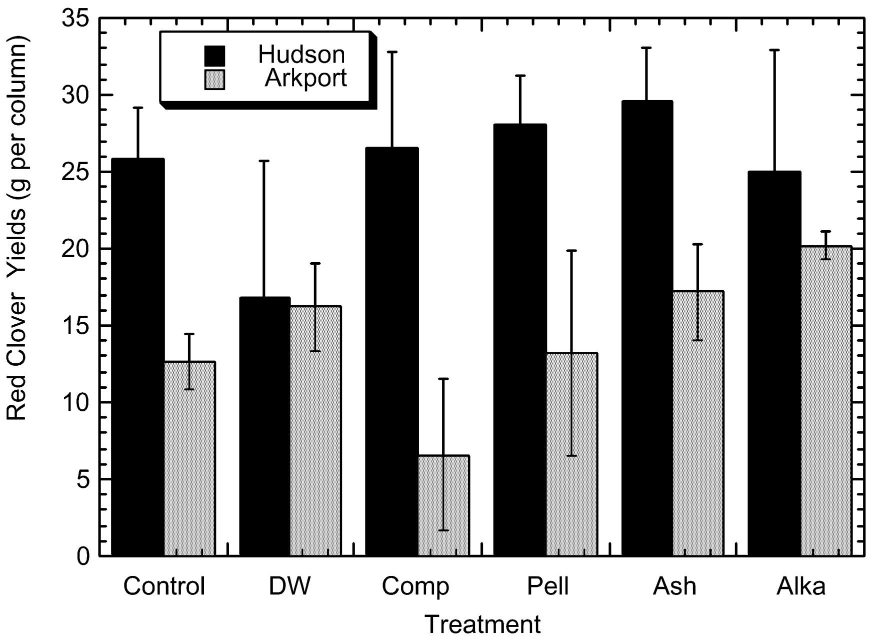

Figure 8. Average red clover yields (dry weight) on the sludge product-amended Hudson and Arkport soil columns. The treatments are dewatered sludge (DW), compost (Comp), sludge pellets (Pell), sludge ash (Ash) and alkaline-stabilized sludge (Alka). Error bars denote±one standard deviation for three yield measurements.

Table 4. Trace metal concentrations in red clover grown on sludge product-amended Arkport soil columns under acid (A) and non-acid (B) soil condition

Treatment	n	Soil pH	Zn	Cd	Cu	Ni	Mo	Mn
Acid treatments								
Dewatered	3	3.9	331 ± 7	1.61 ± 0.15	23.5 ± 5.4	24.5 ± 3.5	2.28 ± 0.59	1122 ± 333
Compost	3	4.9	242 ± 44	0.62 ± 0.13	8.90 ± 0.31	21.1 ± 17.8	2.93 ± 0.20	330 ± 58
Pellets	3	4.6	156 ± 32	0.33 ± 0.10	8.93 ± 1.42	10.3 ± 0.5	5.70 ± 0.52	177 ± 51
Ash	3	6.3	43.0 ± 5.3	0.07 ± 0.02	10.4 ± 0.50	6.1 ± 1.7	8.74 ± 2.91	119 ± 28.8
Control	6	4.5	92.3 ± 13.3	0.63 ± 0.15	10.5 ± 2.2	18.3 ± 1.5	1.08 ± 0.96	529 ± 223
Limed treatments								
Dewatered	3	6.8	36.0 ± 0.1	0.04 ± 0.01	15.1 ± 2.7	3.8 ± 0.3	34.7 ± 8.1	67 ± 19
Compost	3	6.8	47.2 ± 18.0	0.10 ± 0.03	12.2 ± 2.5	2.7 ± 0.40	16.6 ± 3.4	83.7 ± 29.3
Pellets	3	6.6	59 ± 36	0.08 ± 0.03	14.8 ± 4.4	4.5 ± 2.3	24.4 ± 13.6	80 ± 15
Alkaline	6	8.0	20.6 ± 6.2	0.06 ± 0.04	14.4 ± 0.8	1.5 ± 0.5	11.5 ± 2.8	46.1 ± 17.3
Ash	3	6.5	32.2 ± 1.1	0.06 ± 0.03	10.9 ± 0.7	3.5 ± 1.2	9.28 ± 2.45	108 ± 39
Control	3	7.3	16.9 ± 1.7	0.05 ± 0.02	8.89 ± 0.58	3.7 ± 2.4	3.43 ± 1.09	71.3 ± 6.9

Table 5. Relationship of trace metal concentrations (mg/kg, dry wt.) in red clover to the extractable concentration (mg/kg) in Hudson and Arkport soil columns treated with various sewage sludge products ($n = 90$)

Trace metal	Regression equation	r-value	Significance
Mo	$(Mo)_{RC} = 5.15 + 93.0(Mo)_{CaCl2}$	0.765	$P \ll 0.01$
Ni	$(Ni)_{RC} = 3.32 + 17.6(Ni)_{CaCl2}$	0.774	$P \ll 0.01$
Cd	$(Cd)_{RC} = 0.103 + 7.56(Cd)_{CaCl2}$	0.935	$P \ll 0.01$
Zn	$(Zn)_{RC} = 51.9 + 21.6(Zn)_{CaCl2}$	0.823	$P \ll 0.01$
Cu	$(Cu)_{RC} = 10.9 + 1.05(Cu)_{CaCl2}$	0.292	$P < 0.01$

they have lower levels of soil Zn, reach this toxicity threshold only if the pH is less than 4.5. Thus, even the relatively small Zn loading from sludge products (by USEPA standards) may have a significant impact in increasing the potential risk of long-term yield reduction if pH is not maintained above 6.

The problem with attributing yield depression to a single metal toxicity is that the sludges also contained substantial concentrations of other potentially phytotoxic contaminants such as Cu. Since other contaminant application rates increased in proportion to Zn as sludges were applied, the significant regressions of clover yield to clover tissue Zn do not prove that Zn is the phytotoxic agent.

It is important to put the metal loadings in the experiment described here in perspective relative to regulations and guidelines applicable to agricultural soils. The soil column loadings of Cu, Zn and Ni from dewatered, composted and pelletized sludges (see Table 2) are a small fraction of the EPA 503 rule permitted loadings for each metal – 0.09, 0.04 and 0.02, respectively. However, the loadings used would raise soil total Cu , Zn, and Mo into the ranges recommended as upper limits in some European and Canadian standards (Harrison et al.,1999). Soil total Mo exceeded Ontario's upper limit of 4 mg/kg as a result of some of the sludge product applications in this experiment; soil Mo reached 5.5 mg/kg (compared to 1.2 mg/kg in the control) shortly after application of the dewatered sludge (unpublished data). The high bioavailability of sludge-applied Mo was demonstrated by elevated Mo levels in earlier red clover crops grown on these columns (McBride et al., 2003), and again in this study (see Tables 3 and 4). The persistent bioavailability of Mo to clover and other legumes supports a more conservative limit on Mo loading than is presently employed in most countries.

It can be debated whether the accelerated loading used in this study, in an attempt to simulate about 25 years of agronomic use (or several years of soil 'remediation' to establish topsoil on disturbed sites), can be considered to represent the likely state of the soil and metals had 25 years of agronomic application rates been used. Nevertheless, cumulative heavy metal loadings likely to have a significant effect on crops and soil biota can only be reached after several decades of repeated applications under typical field conditions. Because it is unlikely that controlled long-term ($\geq$ 25 years) experiments will be done in the field, the accelerated loading of this experiment gives the best approximation that is practically achievable. The experiment described in this study does not, however, address more immediate impacts from short-term applications, such as rapid leaching into drainage or surface runoff water.

The concentrations of Zn (1500–2000 mg/kg) and Cd (25–50 mg/kg) in the 'old site' Hudson soils are not substantially higher than levels that could be eventually expected from the USEPA permitted cumulative loading of 2800 kg/ha Zn and 39 kg/ha Cd to agricultural soils. Despite the fact that Hudson series soils (with high organic matter and clay content and pH in the 6–7 range), should be much less vulnerable to heavy metal toxicities than coarse-textured or more acid soils, phytotoxicity is severe and Cd uptake into crops quite evident after decades of field 'aging' and repeated cropping. The 'old site' demonstrates the inadequacy of the USEPA cumulative soil metal limits intended to protect productive agricultural soils.

Conclusions

The equivalent of about 25 years of agronomic application of low-metal ('EQ') sewage sludge products to greenhouse soil columns increased the easily-extractable soil levels of Zn, Cu, Mo, S and P, but had little effect on extractable Cd or Ni. These increases were measured after a 6-year period of 'equilibration' during which time multiple crops were grown with accelerated leaching by simulated acid rain. Soil pH had a strong influence on the level of extractable metals, and because the tested sludge products affected pH differently, it was essential to consider pH in the comparison of different sludge treatments with controls. Once soil pH was accounted for, metals (Cu, Zn, Mo) in the organic-rich sludge products (dewatered, pelletized, composted) were found to be similarly extractable. Copper, Zn and Mo applied in the sludge ash had low soil extractability, suggesting that these trace metals were trapped in high-temperature mineral phases formed during sludge incineration, and resisted subsequent weathering in the soil environment. Extractable soil metals in the alkaline sludge treatment were generally low, as soil pH was maintained above 7 by the liming reaction of this product.

As long as soil pH was managed by lime, the sludge products applied at the rates no greater than 135 kg/ha Cu, 125 kg/ha Zn, did not produce obvious long-term metal phytotoxicity in crops, although certain types of sludge products did produce unexplained yield depression in red clover. Of greater concern was the high uptake of Mo by red clover grown on the sludge product-amended soils.

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