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Project Summary

Soil Physicochemical Parameters Affecting Metal Availability in Sludge-Amended Soils

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Laboratory studies were conducted to examine the effects of pH and oxidation-reduction status (redox potential) on soil levels of trace and toxic metals in selected chemical forms. Studies were also conducted to see how metal availability to plants was affected by soil redox conditions. The elements studied included Cu, Zn, Cd, Pb, Cr, Ni, and As.

Chemical availability and plant uptake studies under controlled pH and redox potential indicated that various organic phases predominate in retaining Cu under reducing conditions (i.e., low redox potential). As redox potential is increased, however, a very marked transformation occurs so that potentially available Cu becomes strongly associated with the reducible (hydrous iron oxide) phase under well oxidized conditions. Soluble, exchangeable, and chelate-extractable Cu also increased with increasing redox potential. Results with rice were mixed, but increasing oxidation conditions tended to increase Cu in corn.

Dissolved and exchangeable Zn increased with decreasing soil pH and increased to a lesser degree with increasing redox potential. A very large increase in plant Zn levels occurred with increasing redox potential.

Compared with most other trace and toxic metals studied, a much larger proportion of the total Cd extracted was recovered in the most readily available chemical forms (dissolved and exchangeable). Cd appears to be less strongly associated (immobilized) with high-molecular-weight organics and is weakly bound to hydrous iron oxides. This factor contributes to the potential for ready accumulation of Cd by plants grown in Cd-contaminated soils. In most of the experimental combinations of sludge-soil mixtures and pH used in the laboratory microcosms, plant Cd concentrations increased greatly as the redox potential increased.

Except for exchangeable lead being greater at pH 5.0 than at higher pH levels, changing pH or redox potential had little effect on Pb levels in other chemical forms.

Unlike results for Cd and Zn, oxidation status had little, if any, effect on plant levels of Cr, Ni, and As. Predominant chemical forms in the sludge-amended soils and oxidation effects on levels in these chemical forms are discussed in the report.

This research demonstrates the important effects of soil redox potential in regulating the chemical mobility and availability to plants of Zn and Cd—two key contaminants in sludge materials that may be applied to soils. Where alternatives exist for disposal of contaminated sludge, wet or poorly oxidized soils would be more effective for immobilizing Zn and Cd and would thus result in lower accumulations of these metals in crop plants or native plant populations on uncultivated land.

This Project Summary was developed by EPA's Water Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a

separate report of the same title (see Project Report ordering information at back).

Introduction

The Federal Water Pollution Control Act of 1972 (PL 92-500) has stimulated increasing interest in the use of terrestrial ecosystems to achieve water quality standards. Section 201(b) requires that technology development consider advanced waste treatment techniques and include the reclaiming and recycling of water and the confined disposal of pollutants to prevent other environmental pollution. The application of municipal sewage sludge to soil-crop systems may be the most environmentally and economically feasible method of meeting these requirements in many instances. The benefits of applying municipal sludge to land include (1) reducing the pollution load of river and coastal waters that have traditionally received sewage wastes, (2) recycling water and nutrients through crops to recover these valuable resources, (3) more rapid inactivation or destruction of potentially serious microbial pathogenic organisms than some conventional wastewater treatment methods, and (4) possible improvement of marginal soils to develop land for parks and other urban uses.

The most serious limitation of applying municipal sludge to agricultural soils concerns the fate of pathogens and toxic substances that may be associated with municipal wastes. Toxic heavy metals in sludge-amended soils and the crops grown on them have been studied extensively because of the tendency for these metals to accumulate in soils and to be assimilated by plants. Crop uptake of toxic metals may increase the dietary intake of livestock and humans who consume these plants.

Extensive agricultural research has shown that a number of interacting physical, chemical, and biological factors affect the availability of nutrients and toxic materials in soil-plant systems. For example, the kind and amount of clay minerals and soil organic matter and the presence of additional chemically reactive or adsorptive soil components such as sulfides (if present) and hydrous oxides play an important role in regulating bioavailability. Plant species and management of soils, crops, and waste applications are also important factors. Fortunately, most soils—even those that are highly contaminated—have a large capacity to immobilize toxic metals so that only a small proportion of the metal applied is available to plants. However, all of the metals applied with sludge applications must be considered potentially available for plant uptake. Because of the probable long-term accumulation of potentially available toxic metals in sludge-amended soils and the dynamic nature of soil-plant systems, it is imperative that we understand all of the significant factors and processes affecting their availability.

Soil pH and oxidation-reduction (redox) conditions are two physicochemical parameters that affect metal mobilization and immobilization. Considerable research has been conducted on the effects of soil pH on the chemical availability and uptake of trace and toxic metals by crop plants grown on soils treated with municipal sludge. As presented in the literature review, these studies have conclusively demonstrated that an increase in soil acidity usually enhances the availability of trace and toxic metals to plants. In contrast, very little is known about the effects of soil redox conditions on toxic metal availability, but they are probably as important as soil pH in regulating the availability of some metals.

Very limited published information is available on the effects of soil redox conditions on trace and toxic metal uptake by plants. The early work focused on trace elements, primarily Fe and Mn. In recent years, a few papers have been published on chemical mobility and plant uptake of trace and potentially toxic metals (e.g., Zn) and toxic elements such as Cd in wetland soils. However, little attention has been paid to the processes regulating trace and toxic metal availability under different oxidation conditions and the effects of soil oxidation on the availability of metals to plants in sludge-amended soils. Most soils currently receiving municipal sludge are upland soils classified as moderately well to well drained. Such soils are generally aerobic or oxidized.

Municipal sludge may also be applied to wetland soils characterized by poor internal drainage or water saturation for much of the time. These soils are likely to be anaerobic and chemically reduced. Because of increased restrictions on dumping pollutants in coastal water and the chronic shortage of conveniently located land suitable for disposal, pressures will probably increase to use poorly drained agricultural and wetland soils for waste disposal.

In addition to the various oxidation conditions of different soils, adding large quantities of sludge (frequently as a water slurry) with high levels of organic matter is likely to contribute to intermittent, strongly reduced conditions in all or part of the rhizosphere of an upland soil that is normally considered well drained and oxidized. Thus a wide range of redox conditions may be encountered in sludge-amended soils, resulting in varying degrees of toxic metal availability to plants.

The primary objective of this research was to study the effects of soil pH and, especially, redox conditions on the soil chemical form and the availability of trace and toxic metals to plants grown on agricultural soils receiving municipal sludge applications. The elements included were Cu, Zn, Cd, Pb, Cr, Ni, As, Fe, Mn, Ca, Mg, Mo, Si, P, and Al, but the report evaluated only the first seven of these in detail.

A secondary objective of the research was to focus on the effects of pH and redox conditions on trace metal complex formation with soluble and insoluble organic matter. This important, if not predominant, regulatory process affects the availability of metals in sludge-amended soils.

Research Approach and Findings

Sludge Ratio Study

A simple study was conducted in which mixtures of Chicago reference sludge and Drummer soil were incubated as suspensions under conditions of continuous air purging or oxygen-free nitrogen purging. The sludge: soil ratios used were 0:100, 5:95, 25:75, and 100:0. At the end of the incubation, sequential extractions were made on the suspensions to measure exchangeable and diethylenetriaminepentaacetic-acid-(DTPA-) extractable levels of selected elements to determine the effect of sludge:soil ratios and oxidation conditions on the chemical availability of these elements.

At ratios of 75 and 100 percent sludge, the data suggested that oxidizing conditions were probably not achieved; thus the evaluation of the results was limited to the 0-, 5-, and 25-percent sludge ratios. Except for Mn, there was generally an increase in exchangeable and DTPA-extractable levels of the elements studied with an increase in the sludge ratio. Also, except for Mn and Mo, the largest proportion of the elements was in the

DTPA fraction. This result was especially apparent as the sludge ratio increased, indicating the important role of high-molecular-weight organics in binding these elements in soils and sludge-amended soils. Levels of exchangeable and DTPA-extractable Cu, Zn, Cd, and Pb were generally much greater in oxidized sludge-soil suspensions than in reduced suspensions. Exchangeable and DTPA-extractable levels of Fe, Mn, and P responded to redox potential conditions in the opposite manner. This result was anticipated for Fe and Mn, since these metals are subject to redox-mediated valence state changes, which make them much more chemically mobile under reducing conditions as ferrous Fe and manganous Mn. This preliminary experiment indicated that (1) the addition of metals through sludge increases metal levels in several chemical forms, but the organic-bound pool may be especially important, and (2) soil redox potential affects the levels of metals in various chemical forms. One implication is that soil redox conditions may affect the availability of trace and toxic metals to plants as well.

Effect of Sludge Digestion Method on Plant Uptake of Selected Elements

The ojective of this study was to determine whether sludge derived from aerobic or anaerobic digestion of sewage influenced the chemical availability or plant uptake of trace and toxic elements in sludge-amended soils. Soybean and corn seedlings were grown for 3 weeks in the Drummer soil material amended with 5 percent of aerobically or anaerobically digested Baton Rouge sludge. Only the plant tissue samples were analyzed for elemental content. Each experimental combination was replicated five times.

Soybeans grown for 3 weeks in the 5-percent-amended Drummer soil showed no indication that the addition of sludge or the digestion method affected the above-ground plant tissue content of Cu, Zn, Cd, Pb, Cr, Ni, or As. Corn plants grown in the soil amended with 5 percent anaerobically digested sludge contained significantly more Cu, Cd, Pb, Cr, and As than did the control plants. Regarding the method of digestion, significant differences were obtained only for Cu and Pb: levels were higher for both elements from the sludge that was derived from an anerobic digestion process.

Trace and Toxic Elements in Humic and Fulvic Acids Extracted from Sludge and Sludge-Soil Mixtures

Levels of selected elements in humic, fulvic, and precipitate forms were determined in Baton Rouge sludge materials that had been prepared by either an anaerobic or an aerobic digestion process. In another study, levels of selected elements in the three humic material fractions were determined in extracts of many of the sludge-soil suspensions incubated under controlled pH and redox potential.

Following the incubations of sludge-soil mixtures under controlled pH and redox potential, aliquots of the suspensions were shaken to extract humic and fulvic acids and a precipitate fraction. Fulvic acid was apparently recovered in the greatest amount, though a substantial part of this fraction is composed of extracting reagents (primarily sodium). Cu, Zn, and Ni were most strongly associated with the fulvic acid fraction than with the other two forms. However, the much greater quantity of fulvic acid extracted would result in a greater quantity of most elements of interest in this fraction. Copper was also present at about equal levels in the humic acid fraction. The concentration of all other elements in the humic acid fraction was either about the same as or less than levels in the fulvic acid and precipitate forms. No consistent, unidirectional changes occurred in the concentration of any metal in any of the three fractions with increasing pH and redox potential. However, levels of Cu were generally lower in all three fractions under strong reducing conditions (−150 mv) than in better oxidized treatments at pH levels of 5.0 and 6.5. At pH 5.0, Zn levels tended to decrease with increasing redox potential. Cadmium levels in the humic and precipitate fractions were low (undetectable). Cadmium levels in the fulvic acid fraction generally increased with increasing redox potential.

Effect of pH and Oxidation Conditions on Chemical Form and Plant Availability of Metals in Sludge-Amended Soils

A 10-percent mixture of Chicago reference sludge and Drummer (or Loring) soil material was incubated as an aqueous slurry at different pH levels (5.0, 6.5, and 8.0) and at different redox potential levels (−150 mv, 50 mv, 250 mv, and 500 mv) representing redox conditions ranging from strongly reduced to well oxidized. After a 2-week period, duplicate suspension aliquots were taken and extracted for dissolved, exchangeable (sodium-acetate-extractable), reducible (ammonium-oxalate-/oxalic-acid-extractable), DTPA-extractable, and residual organic-bound metals. At this time, plant seedlings were introduced into the microcosms so that the roots were suspended in the slurry being maintained under controlled pH and redox potential. After 2 weeks of growth in the microcosms, the above-ground tissue was harvested and analyzed for trace and toxic metals.

The chemical availability and plant uptake studies under controlled pH and redox potential provided considerable information on the forms and transformations of trace and toxic metals in sludge-amended soils.

Various organic phases predominate in retaining Cu under reducing conditions, but as redox potential is increased, a very marked transformation occurs in the reducible (hydrous iron oxide) phase, with which potentially available Cu is most strongly associated under well oxidized conditions. The trend was for dissolved, exchangeable, and chelate-extractable Cu to increase with increasing redox potential. Results with rice were mixed, but increasing oxidation conditions tended to increase Cu in the young corn plants grown in the laboratory microcosms.

In the studies using Chicago sludge and Drummer soil, there was a weak trend for readily available (dissolved and exchangeable) Zn to increase with increasing redox potential, and the highest levels were at pH 5.0, as expected. A very large increase in plant Zn levels occurred with increasing redox potential. For example, in the young corn plants, Zn levels increased from around 100 µg/g under strong reducing conditions to greater than 900 and 500 µg/g in well oxidized sludge-soil mixtures at pH levels of 6.5 and 8.0, respectively. Most of the potentially available Zn was found in the reducible fraction under oxidized and reduced conditions.

Compared with most other trace and toxic metals studied, a much larger proportion of the total Cd extracted was recovered in the most readily available chemical forms (dissolved and exchangeable). Cd appears to be less strongly associated (immobilized) with high-molecular-weight organics than most toxic metals and, in particular, is weakly bound to hydrous iron oxides.

This factor contributes to the potential for ready accumulation of Cd by plants grown in Cd-contaminated soils. In most of the experimental combinations of sludge-soil mixtures and pH used in the laboratory microcosms, plant Cd concentrations increased greatly as the redox potential increased. For example, a 20-fold or greater increase in the Cd content of rice plants occurred between −150 mv and 500 mv at pH 6.5 in the suspensions of Baton Rouge sludge and Loring soil and in the combination of pH 8.0 Chicago sludge and Drummer soil. A 50-fold increase in plant content occurred between the redox potential extremes in the Chicago sludge and Drummer soil incubated at pH 6.5. Thus this research supports other studies indicating that Cd contamination of soils and sediments represents a greater environmental risk than contamination with many other toxic metals at equivalent levels because of Cd's relatively high mobility and availability to plants. This study also demonstrates the importance of soil oxidation conditions on Cd mobility and availability to plants.

Pb was most strongly associated with the residual organic phase. Exchangeable Pb was very pH-dependent, and the greatest levels were found at pH 5.0. Changing redox and/or pH had little effect on levels of Pb in other chemical forms.

Unlike results with Zn and Cd, soil oxidation status had little, if any, effect on plant levels of Cr, Ni, and As. Predominant chemical forms in the sludge-amended soils and oxidation effects on levels in these chemical forms are discussed in the full report.

Conclusions

This research demonstrates the important effects of soil redox potential in regulating the chemical mobility and availability to plants of Zn and Cd—two key contaminants in sludge that may be applied to soils. Obviously, most crop species are not grown on soils that range from strongly reduced to well oxidized. Most crops are grown on well drained (oxidized) soils. Rice is an important exception in that it is normally grown on flooded (reduced) soils. However, rice may be grown in upland, oxidized soils as well, and in some regions of the country, substantial acreage is devoted to such dry-land rice. Sugarcane is grown on soils that are somewhat low and wet. The redox potentials of these soils would probably be intermediate but subject to frequent and wide fluctuations. Nonagricultural soils may also be used to dispose of sewage sludge, and the oxidation status encountered in soils of various natural habitats or other uncultivated soils may vary considerably.

In considering the potential problems associated with the disposal or productive use of contaminated sewage sludge, many factors and options must be considered in developing acceptable management plans. This research indicates that the redox status of soils being considered for receiving municipal sludge is also an important consideration, particularly for Zn and Cd. Where feasible alternatives exist, wet or poorly oxidized soils would be more effective for immobilizing Zn and Cd. Sludge applications to these soils would therefore be less likely to result in accumulations by plants.

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The complete report, entitled "Soil Physicochemical Parameters Affecting Metal Availability in Sludge-Amended Soils," (Order No. PB 86-116 621/AS; Cost: $16.95, subject to change) will be available only from:
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