



## Project Summary

# Characterization of Sewage Sludge and Sewage Sludge-Soil Systems

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**Field and laboratory studies were conducted to characterize the chemical properties of municipal sewage sludges, to evaluate the fate of sludge components in soils, and to determine the distribution of trace metals in milling fractions of grains grown on sludge-treated soils. Specific studies included (1) characterizing the organic components in sewage sludges, (2) separating sludges into organic and inorganic fractions, (3) examining the capacity of sludge to retain metals, (4) evaluating sludge through spectroscopic, infrared, and electron spin resonance studies, (5) conducting laboratory soil incubation studies to characterize mineralization and nitrification of nitrogen and decomposition of organic carbon in sludge-amended soils, (6) determining metal speciation with analytical data for soil solution samples, and (7) evaluating the uptake of Cd, Zn, Ni, Cu, Fe, and Mn in oats, corn, wheat, and soybeans grown in soils treated with sewage sludge.**

*This Project Summary was developed by EPA's Municipal Environmental 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 recent emphasis on applying municipal sewage sludge to agricultural cropland necessitates a knowledge of the sludge constituents and their fate in soils. Sludges can be used as an alternative fertilizer because they contain not only macronutrients required by plants (i.e., N,

P, and K), but also essential micronutrients such as Cu, Zn, and Mn. Studies have shown that comparable crop yields can be obtained with conventional fertilizer materials and sewage sludge, but sludges may also have constituents that can be toxic to plants or to animals or humans consuming products grown on sludge treated soils. Trace metals, organics, and pathogens are the three broad groups of sludge constituents that have received the greatest emphasis in research and regulatory activities. Of the metals contained in sludge, Cd has received the most attention as a potential threat to human health, and Zn, Cu, and Ni have been implicated in decreasing crop yields. The polychlorinated biphenyls (PCB's) have received more attention than other sludge-borne organics.

This series of studies was conducted to characterize the chemical composition of sewage sludges, to study the fate of sludge components in soils, and to evaluate the distribution of metals in crops grown on sludge-treated soils.

### Chemical Composition of Sewage Sludges

The organic components in sludge were characterized by several extraction, chromatographic, and spectroscopic techniques. Fatty acid esters (fats and waxes) and phthalic acid esters (plasticizers) constituted 2% to 10% and <1% of sludge oven-dry weight, respectively. Palmitic acid esters and dibutyl phthalate were the predominant components in the respective fractions. Upon H<sub>2</sub>SO<sub>4</sub> hydrolysis of the sludges and subsequent analysis of the hydrolyzates by high pressure liquid

chromatography and colorimetric procedures, hexuronic acids, glucose, and xylose were detected. The sugars were likely monomers of hemicellulose and cellulose polymers, which together made up 0.99% to 2.55% of sludge oven-dry weight. Organic N in the sludges was present primarily as  $\alpha$ -amino acid N, constituting 31% to 36.5% of the organic N. The amino acid distribution in sludge hydrolyzates was determined by an amino acid analyzer and revealed that amino acids of bacterial origin were present (i.e.,  $\alpha$ -amino pimelic,  $\alpha,\epsilon$ -diaminopimelic,  $\beta$ -alanine,  $\gamma$ -amino butyric, and ornithine) as well as those commonly found in plant and animal protein. Sodium-amalgam reduction of the sludges produced few or no phenolic compounds, indicating small concentrations of humic-type materials. Infrared and X-ray analyses of residues from HF-treated sludges and NaOH extracts (humic acids) of sludges indicated the presence of condensed aromatic rings or quinone-like compounds and little or no inorganic crystalline material.

Sludges were separated into light and heavy fractions by an ultrasonic dispersion and heavy liquid separation technique to provide information on trace metal forms in sludges. The light fraction (organics) was 8% to 26% of the sludge dry weight, and the heavy fraction (inorganics) constituted 69% to 88% of the sludge weight. Most of the metals were associated with the sludge light fraction (organic).

Infrared studies were conducted to characterize qualitatively the sewage sludge light (organic) and heavy (inorganic) fractions obtained using the heavy liquid separation technique. Infrared spectra of sludge organic fractions revealed the presence of proteinaceous and polysaccharide-like materials. Infrared absorptions characteristic of carboxyl groups and aromatic compounds were not observed in the spectra of sludge light fractions. The position of the amide-I band in the infrared spectra of the sludge light fractions was used to obtain direct evidence of metal binding sites involving amide N and possibly amide O. A discrete shift in the position of the amide-I band was initiated by extracting indigenous metal cations from the sludge organic fraction. This shift was reversed by saturating the extracted sludge organic fraction with  $\text{Cu}^{2+}$ . Absorption bands of quartz and calcite dominated the infrared spectra of sludge inorganic fractions.

Electron spin resonance (ESR) spectroscopy was used to study the mechanism of

$\text{Cu}^{2+}$  binding by humic acid (HA) extracted from soil and sewage sludge. The ESR data showed that the addition of pyridine (py) and 1,10-phenanthroline (phen) to the soil and sludge Cu-HA complexes resulted in the added nitrogen ligands replacing water coordinated to  $\text{Cu}^{2+}$ . The added ligand did not displace HA oxygen donor ligands also coordinated to the  $\text{Cu}^{2+}$ . The addition of a more basic nitrogen donor, ethylenediamine (en), resulted in the formation of  $\text{Cu}(\text{en})_2^{2+}$  by displacement from  $\text{Cu}^{2+}$  or both coordinated aquo ligands and HA oxygen donors. ESR parameters revealed that two HA oxygen atoms were coordinated equatorially to  $\text{Cu}^{2+}$  in the original soil and sludge Cu-HA complexes. In the sludge  $\text{Cu}^{2+}$ -HA complex, the  $\text{Cu}^{2+}$  ion also appeared to form axial bonds with HA nitrogen donor ligands originating from proteinaceous materials associated with the sludge HA fraction. Characterization of an adduct with glycylglycine showed that the dipeptide formed coordinate bonds with  $\text{Cu}^{2+}$  bound to sludge HA.

The metal retention capacities of calcareous and acidic sludges and sludge fractions were determined. The results obtained from the equilibration of Cd, Cu, Ni, or Zn salts with calcareous and acidic sludges indicated that calcareous sludges have a higher capacity to retain added metals than noncalcareous sludges and that metal retention was directly related to sludge pH. As solution pH increased above 5.0, chemical precipitation of metals, most likely as carbonates, became the dominant mechanism in the removal of Cd, Cu, Ni, or Zn from solution. Metal retention was reduced when pH values of sludge and metal solutions were below 5.0. Most of the Cd, Cu, Ni, and Zn retained by sludge at low pH values was likely the result of complexation by organic matter and sorption by amorphous Fe, Al, and Mn hydrous oxides. The retention capacity for Cd and Cu with heavy and light sludge fractions decreased in the following order:

light fraction > heavy fraction > whole sludge

This order indicates the formation of stable complexes between sludge organics and metal ions. The heavy fraction, which is composed largely of inorganic materials, also retained large proportions of added Cd and Cu. The sludge components responsible for Cd, Cu, Ni, or Zn retention were estimated by selective extraction procedures. The results indicated that three sludge components are

primarily involved in Cd, Cu, Ni, or Zn retention. Sludge components are ranked below in decreasing order of their importance for retention of each metal:

Cd: carbonate > organic matter > hydrous oxides;  
 Cu: carbonate > organic matter = hydrous oxides;  
 Ni: carbonate > organic matter = hydrous oxides;  
 Zn: carbonate > organic matter > hydrous oxides.

## Fate of Sludge Components in Soils

A laboratory soil incubation system was used to study metal extractability (with DTPA), nitrogen mineralization, nitrification, and organic C decomposition in soils amended with municipal and synthetic sludges. The synthetic sludges were prepared to contain varying concentrations of Cu, Cd, Zn, Pb, and Ni at a constant level of organic C and N. The extent of decomposition of municipal sewage sludges (as measured by  $\text{CO}_2$  evolution) appeared to be a function of the organic C content of the sludges. As much as 30% to 47% of the  $\text{CO}_2$ -C evolved from the sludge-treated soils was due to dissolution of calcium carbonate present in the sludges. Significant inhibition of nitrification was found in soils amended with synthetic sludges at rates greater than 60 metric tons/ha, whereas stabilized municipal sludges showed rapid nitrification of all application rates. Generally, the percent of sludge organic N mineralized increased with sludge application rate. Metals (Zn, Cu, Ni, and Cd) extracted from soil with DTPA generally increased with incubation time and were directly related to the amount of sludge-borne metal added to the soil. Similar correlations were obtained between added and DTPA-extractable metals for synthetic and municipal sludges. In general, synthetic sludges offer promise for studying the decomposition rate of municipal sludges in soils.

The decomposition of liquid and dried municipal sewage sludges was determined in soils under laboratory and field conditions. Evolved  $\text{CO}_2$  was continuously monitored in soil + sludge mixtures incubated in the laboratory. Primary, raw, and waste-activated sludges showed the greatest degree of decomposition, whereas digested and composted sludges had the lowest decomposition values during a 112-day incubation. The data indicate that the percentage of sludge organic C

composed in soil will be less for those ridges subjected to intensive stabilization processes at the treatment plant. Carbon dioxide evolution in the field study is monitored for a 24-hr period by sealing cylinders containing soil-sludge mixtures. The cylinders remained open to the environment between sampling periods. Soil moisture and temperature were also monitored. Evolution of CO<sub>2</sub> was initially rapid in all soil and sludge combinations, but it decreased with time owing to consumption of easily decomposable organic substrates in the sludge and gradual lowering of soil temperature in the late fall and winter. Carbon dioxide evolution rates for all treatments were affected by temperature and increased in early spring. Dewatering an anaerobically digested sludge by air-drying reduced the extent of decomposition in soil. Because of CO<sub>2</sub> release from carbonate dissolution, the presence of inorganic C in sludges can interfere with organic C decomposition calculations based on CO<sub>2</sub> evolution. Data from both the laboratory incubation and field study show good agreement concerning relative order and magnitude of sludge decomposition. A first-order model adequately predicts decomposition of most sewage sludges under field conditions. The model failed to predict an increase in the rate of CO<sub>2</sub> evolution in early spring. This increase is possibly due to increased organic C availability induced by freezing and thawing cycles during the previous winter.

Incubation studies using carboxyl-labeled <sup>14</sup>C dibutyl phthalate (DBP) added to soils at 0.1% (w/w) indicate that 90% of the DBP was degraded within 80 days. Decomposition of DBP was shown to be microbially mediated and was a function of soil type, pH, and temperature. Application of DBP at rates of 0.4% (w/w) and the addition of ammonium and CaCO<sub>3</sub> or sewage sludge had little effect on the extent of DBP degradation. Dibutyl phthalate contained in sewage sludge or other waste materials to soils should not pose a long-term persistence problem in soils.

Humic acids (HA) extracted from sludge, soil, and sludge-amended soil were characterized by elemental and functional group analyses, and by visible and infrared spectroscopy. When compared with a soil HA, the sludge HA appeared to be a more aliphatic, N-enriched polymer with decreased amounts of carboxyls and phenolic hydroxyls. Proteinaceous materials associated with the sludge HA appeared to be the major source of N enrichment. Sludge organic matter was

apparently recovered in HA extracted from soil 2 and 14 months after sludge application. The association of sludge-borne proteinaceous and aliphatic materials with the sludge and sludge-amended soil HA fractions was indicated by increased amide and C-H stretch infrared absorptions, as well as by the increased N contents and decreased C:H ratios. The observation of proteinaceous materials associated with HA extracted from sludge-amended soil 14 months after application suggested that these proteinaceous materials were resistant to decomposition, possibly as a result of their incorporation into the HA structure.

Infrared spectroscopy was used to identify the mode by which carboxylates of a soil HA complexed Cu<sup>2+</sup> and Fe<sup>3+</sup>. Carboxylic acid groups of soil HA were converted to carboxylates (CO<sub>2</sub><sup>-</sup>) by forming coordinate bonds with Cu<sup>2+</sup> and Fe<sup>3+</sup>. The separation of the antisymmetrical, ν<sub>a</sub> (CO<sub>2</sub>), and symmetrical, ν<sub>s</sub> (CO<sub>2</sub><sup>-</sup>), stretching vibrations of CO<sub>2</sub><sup>-</sup> obtained from spectra of metal-HA complexes indicated that CO<sub>2</sub><sup>-</sup> formed a unidentate complex (i.e., a single M-O bond) with Cu<sup>2+</sup> and Fe<sup>3+</sup>. The formation of bidentate or bridging complexes between CO<sub>2</sub><sup>-</sup> of HA and Cu<sup>2+</sup> or Fe<sup>3+</sup> was not observed.

Metal-chelate stability diagrams were developed as a function of pH and redox to predict the behavior of five synthetic chelating agents in soils. The metals evaluated include H<sup>+</sup>, Fe<sup>3+</sup>, Fe<sup>2+</sup>, Al<sup>3+</sup>, Mn<sup>2+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, and Ni<sup>2+</sup>. In acid systems, Ni<sup>2+</sup> at 10<sup>-5</sup> to 10<sup>-7</sup> M was the predominant ligand species for all chelating agents. Similar results were obtained in alkaline systems when NiCO<sub>3</sub> controlled Ni<sup>2+</sup> solubility. In the absence of Ni<sup>2+</sup>, either Cd<sup>2+</sup> or Pb<sup>2+</sup> ligand species dominated at alkaline pH for all chelating agents. In acid systems, Cu, Pb, Fe, and Zn are the major chelated species. These chelating agents deserve further study in acid soils as extractants for metals and as reagents for determining metal ion activities through competitive equilibria. The results identify ligands that may be useful in determining various metal ion activities in soils. The diethylenetriamine pentaacetic acid (DTPA) soil test appears to have a sound theoretical basis for evaluating the plant-available Pb, Cd, and Ni in soils.

A cooperative study was conducted with the Tennessee Valley Authority to determine the effects of sewage sludge applications on the heavy metal status of a soil. Sewage sludge from Tuscumbia, Alabama, was applied to an acid soil (pH

~ 5) as a single treatment in 1971 or as annual treatments from 1971 through 1974 in amounts totaling 50 to 800 metric tons/ha. Soil samples (0- to 15-cm depth) obtained from the plots in 1977 were moistened to -0.33 bar water potential and equilibrated for 7 days before displacement of the soil solution. The soil solutions were analyzed for Zn, Cd, Cu, Ni, Pb, Mn, Fe, Ca, Mg, Al, Na, K, PO<sub>4</sub>, SO<sub>4</sub>, Cl, conductivity, pH, and organic C. The metal species present were calculated with a computer program (GEO-CHEM). Sludge application increased soil solution concentrations of Zn, Mn, and Cd, but Cu, Ni, and Pb levels in most solutions were below the detection limits of the analytical methods used. Cd, Zn, and Mn in the soil solution appeared to exist predominately as the free ion. Depending on the model used to represent metal interaction with soluble organic C, complexation by inorganic and organic ligands ranged from 9% to 33%, 3% to 22%, and 3% to 31% of the total soluble Cd, Zn, and Mn, respectively. Cd was complexed with organic ligands to a greater extent than were Zn or Mn. Sulfate, phosphate, and chloride formed inorganic complexes with Cd, Zn, and Mn, but they constituted less than 10% of the total metal present. The general degree of metal complexation by organic and inorganic ligands increased in the following order:



Speciation of Zn and Cd into free metal ion and complexed forms was essentially the same in the soil solution, regardless of metal concentrations in solution and rate or frequency of sludge application. Calculated activities of Cd<sup>2+</sup> indicated undersaturation with respect to known Cd solid phases, whereas Zn<sup>2+</sup> activities were comparable with those of ZnFe<sub>2</sub>O<sub>4</sub>, soil Zn, and Zn<sub>2</sub>SiO<sub>4</sub>. Soluble Zn and Cd were directly related to the amount of metal added and to the extractability of added metal with DTPA. The solubility and DTPA-extractability of Cd were increased more by a single application of sludge than by multiple, annual additions. This relationship was not as consistent for added Zn.

### Distribution of Trace Metals in Milling Fractions of Grains Grown on Sludge-Treated Soils

Oats, corn, wheat and soybeans were grown on soils treated with stabilized sewage sludge from three Indiana cities.

Sludges were applied to a Chalmers silty clay loam soil at rates of 56 to 448 metric tons/ha. Oat samples were separated into groats and hulls, and concentrations of Cd, Zn, Cu, Fe, and Mn were determined in each fraction by atomic absorption spectrophotometry. The effect of sludge application rates on the concentrations of trace metals in whole oats, groats, and hulls was similar for all three sludges used, and they generally decreased in the following order:

Zn = Fe > Mn > Ni > Cu > Cd

Except for Mn, the concentrations of trace metals increased with increasing rates of sludges applied, but the groats contained greater concentrations of Cu, Ni, Zn, Cd, and Mn than the hulls.

The metal concentrations in whole-kernel corn were not significantly increased by sewage sludge applications of 56 to 448 metric tons/ha. Except for one Cd-enriched sludge, Cd concentrations in whole corn and fractions from dry-milling were less than 0.05 mg/kg. As expected, the germ fraction contained the greatest proportion of the fat, ash, and trace metals, and most of the protein was found in the grits fraction. Both the concentration and the percent distribution of metals in dry-milling fractions decreased in the following order:

germ > hulls > flour > meal > grits

The metal concentrations in both wheat and soybean grain were increased by sludge applications. For wheat, the bran contained significantly higher concentrations of all metals than did the flour. Metal concentrations were similar in whole soybean grain and the resulting meal.

## Conclusions

1. Characterization of the organic components in sewage sludges indicated that fatty acid esters and phthalates were predominant forms present in nonaqueous extracts of sludge.
2. A heavy liquid extraction procedure developed to separate sewage sludges into organic and inorganic fractions indicated that most metals naturally present in the sludge were associated with the fraction enriched in organic matter.
3. Municipal sludges had the capacity to retain appreciable amounts of Cd, Cu, Ni, and Zn. The most likely

primary mechanisms involved in sludge retention of added metal salts were precipitation as carbonates and sorption by organic matter and hydrous oxides.

4. Studies conducted to evaluate the spectroscopic properties of sludge organic matter indicated that sludge humic acids were more aliphatic and contained fewer carboxyl and phenolic hydroxyl functional groups than soil humic acids.
5. Infrared investigations indicated that the amide group in residual proteinaceous materials could be involved in the retention of Cu by sludge.
6. Electron spin resonance studies indicated that Cu (II) was bound to oxygen-containing donor ligands in the humic acid fraction of sewage sludge.
7. In laboratory incubation experiments, evolution of CO<sub>2</sub> from sludge-treated soils indicated that elevated amounts of trace metals may temporarily inhibit decomposition, but they do not do so over an extended period. Some temporary inhibition of nitrification was observed in sludge-amended soils.
8. Studies conducted under laboratory and field conditions indicated that

the extent of sludge decomposition in soils was inversely related to the intensity of treatment and processing within the sewage treatment plant.

9. Laboratory incubation studies using dibutyl phthalate indicated that more than 90% of this compound will be degraded within 80 days after application to soils.
10. The free metal ion was the primary species of Zn and Cd found in soil solutions, regardless of total metal concentrations or the rate or frequency of sludge application.
11. For oats, metal concentrations were significantly greater in the groats than in the hulls.
12. Minimal increases in grain metal content were observed when corn was grown on sludge-amended soils.
13. Concentrations of Zn, Cu, Cd, and Ni in wheat and soybean grain were increased by sludge applications. Bran and meal contained the highest metal concentrations for wheat and soybeans, respectively.

The full report was submitted in fulfillment of Grant No. R804547-02 by Purdue University under the sponsorship of the U.S. Environmental Protection Agency.

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*The complete report, entitled "Characterization of Sewage Sludge and Sewage Sludge-Soil Systems," (Order No. PB 84-158 898; Cost: \$28.00, subject to change) will be available only from:*

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