Project Summary

Characterization of Sewage Sludge and Sewage Sludge-Soil Systems

Lee E. Sommers, Darrell W. Nelson, and Allen W. Kirleis

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 H₂SO₄ 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, \( \alpha \)-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 quinine-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 (organics) 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 solutions 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 \( \text{Cu}^{2+} \). The addition of a more basic nitrogen donor, ethylenediamine (en), resulted in the formation of Cu(en)\( _2 \) by displacement from Cu-HA or both coordinated aqua ligands and HA oxygen donors. ESR parameters revealed that two HA oxygen atoms were coordinated equatorially to Cu\( ^{2+} \) in the original soil and sludge Cu-HA complexes. In the sludge Cu\( ^{2+} \)-HA complex, the Cu\( ^{2+} \) ion also appeared to form axial bonds with HA nitrogen donor ligands. The nature of the materials associated with the sludge fraction. Characterization of an adduct with glycyglycine showed that the dipetide formed coordinate bonds with 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:


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 decomposiition 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 CO\( _2 \) evolution) appeared to be a function of the organic C content of the sludges. As much as 30% to 47% of the CO\( _2 \) 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 offered 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 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 sludges subjected to intensive stabiliza-
processes at the treatment plant. 
Carbon dioxide evolution in the field study was monitored for a 24-hr period by 
sampling cylinders containing soil-sludge mixtures. The cylinders remained open to the 
environment between sampling periods. Soil moisture and temperature were also monitored. Evolution of CO2 
was initially rapid in all soil and sludge 
combinations, but it decreased with time 
owing to consumption of easily decom-
posable 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 CO2 release from carbon dioxide dissolution, the presence of inorganic C in sludges 
can interfere with organic C decomposi-
tion calculations based on CO2 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 CO2 evolution in 
early spring. This increase is possibly due 
of increased organic C availability induced 
by freezing and thawing cycles during the 
previous winter.

Incubation studies using carboxyl-
abeled 14C dibutyl phthalate (DBP) added 
soils at 0.1% (w/w) indicate that 90% 
of the DBP was degraded within 80 days. 
Decomposition of DBP was shown to be 
biochemically mediated and was a function 
of soil type, pH, and temperature. Applica-
tion of DBP at rates of 0.4% (w/w) and the 
addition of ammonium and CaCO3 or 
sewage sludge had little effect on the 
extent of DBP degradation. Dibutyl phthal-
ate contained in sewage sludge or other 
new 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 char-
acterized by elemental and functional 
group analyses, and by visible and infra-
red 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 mate-
rals 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 applica-
tion. 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 
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 decomposi-
tion, possibly as a result of their incorpo-
ration into the HA structure.

Infrared spectroscopy was used to 
identify the mode by which carboxylates of 
a soil HA complexed Cu** and Fe**. 
Carboxylic acid groups of soil HA were 
converted to carboxylates (CO2) by form-
ing coordinate bonds with Cu** and Fe**. 
The separation of the antisymmetric, v4 
(CO2), and symmetrical, v2 (CO2), stretch-
ing vibrations of CO2 obtained from 
spectra of metal-HA complexes indicated 
that CO2 formed a undentate complex 
(i.e., a single M-O bond) with Cu** and 
Fe**. The formation of bidentate or 
bridging complexes between CO2 of HA 
and Cu** or Fe** 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+, Fe**, Fe++, Al**, 
Mn++, Ca++, Mg++, Zn++, Cu++, Cd**, Pb**, and 
Ni++. In acid systems, Ni++ at 10^-5 to 
10^-7 M was the predominant ligand 
species for all chelating agents. Similar 
results were obtained in alkaline systems 
with NiCO3 controlling Ni+2 solubility. In 
the absence of Ni++, either Cd++ or Pb++ 
ligand species dominated at alkaline pH 
for all chelating agents. In acid systems, 
Cu, Pb, Fe, and Zn were 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 diethyl-
eteramine pentaacetic acid (DPTA) 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 ~ -0.3 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, 
PO4, SO4, Cl, conductivity, pH, and organic 
C. The metal species present were calcu-
lated with a computer program (GE-
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 inor-
ganic ligands increased in the following 
order:

Zn ≈ Mn ≈ Ni < Cd < Cu

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** indicated 
undersaturation with respect to known 
Cd solid phases, whereas Zn** activities 
were comparable with those of ZnFe2O4, 
soil Zn, and Zn3SiO4. 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 in-
creased 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:

\[ \text{Zn} > \text{Fe} > \text{Mn} > \text{Ni} > \text{Cu} > \text{Cd} \]

Except for Mn, the concentrations of trace metals increased with increasing rates of sludge 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 grots fraction. Both the concentration and the percent distribution of metals in dry-milling fractions decreased in the following order:

\[ \text{germ} > \text{hulls} > \text{flour} > \text{meal} > \text{grits} \]

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 CO₂ 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 decompositon 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.

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