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Project Summary

Toxic and Priority Organics in Municipal Sludge Land Treatment Systems

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Research was conducted to investigate the fate of organic priority pollutants applied to plant-soil systems at rates characteristic of municipal sludge land treatment. A single chemical was applied at rates that were 0.1, 1.0, 10, and 100 times the expected values received during an annual application of municipal sludge. The ^{14}C-chemicals investigated were in the following groups: polynuclear aromatics, phthalic acid esters, and substituted aromatic compounds. None of the organic priority pollutants studied was entirely excluded from all plant species at the rates of soil application used. The ratio of chemical concentration in the fresh plant to the level loaded initially onto the soil (bioaccumulation) was most typically less than 0.01 and always less than 1.0. Of the crops studied (fescue, corn, soybeans, and wheat), no vegetation type routinely evidenced the highest uptake of the organic chemicals used. Plant uptake of organics appears to be largely governed by chemical losses from the soil over time and the water solubility of a given chemical. The presence of sludge did not appear to alter significantly the crop uptake or soil loss of these compounds. If corroborated, these data would allow a large expansion of design information for municipal sludge land treatment systems.

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

Before publication of the specific list of priority pollutants in 1976, attention to organic chemicals in municipal wastes was restricted by the lack of information about what compounds were present or of concern. Research was therefore limited in scope. With publication of the priority pollutant list, a program was undertaken to measure these specific organics in municipal wastes, effluents, and sludges. For organic chemicals, the priority pollutant list has stimulated recognition of a substantial data base that already exists on the behavior of organic compounds in the terrestrial system. This data base has been built by research on pesticides and residues, other agricultural chemicals, soil sterilization, chemical spills, organic fertilizers, and soil-plant behavior. This very large data base is an excellent starting point for evaluating the impacts of specific organic compounds on applications of municipal effluents and sludges. Though significant transferable information exists for estimating behavior, relative assimilation capacities, and critical levels for specific organics, further research is also needed on the organic priority pollutants present in the municipal sludge or effluent.

Experimental Procedures

Selection of the organics (nonpesticides) to be studied was based on data from the U.S. Environmental Protection Agency evaluations of municipal sludge. Since a major disposal alternative for municipal sludge is application to land, those organics in highest concentration were chosen for these experiments. As an ex-

perimental plan, chemicals were tested in similar groups: phthlate esters [bis (2-ethylhexyl), di-n-octyl, di-n-butyl, and diethyl], polynuclear aromatics [naphthalene, anthracene, phenanthrene, and benz(a)anthracene], and chlorinated aromatics (chlorobenzene and p-dichlorobenzene).

A rationale was established for the loading rates of individual organic chemicals used in these experiments. As a reference loading rate (1X), the sludge nitrogen loading of 500 kg/ha per year was selected as an intensive-use design criterion. From extensive municipal sludge characterizations available, the nitrogen content was taken as 5% on a dry solids basis. From the available priority pollutant data, the average total solids concentration was 57,000 mg/L for primary sludge. The average concentration in wet sludge was determined for each organic compound. This organic compound concentration was combined with the dry solids concentration and nitrogen loading rates to determine the reference study rate for each chemical. Each investigation usually involved multiples of the reference rate, typically 10X and 100X.

The experiments were conducted in a greenhouse with temperature and humidity control. The study of organic priority pollutants was undertaken primarily using ^{14}C-labeled compounds. A Norfolk fine, loamy, siliceous, thermic, typic, paleudult soil was selected. The vegetation species used were fescue, corn, wheat, and soybeans. Most plants were sampled after early growth of about 30 days, but the wheat and soybeans were allowed to grow to maturity. These latter species were then sampled, with the plant and seeds being analyzed separately for chemical uptake.

The primary determination of plant uptake of an organic chemical was by ^{14}C analysis. This quantification after the initial loading period was necessarily a combination of metabolites and parent compound. Thus such data represent maximum uptake of parent compound. In a number of situations, thin-layer chromatography (TLC) was used to verify the percentage of ^{14}C detected that was actually parent compound. These data were used to judge the overall behavior of the parent compounds.

The loss of each chemical from the soil system was determined to evaluate this major pathway. Losses were a combination of microbial decomposition and volatilization. Determination of the chemical concentration in the soil at the start and end of the plant growth cycle was used to assess overall loss. The rate of loss was thus a minimum measure, since decomposition was often substantially achieved over shorter time periods.

Results

Phthalic Acid

The phthalic acid loading rate to the soil was 0.6, 6, 60, and 600 ppm; also, a control sample received no phthalic acid. Height and dry weight of corn (21-day), tall fescue (45-day), immature soybean (21-day) plant, mature soybean plant, soybean seeds, wheat seeds, and mature wheat straw were not affected by the phthalic acid applied to the soil. The height of immature wheat (40-day) was affected at the highest chemical loading rate. The phthalic acid uptake ranged from less than detectable to 23 ppm and was significantly above the control for all plants and plant materials except soybean pods. Fescue and immature wheat plants exhibited the highest concentration of phthalic acid, and mature wheat plants and wheat seeds exhibited the least. Most of the phthalic acid was lost from the soil by the end of the study, with an average of only 5.7% recovered in plants and soil.

Phthalic Acid Esters

The loss from soil and uptake by vegetation was investigated at initial loading rates of 0.022, 0.22, and 2.2 ppm for all the phthalate esters except di(2-ethylhexyl), which was 0.44, 4.4, and 44 ppm. The height and dry weight of young corn, fescue (30-day), mature wheat, and mature soybeans were not affected phytotoxically at these chemical loading rates. Plant uptake (^{14}C basis) of phthalate esters was typically at less than detectable limits (LDL) — up to 1 ppb for the loading rates corresponding with municipal sludge practice, except for di(2-ethylhexyl), which was between LDL and 28 ppb. Crop levels increased with increasing soil loading rate, but the bioaccumulation (ratio of chemical concentration in the dry plant to the level initially applied to the soil) was always less than 0.1 and averaged 0.06 in plants and 0.03 in the seeds harvested. The plant bioaccumulation ratio is typically lower than the above volume by a factor of 4.5 when the chemical concentration of the fresh plant is used. The percentage of ^{14}C that was actually found to be phthalate ester (by TLC method) in the plant ranged between 9% and 35%. After correcting for the TLC results and the ratio of extraction to plant-bound ^{14}C, the bioaccumulation factor (dry-weight basis) is about 0.04 for plants and 0.07 for seeds. Loss of phthalate ester after incorporation in the surface 15 cm of soil appears to be by first order process (coefficient of loss about 0.3 $days^{-1}$) followed by a much slower rate of decrease. In an overall ^{14}C balance, between 1% and 25% of the radiolabel was still in the plants, roots, or soil at the time of harvest.

Polynuclear Aromatics

For each chemical in this group, the loading rate to the soil was 0.1, 1.0, and 10 ppm; also, a control sample received no polynuclear aromatic compound. Neither the chemical, the application rate, nor the replication had significant effects on total dry weight or height at harvest for any of the crop plants studied. Thus no phytotoxic response for these four vegetative species was observed over the range of chemical loading. The average chemical uptake levels ranged from LDL to 0.59 ppm for all plants and varied directly with the loading rate applied to the soil. Overall, immature wheat, corn, and mature soybeans had the greatest uptake, whereas soybean seed, mature wheat plants, and wheat seed had the least. Uptake also varied by chemical. For all plants at all rates, the uptake was ranked anthracene > benz(a)anthracene > naphthalene > phenanthrene. Regression equations were produced to predict plant uptake from soil loading rates.

Soil retention reflected chemical structure, water-solubility, and vapor pressure. Benz(a)anthracene, with the largest structure, lowest water solubility, and lowest vapor pressure, was most resistant to loss. In contrast, naphthalene, with the simplest structure, highest vapor pressure, and highest water solubility, was lost from the pots at the greatest rate. Plant uptake accounted for very little of the mass of applied radiolabel — less than 0.5%.

Chlorinated Aromatics

The soil loading rate was 0.0094 ppm for chlorobenzene and 0.2 ppm for p-dichlorobenzene, based on the projected levels from cumulative annual municipal sludge land treatment. In addition, a control sample received no added chemical. No effect was observed in regard to phytotoxicity at these soil loading rates of chloro- and p-dichlorobenzene. The uptake of chlorobenzene by plants was from 0 to 23 ppb, with the latter concentration being achieved by fescue grass. For p-dichlorobenzene, the uptake range was 0

to 1 ppm, with immature wheat having the highest concentration. This group of chemicals was the only one to evidence a ^{14}C bioaccumulation factor greater than 1.0 on a dry-plant basis. The factor for green plants was less than 1.0. Verification of the actual amount of parent compound was not possible. The soil concentrations after about 45 days were 8% of the initial loading for the chlorobenzene and 4% for p-dichlorobenzene. Thus losses from the soil system were extensive.

Organic Chemicals in the Presence of Municipal Sludge

A limited series of studies was conducted in which organic compounds were added to the soil in the absence of municipal sludge and at two rates of sludge addition (0.16 and 1.6 dry tons of sludge per acre). The chemicals used in separate pots were di-n-butyl phthalate ester (0.22 ppm), chlorobenzene (0.0094 ppm), and p-dichlorobenzene (0.2 ppm). For these three chemicals, plant uptake by the four species used showed no increase or decrease with the presence of municipal sludge. That is, there was no statistically significant dependence on the presence or the rate of sludge addition. The exception to this was with di-n-butyl phthalate, in which the uptake was lowered by a factor of 2 to 3 when sludge was also present. Over the duration of one plant cycle, the loss of these organic compounds from the soil was essentially the same whether sludge was present or not.

Summary and Conclusions

Important, previously unavailable, quantitative data were obtained for each separate chemical group studied. However, the aggregate behavior of all chemicals leads to additional conclusions about municipal sludge land treatment. Two factors seemed to unify the experiments: (1) The chemical concentration in soil at the end of the experiment was a measure of the chemical concentration in soil over the duration of the experiment, with higher concentrations indicating more compound available for uptake, and (2) the water solubility of a chemical was a measure of its availability in the water phase, with lower solubility implying that any chemical present might be bound to the soil (lipophilic phase).

An initial conclusion is that probably all organic compounds have properties that permit uptake by vegetation. Such uptake occurs in natural soils and is limited by the degree of solubility *and* by the magnitude of competing mechanisms (compound decomposition, volatilization, absorption, etc.) occurring in the soil. All compounds used in these experiments were found in some vegetation, although for many plants, no detectable concentrations were found. A similar conclusion can be reached concerning all inorganics (such as metals); and it simply reflects the equilibrium distribution of all chemicals between soil and water with the subsequent dynamic processes by which plants take up water from the soil.

Among the chemicals investigated, the ratio of chemical concentration in the fresh plant to that in the soil at the beginning of the experiment appears to indicate low bioaccumulation. That is, this ratio was always less than 1.0 and most often than 0.1. In the majority of cases, the ratio is less than 0.01. The actual ratio is probably far lower since ^{14}C — and not exclusively the parent compound — are being measured at the end of the experiment, whereas the initial soil loading is clearly the parent compound.

The factors affecting plant uptake are complex and involve competing soil behavior for each specific organic compound. If one qualitatively diagrammed the factors of relative availability for a chemical in a soil system and of relative loss by competing mechanisms, the crop uptake would appear to have certain trends. For chemicals in which competing losses are high (i.e., volatile or microbially labile), the compound is not available for uptake. Likewise, if a compound is present but not easily dissolved in water, the chemical will then be bound to the soil (the organic phase) and will not be readily available. Conversely, compounds that are only slowly lost by competing pathways and are highly water soluble would be predicted to have generally higher rates of plant uptake. The compounds studied in this project offer few, if any, exceptions to this qualitative behavior.

The specific conclusions of this report are:

1. Measurement of radiolabel (which can be parent or metabolites) proved to be an indication of the parent ^{14}C compound.
2. After a full growth cycle, a certain fraction of ^{14}C and possibly parent compound remained unextractable from the plants.
3. All organic compounds studied were taken up by plants, but the bioaccumulation factors appear to be significantly less than 1. This condition represents a major safety factor, since with the losses of an organic compound (e.g., decomposition), uptake of successive crops will approach the lowest level of detection.
4. For the three organic chemical groups studied, the bioaccumulation factor (chemical concentration in the fresh plant: chemical level applied to the soil) was always less than 1.0; most often it was less than 0.1, and in the majority of cases it was less than 0.01.
5. No single crop (among corn, fescue, soybean, and wheat) was routinely the species with the highest uptake.
6. The competing phenomena of loss from the soil and solubility (bioavailability) appeared to control the levels of an organic chemical taken up by vegetation. These phenomena are complex.
7. In experiments with three organic compounds, the presence of municipal sludge as a large organic addition did not appear to significantly alter the crop uptake or decomposition of the organic chemicals. Should these results prove even qualitatively correct, large amounts of available information on organic compounds in terrestrial systems could be used in estimating the effects of specific organics on land disposal of municipal sludges.
8. Organic compound studies in municipal sludge land treatment systems will remain complex, expensive, and time-consuming investigations for the near future.

The overall specific recommendations for future research are as follows:

1. Investigations should be initiated to expand the number of groups of organic chemicals in which representative compounds are evaluated as to their behavior in soil-plant systems.
2. Designers and evaluators of municipal sludge land treatment systems must maintain some perspective about the effects of all the various sludge constituents (e.g., pathogens, metals, organics, anions) when evaluating or designing municipal sludge land treatment systems.
3. With the limited information available as a part of this report, and with data more broadly available, preliminary consideration of the risk sequence probable with municipal sludge and crops grown on such systems should be undertaken.

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The complete report, entitled "Toxic and Priority Organics in Municipal Sludge Land Treatment Systems," (Order No. PB 86-150 208/AS; Cost: $16.95, subject to change) will be available only from:
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