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Project Summary

Trace Organics and Inorganics in Distribution and Marketing Municipal Sludges

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This project was undertaken to complement a study of the occurrence of pathogens in distributed and marketed (D & M) municipal sludge products. The purpose was to provide a data base of priority pollutant metals and organics from sludges produced at facilities in 26 cities across the U.S. In addition, efforts were made to characterize the major organic components in sample extracts from each city using GC/MS.

For two of the cities, where large composting and marketing/distribution operations were in place, composites of weekly samples from eight different sites were prepared. Five to six composites from each of these sites were prepared from eight weekly samples collected at each site. For the other 24 cities, 15 of which had ongoing D & M operations, less intensive analyses were carried out for the survey: four monthly samples from each site were composited, and these 24 composites were analyzed with the composite samples from the two weekly-sampled cities.

Analytical methods were selected prior to initiation of the project; they followed standardized preparation, cleanup, and analytical procedures. Modifications were required in some instances in order to deal with the complicated sample matrix presented by composted sludge. The modifications for arsenic, selenium, and thallium were successful in dealing with the matrix. For extractable organics, additional cleanup methods are still required to achieve suitable detection limits for some components.

Of the 15 trace metals analyzed, all but Be and Tl were detected 100% of the time in all 67 samples analyzed: Be was at low but detectable concentrations in 97% of the samples, but Tl was never detected. The relative standard deviation of individual metal concentrations for each site where multiple composites were analyzed was less than 30%. In contrast, the range of metal concentrations from site to site varied up to two orders of magnitude for some metals. Comparison of these results with literature reports of municipal sewage sludge evaluations suggested that none of the sludge products tested would be classified as hazardous waste under RCRA criteria. Comparison of the analytical data to EPA proposed criteria for D & M sludge products indicate that copper may be a problem in sludge from one city, and that several D & M products across the country may have a consistent problem with lead.

Relatively few of the target organic compounds were detected in any of the samples. One phthalate (DEHP) was detected in all samples. Some two, three, and four-ring PAH, DDT metabolites, phenol, and chlordane were detected in several samples. Sample matrix problems in the pesticide analysis prevented a complete survey by GC/EC. Six other target compounds were detected in one sample each. The PCB mixture,

Aroclor 1248, was detected in two samples by GC/EC, but the concentrations were too low to be confirmed by GC/MS. The reported levels did exceed the draft D & M criteria, however.

The GC/MS characterization of major organic components in 26 sludge extracts did not reveal any "new" compounds. The ion chromatograms of most samples were dominated by petroleum and carboxylic acid-type compounds.

This Project Summary was developed by EPA's Health Effects Research Laboratory, Research Triangle Park, NC, 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 land application of municipal wastewater treatment sludges is widely practiced both as an economic treatment or disposal method and to provide an economic soil nutrient amendment for agricultural use. Concerns over the general disposal of sludge to land have focused on several possible adverse impacts from sludge-borne chemical and microbial agents, including phytotoxicity, domestic animal toxicity, and human health. Human health issues primarily emphasize pathogenic microorganisms, and to a lesser extent, trace metals and organics which might enter the food chain via contamination of drinking water, accumulation in and on edible crops, or accumulation in animals and animal products used for food.

Most studies of sludge products and trace chemicals in sludge applied to land have revolved around specific sludges applied under controlled, planned conditions, – either laboratory, pilot, or full scale operations. Sludges used in planned land applications are usually stabilized via one or more treatments such as digestion, chemical treatment, dewatering, heat-drying, and composting.

The EPA published a process design manual, "Land Application of Municipal Sludge" (1), setting guidelines for projects and reviewing existing information and data bases. In a separate report, EPA identified approximately 50 individual metals and organics of probable concern in different disposal management options (2). These options included: landspreading and distribution/marketing (agricultural); landfilling; incineration; and ocean disposal.

In a separate but obviously related issue, the "Domestic Sewage Study" (3) addressed concerns over the industrial disposal of toxic wastes into municipal treatment systems and the domestic sewage and sludge exclusion from RCRA. This study proposed a list of 165 chemicals for analysis in municipal treatment systems. As part of a cooperative study (4) between the Association of Municipal Sewage Agencies (AMSA) and EPA, 18 sludges were evaluated using the "Toxicity Characteristic Leaching Procedure" (TCLP). A wide range of sludge types was included in that study, and although none exceeded the proposed TCLP limits for hazardous wastes, some were close to the proposed limits (5). The EPA is currently in the process of issuing regulations for sludge management, and draft criteria were made available to AMSA in mid-1987.

Although there is much data to be found in the literature for metals, there is comparatively less available for trace organics, and in either case, little recent data on composted D & M sludges are available. The project reported herein was undertaken to address two goals:

1. provide a data base of 15 trace metals and 121 toxic organic compounds in stabilized sludge products from 26 cities which are distributed and marketed for various land application uses.
2. characterize selected sludge extracts from each city for non-target organic chemicals which might predominate in individual sludges.

Experimental Procedures

The following is a brief discussion of the analytical procedures employed and some of their limits relevant to data interpretation. Few problems arose in the acid digestion and ICP or AA analyses of Ba, Be, Cd, Cr, Cu, Pb, Mn, Ni, Ag, Zn, or Hg following guidelines in the EPA Methods SW 846 procedures. For the graphite furnace AA analysis for Tl, however, Smith-Hieftje background correction was required. For As, Se, and Sb analyses by hydride generation AA methods, 6.5 N hydrochloric acid was required to minimize the transition metal inhibition of the hydride generation step. Graphite furnace analyses of As and Se were precluded due to severe background interferences.

The volatile organics were analyzed by purge and trap methods using capillary gas chromatography/electrolytic conductivity/photoionization detectors, following guidelines set forth in EPA methods SW 846. While these techniques were suitable for the target compounds in the composted sludge matrix, a number of unidentifiable components were detected by the photoionization detector. It is unlikely that these unknowns were present in the extracts used for GC/MS characterizations described below.

Initial efforts to analyze for pesticides and PCBs by capillary GC with electron capture detector met with mixed success. Sample extract fractions had to be treated with KOH, mercury, and sulfuric acid in addition to silica gel cleanup; each of these fractions required dual column analyses before and after the chemical treatment. This tedious process was successful, in some instances, in yielding data. More often than not, however, interferences remained. GC/EC was abandoned in favor of GC/MS after 15 samples were analyzed.

The GC/MS procedures followed the extraction and GPC cleanup methods described in EPA Methods SW 846. Most of these samples had been processed, and many of the analyses completed prior to availability of the draft D & M sludge criteria. Therefore, in many samples, the complex organic matrix in extracts from most sites interfered with the instruments' ability to detect several of the target compounds at levels low enough to be interpreted relevant to the proposed D & M criteria. Although experiments are being continued in an effort to improve relative detection limits in these matrices, results were not available for this report.

Efforts to characterize major unknown organic components were limited to computer comparisons of GC/MS peaks to the NBS mass spectral library. In none of the cases was a tentative identification made. Manual review of those components with a high degree of fit with an NBS library compound (>80%) allowed probable compound class assignment for many peaks. Virtually all of the major components classified appeared to be aliphatics or carboxylic acid type compounds. A majority of the sample extracts exhibited a hydrocarbon "hump" in the ion chromatograms. The peaks reviewed, therefore, were superimposed on this background. As a result, a significant portion of the major

peaks were multi-component peaks whose identities remain completely unknown.

Conclusions

All of the municipal sludge products analyzed from 26 cities contained measurable levels of heavy metals; concentrations ranged over two orders of magnitude between sites. Based upon comparisons with reported evaluations of municipal sludges in the literature, it is unlikely that any of the distributed and marketed sludge products tested in this study would be classified as hazardous waste. However, in comparing measured concentrations with EPA-proposed D & M sludge criteria, copper (>1100 mg/kg) and lead (>200 mg/kg) concentrations from several sites appeared to be high enough to consistently exceed these criteria for land use.

Volatile priority pollutant organics were rarely detected; toluene was found at 86 µg/kg in one sample and p-dichlorobenzene at 110 µg/kg in another. Hence this group of compounds appears to have little significance in sludge products. Few samples contained detectable amounts of any of the extractable priority pollutant organics. Chlordane, DDT metabolites, and two- to four-ring PAH were frequently detected, but incidence was clearly site specific. Of these, Pyrene was detected 18 times, ranging from 0.4 to 4.4 mg/kg. Bis-(2-ethylhexyl)phthalate was detected in all 67 samples tested ranging from 1.9 to 130 mg/kg.

Phenol was found three times; di-n-butylphthalate, 2-nitrophenol, N-nitrosodimethylamine were found once each. Aroclor 1248 was detected twice. Where analytical detection limits were sufficient to address the proposed D & M criteria, the only organic which exceeded these guidelines was the Aroclor mixture. In general, the priority pollutant organics do not appear to be cause for concern in these types of products, but site-specific evaluations appear to be warranted based on the scatter of data among the sampling sites.

No new toxic organics were identified in GC/MS characterizations of the major organic components in samples from each city. The preponderance of the materials appeared to belong to aliphatic and carboxylic acid classes of compounds. A majority of the sites contained molecular profiles suggesting a high petroleum contribution.

The molecular complexity of many of the sludges presented matrix problems which inhibited detection limits for the standardized extraction, cleanup, and analytical methods used. The resulting detection limits were not sufficient to address the proposed D & M sludge criteria levels for at least five of the organics on that list in the majority of samples analyzed.

Recommendations

This project was initiated prior to availability of draft criteria for use of D & M sludge products, and completed before final recommendation of the criteria. Therefore, once D & M sludge product criteria are finalized, data developed in this survey should again be reviewed.

Where existing survey data are found to be insufficient for comparison to the finalized criteria due to analytical matrix problems and poor detection limits, sites should be re-surveyed. Compounds which appear to be candidates at this time include toxaphene, benzo(a)pyrene, hexachlorobenzene, heptachlor, and aldrin/dieldrin. In addition, molybdenum was not analyzed in this study, but appears on the draft criteria list.

Appropriate modifications of existing GC/MS analytical techniques, including more comprehensive fractionation/cleanup steps, must be developed to accomplish these tasks.

Since data indicate the probability of site-specific problems, (e.g., copper, lead, PCB) in terms of D & M land use criteria, monitoring programs are needed to better define the extent of the apparent problems at these sites.

References

1. *Land Application of Municipal Sludge - Process Design Manual* EPA-625/1-83-016. U.S. EPA, Cincinnati, OH. 1983
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4. Walker, J. M., *Cooperative Testing of Municipal Sewage Sludges by Toxicity Characteristic Leaching Procedure and Compositional Analysis*, Draft Report, Residuals Management Branch WH-595, U.S. EPA office of Municipal Pollution Control, Washington, D.C. 1987.
5. *Federal Register*, 51, 21648 (June 13, 1986) 40 CFR Parts 261, 271, and 302.

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The complete report, entitled "Trace Organics and Inorganics in Distribution and Marketing Municipal Sludges," (Order No. PB 88-160 585/AS; Cost: $25.95, subject to change) will be available only from:
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