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Analysis of Municipal Sewage Sludge Samples by GC/MS/Computer for Polychlorinated Biphenyls and Other Chlorinated Organics

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The presence of halogenated organics in the environment has long been a public and scientific concern. The contamination of water supplies by pesticides, halogenated solvents, chlorination products, and polychlorinated biphenyls (PCBs), has been studied extensively. The analysis of sewage sludge can also be indicative of the environmental pollution by halogenated organics. In general, these compounds exhibit low water solubility and would be expected to partition from water onto lipophilic solids.

The presence of chlorinated organics in sewage sludge is of concern because of the potential for further environmental pollution. The sludge may eventually be digested sufficiently to be reinjected into the sewage plant effluent, it may be dried and transported to landfills, or it may be used as agricultural and gardening fertilizer and soil builder.

The major emphasis of this research was to analyze a series of municipal sewage sludge samples for medium volatility halogenated hydrocarbons. Gas chromatography/ mass spectrometry/computer (GC/MS/COMP) was chosen as the analytical technique to provide selectivity necessary to identify these compounds in the complex matrix.

MATERIALS AND METHODS

Sample Collection. Duplicate sludge samples were collected in clean wide-mouth one-L bottles from municipal wastewater treatment plants. Table 1 lists the locations where the sludge samples were taken. While most of the plants are in large metropolitan areas, they represent a variety of common wastewater treatment processes and a variety of sludge sample characteristics.

Extraction and Cleanup. Samples (∿ 300 g) were extracted at pH 11 six times with a total of 350 mL chloroform to remove neutral and basic compounds. The extract was dried with sodium sulfate, vacuum filtered and concentrated to 2.0 mL using a Kuderna-Danish apparatus. In cases where the sample background interfered significantly, an aliquot of the sample was chromatographed on a 1.0 x 30 cm silica gel column (SNYDER AND REINERT 1971). PCBs and related compounds were eluted with 50 mL hexane; pesticides and other compounds were eluted with 50 mL toluene. The procedure was validated using sludge fortified with PCBs and pesticides.

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TABLE 1

Summary of Sewage Sludge Sample Collection

Sample Code	Municipality	Location	Site
NBM	New Bedford, MA	New Bedford Wastewater Treatment Plant	Between Centrifugation and Incineration
PH	Philadelphia, PA	Northeast Sewage Treatment Plant	Anaerobic Digester No. 6
RAH	Raleigh, NC	Neuse River Wastewater Treatment Plant	Aerobic Digester and and Centrifuge
CHI	Chicago, IL	Metropolitan Sanitary District of Great Chicago-Stickney West-Southwest Plant, Cicero	No. 6 Digester
HOU	Houston, TX	Sims Bayou Sludge Disposal Plant	Flash Dried Sludge
KC	Kansas City, KS	Kaw Point Sewage Treatment Plant	No. 2 Digester
DN	Denver, CO	Denver Metropolitan Sewage Treatment Plant	Primary Digestion
SF	San Francisco, CA	SE San Francisco Water Pollution Control Plant	After Digestion and Elutriation
SEA	Seattle, WA	Metro West Point	Secondary Digester

Sample Methylation. Acidic components of the sludge samples were treated with diazomethane and dimethyl sulfate (KEITH 1975, 1976, a, b). These procedures were validated by fortification of a sewage sludge sample with a series of chlorinated acids, phenols, and biphenylols.

Sample Analysis. Analysis of all samples for PCBs was accomplished using a Finnigan 3300 quadrupole GC/MS with a PDP/12 computer. The 180 cm x 2 mm i.d. glass column, packed with 2% OV-101 on Chromosorb W, was held at 120° for three min, programmed to 230° at 12°/min and held isothermally until all peaks had eluted. Helium flow was 30 cc/min. The ionization voltage was nominally 70 eV and multiplier voltages were between 1.8 and 2.2 kV. Full scan spectra were obtained from m/e 110-500. Method development and some initial samples were analyzed under the temperature conditions: 150° for three min, programmed to 230° at 8°/min and held isothermally until all peaks had eluted. These temperature conditions, however, were found to be too severe for adequate resolution of some of the early-eluting compounds (e.g., chlorobenzenes), so the lower initial temperature conditions were utilized.

PCBs were quantitated by GC/MS/COMP using the selected ion monitoring (SIM) mode to provide maximum sensitivity and precision. SIM has been used successfully in similar research on polychlorinated naphthalenes (ERICKSON et al. 1977, c, 1978). Selected ion monitoring is an operational mode for the mass spectrometer where up to nine m/e values are step-jumped at short time intervals. Since this technique allows integration of ion intensity of the desired ions for a longer period than the customary full-scan mode, the sensitivity of the instrument is increased by approximately two orders of magnitude. By judicious selection of values to be monitored, interference by unwanted compounds can usually be minimized.

Ten ions were selected for monitoring: one from the parent cluster for each of the chorinated biphenyls ($C_{12}H_9Cl$ through $C_{12}Cl_{10}$). Although the parent ions were not necessarily the most intense, the probability of interference by PCB fragment ion or other contaminants was reduced. Ions were chosen from the M (parent), M + 2, or M + 4 values according to an optimum combination of greatest intensity and least interference from other PCBs.

PCBs were quantitated using an external standard and a previously determined relative molar response (RMR). The standard chosen was anthracene (parent ion mass 178; 27 ng/mL), which does not interfere with PCB determination nor do PCBs or their fragment ions interfere with the determination of anthracene.

The calculation of the RMR for the quantitation of sample components precluded the need for a calibration curve. The RMR was calculated as the integrated peak area of a known amount of compound, A^{o}_{unk}, with respect to the integrated peak area of a known amount of standard, $A°_{std}$ (in this case anthracene), according to the equation:

(Equation 1)

$$RMR = \frac{A°_{unk}/moles_{unk}}{A°_{std}/moles_{std}} = \frac{(A°_{unk})\ (mw_{unk})\ (g_{std})}{(A°_{std})\ (mw_{std})\ (g_{unk})}$$

From this calculated value, the concentration of a compound identified in a sample was calculated by rearranging Equation 1 to give:

(Equation 2)

$$g_{unk} = \frac{(A_{unk})\ (mw_{unk})\ (g_{std})}{(A_{std})\ (mw_{std})\ (RMR)}$$

The use of RMR for quantitation in GC/MS has proven successful in repeated application to similar research problems (ERICKSON et al. 1977 a,b,c, 1978, PELLIZZARI 1977, BURSEY et al. 1977).

RESULTS

The results of the sample analysis are summarized in Table 2. A total of 35 chlorinated compounds was found in sewage sludge, although not all compounds could be identified. In cases where a compound was identified, but no standard was available for retention time comparison, the identification was labeled "tentative". In some cases where the spectral quality was insufficient to definitely assign a molecular weight and/or chlorine content to an unidentified compound, it was labeled as "tentative". It must be noted that a large number of spectra contained what appeared to be chlorine isotope clusters which are not reported. This could be due to interferences, very low levels, or spurious peaks.

Although no structure could be assigned, the mass spectra indicated possible structures for three compounds in Table 2. The compound containing two chlorines with MW = 187 (RT = 2.3-2.7 min) may have the molecular formula $C_8H_7NCl_2$ and could be a dichloro-dihydroindole or related compound. Two distinct compounds were observed with four chlorines and MW = 240. These compounds appear to be isomers of tetrachlorostyrene ($C_8H_4Cl_4$). This identification is plausible since hexa- through octachlorostyrenes have been observed in Great Lakes water samples (KUEHL et al 1976). Unfortunately, an authentic sample was not available for correlation of retention time. The 4,4'-dichlorobenzophenone identification was confirmed by comparison of the retention with an authentic sample. The two peaks identified as DDE isomers are probably the two common isomers, o,p'-DDE and p,p'-DDE which generally are separable by GC.

The PCB concentrations in the neutral extracts of NBM sludge were judged sufficient to warrant quantitation. Therefore, the hexane eluate of that fraction was submitted to GC/MS analysis

TABLE 2

Summary of Chlorinated Compounds Found in Sewage Sludge

Compound[a]	Retention Time (min)[b]	Samples Observed
dichlorobenzene	0.5	PH
mw = 195, Cl_1	0.8	PH
mw = 221, Cl_1	0.9	RAH
trichlorobenzene	1.0	NBM, PH, DN, SEA
chloroaniline (tent.)	1.2	RAH
dichloroaniline	2.1-4.7 (1.1)	PH, RAH, KC, HOU
tetrachlorobenzene	2.2 (0.7)	NBM, PH, RAH, KC
mw = 187, Cl_2	2.3-2.7 (0.6)	HOU, DN, SEA
mw = 171, Cl_2	3.0	KC
mw = 240, Cl_4[e]	3.0, 4.3 (1.1)	PH, RAH
trichloroaniline[d]	3.2, 4.4	NBM
dichloronaphthalene	3.7	NBM
trichlorophenol	3.7	KC
mw = 302, Cl_1	4.5	RAH
mw = 210, Cl_3	5.1	KC
chlorobiphenyl	6.2	NBM
dichlorobiphenyl[f]	6.3-8.2	NBM
trichlorobiphenyl[f]	7.5-9.6	NBM, KC
mw = 192, Cl_1	7.6	HOU
mw = 288, Cl_1	8.6-11.1 (5.8)	PH
tetrachloronaphthalene	8.6	NBM
mw = 218, Cl_1 (tent.)	9.1	DN
mw = 256, Cl_1	9.1	HOU
tetrachlorobiphenyl[f]	9.3-10.2	NBM
dichlorobenzophenone	9.2 (7.2)	PH
mw = 269, Cl_1	9.9	PH
mw = 256, Cl_2	10.1	SF
pentachlorobiphenyl[f]	10.2-11.1	NBM
mw = 288, Cl_3	10.5	HOU, DN
mw = 280, Cl_1	10.7	HOU
mw = 241, Cl_1	10.8	PH
mw = 285, Cl_1	12.6	PH
DDE[e]	12.7, 13.2 (8.6)	PH, RAH
mw =356, Cl_2	12.8	PH
mw = 397, Cl_1	15.0	PH

(continued)

[a] Unidentified compounds are listed with the apparent molecular weight and number of chlorines. If the identification of a compound is tentative, it is denoted by (tent.)

[b] Retention times are listed for the chromatographic temperature conditions, 120° for 3 min, then 12°/min to 230°, then hold. Values in parentheses are for chromatographic temperature conditions, 150° for 3 min, then 8°/min to 230°, then hold.

[c] See Table 1 for abbreviations.

[d] Differences in retention times possibly indicate different isomers.

[e] Two separate isomers observed in some samples.

[f] Several isomers observed.

in the SIM mode for quantitation. The quantitative results are shown in Table 3.

Table 3
Quantitation of PCBs in Hexane Eluate of Neutral Extract of New Bedford Sludge

Compound	Amount Found (μg/ml)	Sludge Concentration (μg/ℓ)
$C_{12}H_9Cl$	8.5[a]	57
$C_{12}H_8Cl_2$	220a	1500
$C_{12}H_7Cl_3$	760a	5100
$C_{12}H_6Cl_4$	470a	3100
$C_{12}H_5Cl_5$	57	380
$C_{12}H_4Cl_6$[b]	76	510
$C_{12}H_3Cl_7$[b]	24	160
$C_{12}H_2Cl_8$	-	-
$C_{12}HCl_9$	-	-
$C_{12}Cl_{10}$[b]	14	93
Total PCBs	1600	10,800

[a] Average of two determinations.

[b] Not identified in mass spectra summarized in Table 2. Identification confirmed by comparison of the intensities of two or more ions in the parent cluster.

DISCUSSION

The results presented here establish the presence of a wide variety of chlorinated compounds in municipal sewage sludge. This study must be regarded as preliminary and further research will undoubtedly expand the list of compounds found. It should be noted that there was no evidence for the presence of brominated organics in any of the samples.

The analysis of some of the methylated fractions suggested that these procedures did not effectively methylate phenols and acids. Further research is necessary to assure that acidic components of sewage sludge are being properly analyzed.

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