POLYCHLORINATED BIPHENYLS IN SOLID WASTE AND SOLID–WASTE–RELATED MATERIALS

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Municipal refuse along with various solid–waste processing samples were analyzed for polychlorinated biphenyls (PCBs). In all cases, the samples required drying, particle–size reduction, separation of extraneous material, and extraction with an organic solvent. The extracts were cleaned–up by chromatography and analyzed by gas chromatography. The qualitative results obtained indicate that PCBs were present in several of the samples analyzed. These results are consistent with findings, by other investigators, that there is PCB contamination in many parts of the environment and they indicate that disposal of solid waste contributes to this contamination.

Recently, analysts involved with environmental pollutants have come to realize that polychlorinated biphenyls (PCBs) are widely distributed in the environment (Risebrough *et al.* 1969). These compounds were not discovered in the environment until 1966, in Sweden, and 1967, in the U.S., despite the fact that they have been available commercially for 40 years (Gustafson 1970). Concentrations of PCBs in fish and birds are highest in such industrial outfalls as San Francisco Bay and San Diego Bay, and concentration gradients apparently exist from these areas to more remote regions (Risebrough 1968, Risebrough *et al.* 1968).

Polychlorinated biphenyls are produced by various manufacturers in a number of countries. Some of them are marketed under the name of Aroclor® (a mixture of chlorinated terphenyls) by Monsanto Chemical Co., St. Louis. They represent "a series of inert, chemically–resistant, fire–retarding plasticizers compatible with a wide variety of resins" and they vary "from mobile, oily liquids to white crystals and hard transparent resins" (*Monsanto Co.* 1968). They are used in synthetic resins, synthetic and natural rubbers, cellulose resins, paint, varnish, wax, asphalt, and in allyl starch. They also find applications for dust prevention, moisture proofing, sealing, impregnation, and vapor suppression to prolong the residual life of pesticides (Lichtenstein *et al.* 1969).

The objective of this study was to analyze for PCBs in municipal refuse and in the products of processed refuse. This involved analyzing samples, of varying geographic

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origin, from a compost plant, raw municipal refuse, incinerator fly ash, incinerator gaseous stack emissions and residue, and leachate from a sanitary landfill.

Material and methods

Sample preparation. The raw municipal refuse (Saint Bernard, Ohio) was a grab sample from a 10-cubic yard packer truck which was ground in a large hammermill to approximately 1" x 1" in size. Subsequently, the refuse was ground in a Wiley Mill, to pass through a 2–mm screen, and dried in a laboratory oven at 105°C to constant weight. After drying, a portion of the sample was weighed into a pre-extracted extraction thimble.

The liquid condensate from incinerator stack and the products trapped in ethylene glycol were obtained from an experimental, high-temperature, low-capacity refuse incinerator (located at the Environmental Protection Agency facility at Center Hill). A sample probe was placed in the stack and a portion of the gaseous emissions were diverted through this probe. The diverted emissions were routed through a series of water-cooled condensers and then through a gas-diffusion bubbler containing ethylene glycol. (The ethylene glycol trap was used to extract any organic material that may have been volatilized in the incineration process.) The liquid condensate was collected and utilized as a solid-waste processing sample along with the ethylene glycol sample. These samples, along with the sanitary landfill leachate sample (Walton, Ky.), were extracted using the procedure described by the FWPCA Method for Chlorinated Hydrocarbon Pesticides in Water and Wastewater (*U.S. Department of the Interior* 1969).

The residue- and fly-ash samples were collected from municipal incinerators, as listed in Table I, and were prepared according to a unpublished procedure of Cohen and Allen (1972). Briefly, this involved various sorting, grinding, quartering, and drying procedures designed to reduce the sample size and still obtain a homogeneous sample. The final treatment utilized a pulverizer to reduce the size of particles so that they would pass a 60-mesh sieve. The pulverized, sieved material was used as the sample for this study.

The compost samples came from the joint U.S. Public Health Service-Tennessee Valley Authority Composting Project at Johnson City, Tennessee. The samples were all from the same windrow and were initially ground and mixed at the compost plant. Before shipment to this lab, these samples were dried at 100°C; on arrival, the large pieces of glass, ceramics, metals, and rocks were removed. The samples were then processed in the same manner as that used to prepare the raw refuse sample for extraction. Table I shows the samples used in this study and the quantity of laboratory sample extracted.

Analytical methods. All solids were extracted using a soxhlet apparatus and between 200 and 250 ml of hexane-acetone mixture (9:1 by volume) as the extraction solvent.

All samples were extracted for at least 12 hours, the solvent evaporated to dryness, and the residue redissolved in 6% ethyl ether. The PCBs were eluted from a 22–mm I D, 250–mm long column containing a small layer (one–half inch) of anhydrous granular sodium sulfate followed by a 15–g charge of activated florisil which was then covered with about three–fourths of an inch of granular sodium sulfate. The eluate was collected and evaporated to 1 ml. A portion (usually 100 μl) was applied to a 20– x 20–cm thin–layer chromatography plate, for further separation, along with several standard PCB solutions (hexane). The system employed was that described by Lichtenstein, *et al.* (1969).

Table I. *Samples Analyzed for PCB Content*

Sample	Description	Quantity extracted	Evidence of PCBs
1	Raw municipal refuse (Saint Bernard, Ohio)	50.9 g	No
2	Liquid condensate from incinerator stack (Saint Bernard, Ohio)	250 ml	No
3	Gaseous emissions from incinerator stack (Saint Bernard, Ohio)	300 ml[a]	No
4	Incinerator residue fines (Media, Penna.)	90.1 g	Yes
5	Incinerator residue fines (Greenwood, S. C.)	254.0 g	Yes
6	Incinerator fly ash (Media, Penna.)	115.7 g	Yes
7	Incinerator fly ash (New Orleans, La.)	87.8 g	Yes
8	0–Day compost (Johnson City, Tenn.)	50.1 g	No
9	15–Day compost (Johnson City, Tenn.)	63.0 g	Yes
10	30–Day compost (Johnson City, Tenn.)	71.7 g	Yes
11	42–Day compost (Johnson City, Tenn.)	69.3 g	Yes
12	Finished, screened compost (Johnson City, Tenn.)	76.6 g	(Trace)
13	Sanitary landfill leachate (Walton, Ky.)	1000 ml	No

[a]Approximately 19 standard cubic feet of gaseous emissions were passed through this amount of ethylene glycol.

This system utilized a 250-μ aluminum oxide coating and a heptane–acetone mixture (99:1 by volume). After development, the area of standard PCB spots was sprayed with a solution of Rhodamine B (0.1 mg/ml in ethanol), covering the extract portion so that it was not contaminated by the spray. Fig. 1 shows the chromatographic position of the PCBs on the chromatographic plate of TLC system employed. The standard spots were marked and the area of sample with the same Rf value as the standard spots was removed and extracted three times with 10-ml portions of hexane. The extract was

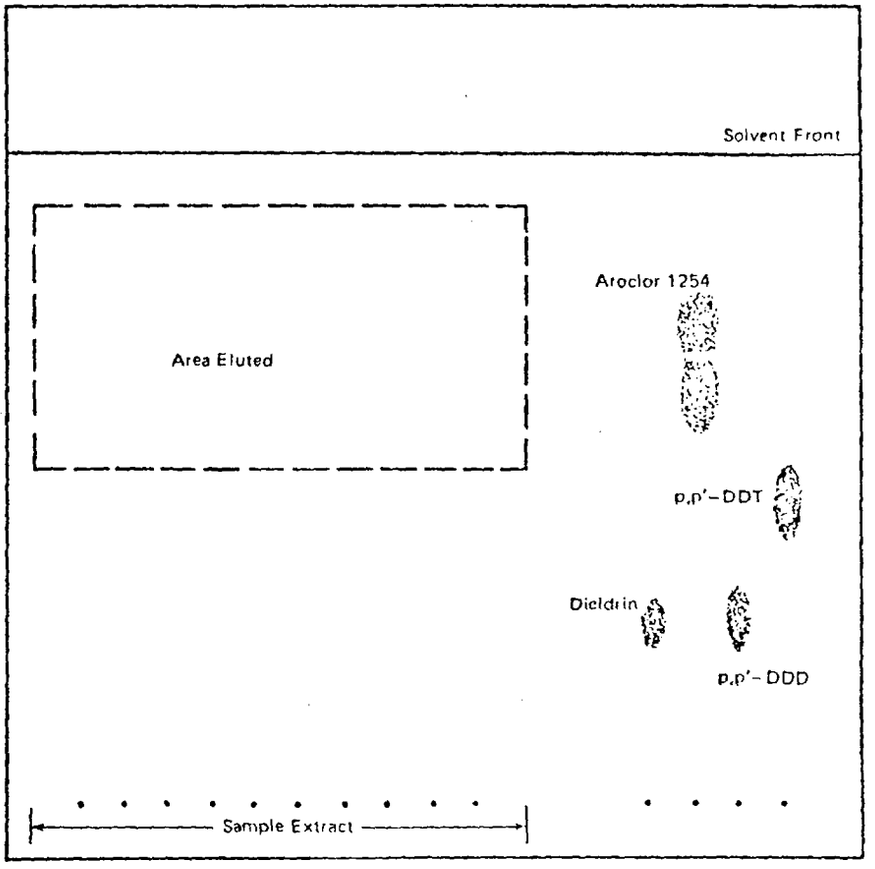

Fig. 1. Thin layer chromatogram of PCB and pesticide chemical standards showing area eluted from chromatographic plate for PCB analysis. Solvent: acetone-heptane mixture (1:99 by volume)

evaporated to 1 ml and retained for final analysis by electron–capture gas chromatography (GC). A Barber–Coleman Series 5000 Bench Model Gas Chromatograph[1], with (^{3}H)–electron–capture detector was used. A coiled glass column (4 ft. x 4- mm ID), packed with one percent by weight of SE–30 on 60/80 mesh Gas Chrom Q, was employed. The GC conditions were: column temperature – 188°C; injection–block temperature – 185°C; detector temperature – 210°C; gas–regulator pressure – 8 psi; gas – nitrogen, prepurified.

All solvents used in the course of this work were of a pesticidal quality suitable for pesticide analysis and the glassware was cleaned with chromic acid before use. All thimbles used in the soxhlet extraction were pre–extracted, using the solvent system employed to extract the samples.

Results and discussion

The results of the electron–capture gas chromatography indicate the presence of several PCBs in at least three of the samples extracted, with most other samples showing only traces. The data for the compost samples indicate the presence of PCBs; this finding is not surprising because the compost originated from a municipal refuse source that, no doubt, contained plastics which are associated with PCBs. PCBs are indicated in the chromatograms from incinerator residue and fly ash, pointing up the heat–resistant characteristics of PCBs. The presence of PCBs in the fly ash can also lead to the existence of PCBs in gaseous emissions from incinerators; however, they are not detected in gaseous emissions from the incinerator available during this study. PCBs in the incinerator residue fines indicate the need for careful disposal of these materials to avoid further contamination of soil or ground–water supplies.

Fig. 2 to Fig. 4 show gas chromatograms obtained from Aroclor standards while Fig. 5 to Fig. 7 show the similar chromatograms obtained from sample extracts. The PCBs in the samples are tentatively identified as Aroclor 1254 in the incinerator residue fines (sample 4), Aroclor 1254 and 1262 in the incinerator fly ash (sample 7), and Aroclor 1248 and 1254 on the 42–day compost (sample 11). Table II lists the retention time for the various peaks of the three Aroclor standards and the retention time (in mm of chart travel) of various peaks from the samples and shows the similarity in retention times.

No attempts at quantitation were made due to the difficulty of determining the amount of PCBs present without the use of a mass spectrometer.

The results reported in this paper indicate that disposal of municipal solid waste is one way in which PCBs enter the environment.

[1]Mention of commercial products does not imply endorsement by the U.S. Environmental Protection Agency.

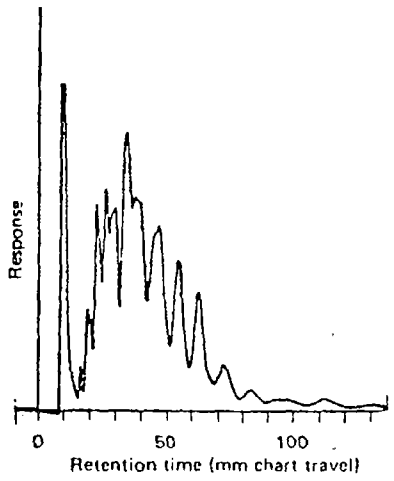

Fig. 2. Gas chromatogram of 50 ng of Arochlor 1248

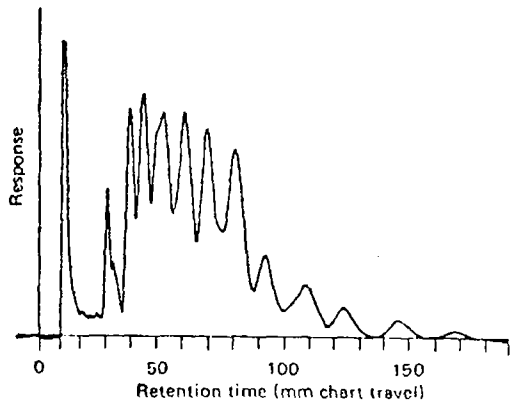

Fig. 3. Gas chromatogram of 40 ng of Arochlor 1254

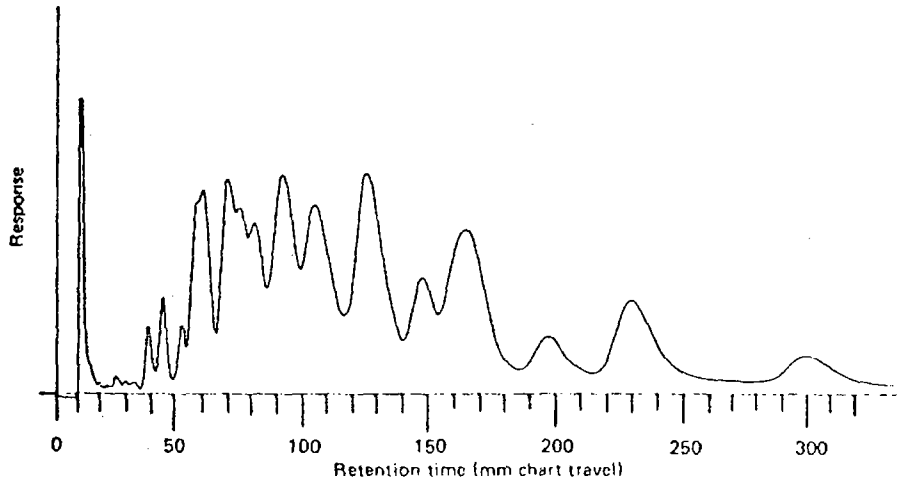

Fig. 4. Gas chromatogram of 50 ng of Arochlor 1262

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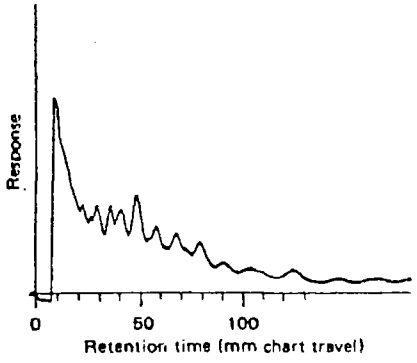

Fig. 5. Gas chromatogram of a 10-µl aliquot of extract (1 ml) obtained from incinerator residue fines (sample 4 in Table 1)

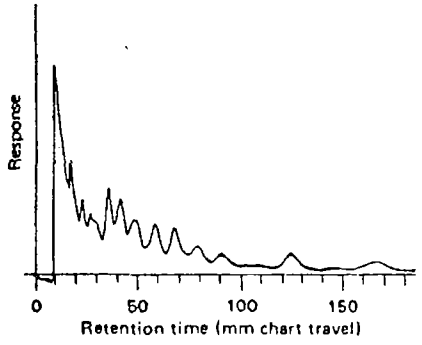

Fig. 7. Gas chromatogram of a 10-µl aliquot of extract (1 ml) obtained from 42-day compost (sample 11 in Table 1)

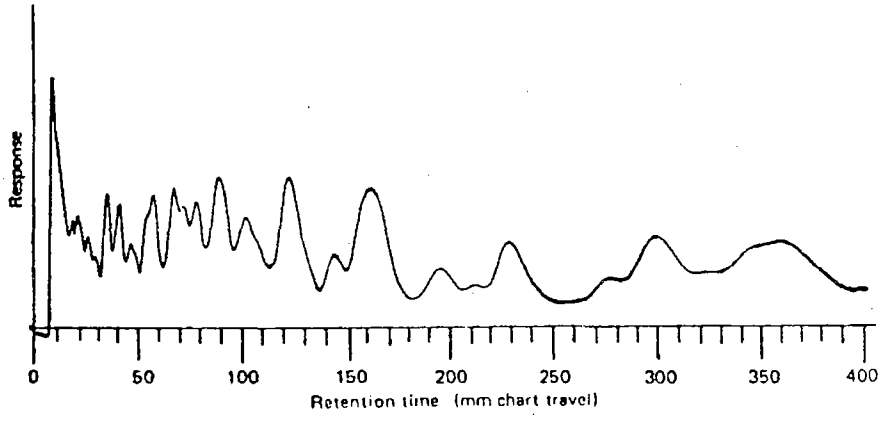

Fig. 6. Gas chromatogram of a 10-µl aliquot of extract (1 ml) obtained from incinerator fly ash (sample 7 in Table 1)

Table II. *Comparison of Retention Times Obtained for Arochlor Standard Solutions and Extracts of Various Waste Samples*[a]

Sample designation	Retention times (mm chart travel)
Arochlor 1248	16, 18, 21, 25, 28, 32.5, 36, 44, 51, 58, 68, 78, 105
Arochlor 1254	28, 38, 44, 51, 61, 69, 81, 93, 111, 126, 148, 172
Arochlor 1262	37.5, 43, 51, 60, 70, 75, 81, 92.5, 105.5, 127, 149, 167, 201, 235, 307
Sample 4, extract	23, 27.5, 31, 37, 43, 50, 60, 69, 81, 93, 106, 128
Sample 7, extract	21, 23, 28, 37, 43, 49, 60, 70, 74, 80, 91, 105, 126, 148, 166, 199, 233, 303
Sample 11, extract	18, 23, 28, 37, 43, 50, 60, 69.5, 81, 93, 128, 171
Sample 13, extract	18, 24, 28, 31, 37, 43, 50, 60, 70, 82, 93, 106, 112, 128, 152, 170, 207, 240

[a] Sample numbers are those given in Table I. Retention times are measured from the injection point with a chart speed of 2.54 mm/min. The injection point corresponds to the coordinate marked "Responses", in the figures. All retention times were measured on the original chromatogram. Fig. 4 and Fig. 6 have been reduced; therefore, the peaks in these two figures do not occur at the respective retention times given in this table.

Acknowledgments

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