Sources of Compounds Interfering with the Analysis of Extracts for Dieldrin and DDT by GLC

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Polychlorinated biphenyls (PCB's) in animal tissues have been reported by several authors (1, 2, 3, 4). These compounds seem to be as widely distributed in the environment as the most common chlorinated hydrocarbon insecticides dieldrin and DDT. Some increase the toxicity of dieldrin and DDT to Drosophila melanogaster and houseflies (5), while another was found to have a steroid degrading potential in pigeons four to six times that of p,p'-DDE (4).

Unidentified peaks in chromatograms of extracts of soil and water make it difficult to interpret analytical results. One of these peaks interfering with the quantitation of aldrin has been identified as being caused by sulfur (9). The findings that PCB's may be responsible for unidentified peaks in chromatograms of extracts of fish and birds offers an explanation for unidentified peaks found in chromatograms of extracts of soil and water.

After studies on the relationship between dieldrin and p,p' -DDT and bog soil characteristics (6,7) the question arose how these two insecticides could reach fresh water bodies when they are practically immobile in the soil. Again, there was a possibility that the occurrence of PCB's in the environment could partly explain this problem.

In rural areas chances are remote that fallout from the chemical industry contributes significantly to the contamination of soil and water with chemicals. Therefore, other possible sources of compounds which may interfere with the gas chromatographic analysis of extracts for dieldrin and DDT were considered.

MATERIALS AND METHODS

Rubber from various automobile tires, "tar" from a road surface, fabric made of synthetic fiber, fabric made of synthetic fiber (90%) and cotton (10%), pieces of rubber base board, several lubricants, kerosene and gasoline were shaken with 200 ml of distilled water over-night on a wrist-action shaker. Prior to the analyses the water was filtered through acetone-washed filter paper, or was separated from liquids in separatory funnels. It

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was extracted with two 25 ml portions of redistilled n-hexane, and after drying with anhydrous Na_2SO_4, the hexane was evaporated until 1 ml of concentrated extract was obtained. Five 1 volumes of this extract were analyzed by GLC. The hexane of the remaining sample was then evaporated, the sample subjected to nitration (8), extracted with hexane and brought to 1 ml. Again, 5 1 were analyzed by GLC. Distilled water controls, with and without insecticide standards, were treated and analyzed like the samples. Volumes of 50 ml of hexane were concentrated to 1 ml, and 5 1 were analyzed by GLC. Attempts to separate PCB's from dieldrin and DDT by column chromatography did not show clear-cut results as reported (1, 8).

The gas chromatograph was a Barber Colman Pesticide Analyzer (Model 5360) with EC detector and 6' x 4 mm I.D. Pyrex column packed with 10% DC-200 on Anakrom ABS 90/100 mesh. Operating parameters were: Column 190°C, detector 200°C, injector 210°C, N_2 flow rate 130 ml per minute, range 1 x 10^{-9} amp. The detector voltage was set to produce a 25% FSD with 0.5 ng of aldrin at 5 mv.

Thin-layer plates (Eastman Chromagram Sheet 6060) were prewashed with acetone: water (1 : 1) and developed in a n-heptane with 2% acetone. Spots, which were visible only when the insecticide standards were used, were visualized with iodine dissolved in ethanol.

RESULTS

Five μl of hexane evaporated from 50 to 1 ml, and hexane extracts of distilled water did not produce peaks with retention times of dieldrin and p,p'-DDT at the setting described above and used throughout the whole study (Small peaks showed up at 1 mv). However, one exception should be mentioned. Distilled water from one of the storage tanks was syphoned through 1.5 m of rubber tubing. Water which remained overnight in the rubber tubing contained 0.2 ppb "p,p'-DDT" and no dieldrin, whereas water taken directly from the storage tank contained less than 0.1 ppb "p,p'-DDT".

Nitration was used because separation of the two insecticides from the interfering compounds with Florisil (8), hexane and 20% diethyl ether in hexane was inconsistent. The recovery of 1 g p,p'-DDT was 98.6%, that of dieldrin 100%, at a flow rate of 3 ml/min. At this rate peaks appeared in the chromatograms of ether-hexane eluates (Samples 9, 10 and 11) which could not be removed by nitration, whereas 1 g quantities of dieldrin and p,p'-DDT did not produce peaks after nitration. Nitrated extracts of samples 1 - 5 and 12 and 13 could not be analyzed by GLC because of compounds which overloaded the columns.

TABLE I

Peaks with retention times 1 and 1.68 (rel. to dieldrin) quantified as ppb. dieldrin and DDT in the water after shaking with various substances.

No.	Substance	Quantity in g.	"Dieldrin" ppb.	"DDT" ppb.
1	Rubber[1]	8.1	0.06	0.34
2	Rubber[1]	8.9	0.08	0.37
3	Rubber[1]	9.0	0.24	0.56
4	Rubber dust of 1	1.3	0.07	0.29
5	Rubber dust of 2	1.1	0.07	0.26
6	Tar[2]	31.4	0.13	0.48
7	Base board, rubber	21.0	0.00	19.20
8	Compressor lub.	10.0	0.08	0.74
9	Fabric, 90% synthetic, 10% cotton	11.0	0.16[3] 0.13[4]	0.61[3] 0.64[4]
10	Fabric, 100% synthetic	3.0	0.52[3] 0.54[4]	0.29[3] 0.32[4]
11	Used engine oil	20.0	0.05[3] 0.06[4]	0.22[3] 0.19[4]
12	Gasoline	20.0	<0.03	0.14
13	"White"Kerosene	20.0	<0.03	0.11

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[1] Used automobile tires
[2] Piece of tar cover of a road
[3] Prior to nitration
[4] After nitration

DISCUSSION

The results given in Table 1 show that there are a variety of sources of compounds which may interfere with the quantitation of dieldrin and p,p'-DDT by GLC. The results also suggest the sources of these interfering compounds in the environment: Rubber tire or engine oil - road surface - runoff water. It would be speculative to draw conclusions at this state of the work. The problem is still under study.

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