

Determination and Distribution of Organochlorine Residues and Heavy Metals in Tar Balls

by

Mete SUNAY, Turgut I. BALKAS, Ilkay SALIHOGLU and Gerald RAMELOW
Marine Science Department, Middle East Technical University, P.K. 28,
Erdemli-Içel (Turkey)

Abstract

The accumulation of organochlorine residues (e.g. aldrin, dieldrin, heptachlor, endrin, DDT's and PCB's) and heavy metals (e.g. Pb, Cu, Mn, Zn, and Cd), in various tar ball samples was investigated, after development of analytical techniques. The enrichment factors with respect to those in seawater were calculated.

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Introduction

Tar balls represent products of different degrees of the physical, chemical and biological weathering of petroleum and are mostly formed in situ from spilled crude oil. Since degradation is limited to their surface boundary, tar balls usually contain a weathered crust. Some volatile and degradable compounds can be effectively trapped inside, either by extraction from seawater or by adsorption from the atmosphere.

The results of several investigators (SEBA & CORCORAN, 1969, MORRIS 1974, DUCE 1972, PROTOWICZ, 1972 & SZEKIELDA, 1972) have indicated that the actual enrichment factor of metals and pesticides in the surface films and slicks may be in the order of 10^4 . Because the pesticides and PCB's are soluble in oil, they can be concentrated in tar balls in great amounts. Proteins, organic acids and some surface active organics may provide complexing sites for metals (SEBOR 1975, KASHIKI 1971). In addition, the possibilities of complex formations of pesticides with some organic polyelectrolytes (e.g. humic acid), are examined (WERSHAW *et al.* 1969).

Experimental

Materials : The adsorbents Celite-545, magnesium oxide, sand and sodium sulphate were purified and activated before use. The solvents, acetonitrile and petroleum ether, were redistilled.

Instrumentation : For pesticide and PCB analyses a Varian Aerograph 2700 model, Gas Chromatograph with an electron capture detector was used. The columns used were coiled glass and packed with 1.5% OV-17 and 1.95% OV-210, coated on 80-100 mesh Varaport 30. Samples were injected with Hamiltonian microliter syringes. The carrier gas was nitrogen. Highest purity pesticides and PCB's, supplied by Applied Spell out, were used as standards.

Chimie Étud. Pollutions, pp. 165-170, Antalya, C.I.E.S.M. (1978).

Heavy metals concentrations were determined by using a Perkin-Elmer 305 B model atomic absorption spectrophotometer with a Perkin-Elmer HGA-74 graphite furnace atomization. Deuterium arc background correction was carried out. The sheat gas was nitrogen. The highest purity, cyclohexanobutyric acid salts of metals, supplied by Merck, were used as the standard materials.

Sample preparation : Approximately 0.5 g of tar was dissolved in 20 ml of ethyl ether and the solution cleaned of petroleum hydrocarbons by eluting through a glass column filled with uniformly mixed, 2 g of Celite-545, 2 g of magnesium oxide and 100 g of 0.50-0.65 mm mesh size sand. The organochlorine residues retained on the column were then eluted with 200 ml of 80% Acetonitrile water (v/v). To the eluant, 100 ml of petroleum ether and 600 ml of 2% Na_2SO_4 (w/v), were added, and the solution was shaken in a separatory funnel, for about 3 minutes. The petroleum ether layer was separated, dried through an anhydrous Na_2SO_4 column. The volume was reduced to a certain amount and injected into the GC column.

For heavy metal analysis, approximately 0.02 g of tar was dissolved in 10 ml of xylene, and dilutions were carried out for viscous solutions, then injected into the graphite furnace.

Results and discussion

The tar samples were collected from the Erdemli campus and Akkuyu beach. This shoreline near Mersin may be considered as a polluted area because of the operations of the petroleum refineries and many industrial facilities around Mersin harbour, as well as the organochlorine residues, which are widely used for agricultural purposes. The sampling was carried out during the summer periods of 1977 and 1978, when there was enormous pollution along the shore, probably due to the dense tanker traffic and favourable climatic conditions (e.g. temperature, waves, winds etc.) The average distribution of tar balls on the beaches for two years sampling were calculated as approximately 30-35 g/m² and 25 g/m² for Erdemli and Akkuyu bay, respectively.

For the isolation of organochlorine hydrocarbons from petroleum hydrocarbons and lipids, two methods, one developed by TOLBERT (1966) using celite and the other developed by PORTER (1973) using florasil as the adsorbent, were compared in terms of their recovery, ease and rapidity of elution, cost and activation properties. The recovery of celite was about 90% for PCB's, 77-80% for aldrin, dieldrin and endrin, 72-89% for DDT's, which were comparable and in agreement with the recovery of Florisil. In addition, celite showed great advantages in terms of elution rate, cost and activation properties compared to florisil, especially for the analysis of very viscous, slurry tar ball solutions.

The difficulty in the identification of pesticides in the presence of PCB's was eliminated by the application of some confirmatory tests (MILLS 1972, TROTTER 1975). Taking into account the problems in the identification of PCB isomers separately, the total PCB content was calculated, as advised for most of the environmental studies.

The results are tabulated in Tables I and II. The PCB's are in the range of 15-600 ppb, and pesticides, 1-50 ppb. They are considerably higher than in seawater. Enrichment factors of 10^2 - 10^3 for DDT's, aldrin, dieldrin and endrin and about 10^5 for PCB's, are found. Finally, very different values obtained for the same samples in replicate analyses, indicate the uneven distribution of organochlorine residues in the tar balls.

Because the xylene solutions of tar balls produced very unstable, noisy flame, the nonflame graphite atomizer was chosen for the analysis of metals in tar balls.

Since the exact composition of tar is not known, the standard addition method was used throughout the quantitative analyses, by assuming that the samples were of the same origin.

As can be seen from the Table III, the metal concentrations are also much higher than those in seawater and crude oil (BERNHARD 1975, BRODIE 1971), in the order of 2×10^1 to 10^4 for Cd, Mn, Zn, and Cu, but about 10^5 for Pb, as compared to concentrations in unpolluted seawater.

TABLE I. Concentrations of Chlorinated Pesticides and PCB's
in Tar Balls (ng/g).
(sampled during summer periods of 1977)

<u>Sample No.</u>	<u>Aldrin</u>	<u>Dieldrin</u>	<u>total DDT</u>	<u>total PCB</u>
			0.9	64
1	1.5	-	37.3	177
2	15.2	N.D.	N.D.	208
3	18.8	N.D.	N.D.	15
	31.5	N.D.	2.0	360
4	11.9	N.D.	22.6	99
5	18.0	N.D.	32.6	60
	24.3	N.D.	6.2	359
6	11.1	N.D.	100.5	96
7	25.2	4.6	56.1	131
	10.7	3.9	5.3	380
8	10.8	1.8	5.8	348
	9.3	N.D.	31.6	329
9	7.3	N.D.	50.5	478
	8.6	N.D.	N.D.	16
10	24.0	N.D.	11.4	271
11	42.6	N.D.	N.D.	66
12	18.2	N.D.	50.6	295
13	31.5	N.D.	33.2	322
14	8.1	5.5	1.9	58
	4.6	N.D.	N.D.	24
15	47.0	5.8		

N.D. Not detectable.

TABLE II, Concentrations of Chlorinated Pesticides in Tar Balls
(ng/g).
(sampled during summer periods of 1978)

Sample No.	Aldrin	Heptachlor	Dieldrin	total DDT	total PCB	Endrin
1	3.5 6.7	18.2 14.1	10.3 3.9	N.D. 2.0	147 54	N.D. 1.8
2	5.5 5.3	10.9 10.1	8.0 1.7	N.D. 18.0	117 35	2.5 N.D.
3	2.5 6.3	10.9 11.2	2.6 1.5	N.D. 2.8	131 30	N.D. 2.5
4	5.1 8.5	20.1 10.0	6.1 2.7	9.5 N.D.	123 158	3.9 N.D.
5	5.5 5.1	5.2 6.5	3.0 2.4	N.D. N.D.	94 113	N.D. N.D.
6	3.9 3.4 3.2	N.D. N.D. N.D.	N.D. N.D. N.D.	N.D. N.D. N.D.	104 108 107	N.D. N.D. N.D.
7	4.6 20.1	5.9 3.7	4.2 2.0	7.4 2.2	134 73	N.D. N.D.
8	18.7 7.0	40.2 11.7	3.8 2.8	29.4 18.5	85 73	N.D. N.D.
9	17.0 4.3	44.6 9.6	3.1 1.5	5.1 18.0	66 36	N.D. 2.9
10	7.9 9.3	8.8 18.7	3.8 4.4	N.D. 12.8	79 51	N.D. 1.4
11	7.7	11.2	2.6	22.6	43	3.6
12	8.6 7.5	15.0 10.0	N.D. N.D.	4.0 7.3	74 77	N.D. N.D.

N.D. Not detectable

TABLE III. Concentrations of Heavy Metals in Tar Balls
($\mu\text{g/g}$)
(sampled during the summer periods of 1977)

<u>Sample No.</u>	<u>Zn</u>	<u>Cu</u>	<u>Mn</u>	<u>Pb</u>	<u>Cd</u>
1	49.9	6.6	1.7	7.0	0.10
2	40.1	12.4	2.9	17.0	0.20
3	68.0	41.9	3.9	13.4	0.12
4	56.6	7.1	5.6	11.7	0.12
5	27.8	19.5	2.0	7.1	0.09
6	30.7	2.4	2.1	7.8	0.11
7	68.8	42.4	3.4	8.0	0.07
8	176.4	20.9	4.3	19.4	0.22
9	25.9	25.0	2.1	6.1	0.15
10	37.3	7.8	3.6	17.8	0.43
11	66.1	20.4	2.6	8.5	0.67
12	38.6	9.0	3.6	7.1	0.12
13	44.0	7.7	3.4	19.1	0.13
14	34.8	12.2	5.1	11.0	0.12
15	71.1	16.1	4.0	12.4	0.09
Ave.	55.8	16.8	3.4	11.6	0.14

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