Bull. Environm. Contam. Toxicol. 23,196-202 (1979)

Comparison of Dry and Wet Surfaces for Collecting Organochlorine Dry Deposition

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Aerial transport appears responsible for the global dispersion of PCB and chlorinated pesticides (NAS 1978), and on a local scale atmospheric input by rain or particle deposition has been shown to contribute significantly to the pollutant budgets of Lake Michigan (MURPHY & RZESUTKO 1977) and the Southern California Bight (YOUNG et al. 1976, McCLURE 1976).

Collection techniques for organochlorines (OC) deposited by particle settling and turbulent impaction (dry deposition or "dry fallout") vary widely. Silicone oil coated nylon screens (SODERGREN 1972), mineral oil sprayed glass plates (McCLURE & LaGRANGE 1977, YOUNG et al. 1976), and even glass plates cooled with dry ice to minimize revolatilization (HEESEN & JOHNSON 1976) have been used to retain aerially deposited OC. Our intent was to develop a method that would mimic as closely as possible the collection characteristics of a water surface, since we were interested in measuring OC fallout in the coastal zone and the open ocean. Screens can trap particles by filtration as well as impaction, and we felt that a hydrophobic surface like oil might scavenge OC vapors as well as particles. We therefore compared the fallout collection characteristics of several hydrophilic surfaces (water, ethylene glycol-water, glycerin-water) with those of a dry pan.

MATERIALS AND METHODS

Measurements of OC fallout were made at Kingston, Rhode Island, a small university community located about 60 km from the nearest major city (Providence, RI) and in Columbia, South Carolina, a metropolitan area with a population of 380,000. Fallout stations were located on rooftops on the University of Rhode Island (URI) and University of South Carolina (USC) campuses, about 15-30 m above ground.

Several different surfaces were evaluated for fallout collection. At URI, flat bottomed glass dishes 0.074 sq. m area and 4.5 cm deep were used dry or filled to a depth of 1-2 cm with 20% ethylene glycol-water. Collections at USC were made with 64 x 46 x 2 cm deep aluminum pans (area = 0.29 sq. m) used dry, filled to about 1 cm with water, or sprayed with a light coat of 50% glycerin-water (using an all-glass TLC atomizer). Dry and wet surface collection pans were

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0007-4861/79/0023-0196 $01.40

exposed side by side for equal intervals ranging from 22-116 h.

The contents of a collector were transferred to a 3.8-L brown glass jug with the aid of distilled water and dichloromethane or acetone rinsings. In the case of dry or glycerin-water sprayed pans, the surfaces were repeatedly scraped with a piece of teflon between rinsings to ensure quantitative transfer of deposited material to the jug. Pesticide quality dichloromethane (200 mL) was added, and the jug was rolled for several hours on a jar mill to extract the OC. The dichloromethane was separated from the aqueous layer, filtered through glass wool, and concentrated to 5-10 mL on a flash evaporator. The extract was transferred to a Kuderna-Danish concentrator apparatus and the dichloromethane was removed by refluxing with hexane and evaporating to 1-2 mL. The extract was cleaned up by alumina column chromatography (4 g activity grade III, 20 mL petroleum ether eluate) and the OC were separated into several fractions on a silicic acid column prior to GC analysis (BIDLEMAN et al. 1978).

Analyses were carried out by electron capture gas chromatography using two of the following columns: 1.5% SP-2250/1.95% SP-2401; 4% SE-30/6% SP-2401; 3% OV-225. All columns were glass, 0.4 cm i.d. x 180 cm long, and were operated isothermally at 180-200°C under 50-70 mL/min nitrogen flow. The peaks identified as PCB, DDT, and chlordane were unaffected by 7% fuming sulfuric acid treatment. DDT and cis-chlordane were confirmed for a number of samples by dehydrochlorination with alcoholic KOH to DDE and 3-chlorochlordene (trans-chlordane does not readily convert under these conditions, (CHAU & COCHRANE 1969).

Aqueous solutions used to fill or spray fallout collectors were pre-extracted with dichloromethane to remove organic contaminants. Traces of the dichloromethane were removed from the solutions before use by heating on a hot plate or steam bath. Woelm neutral alumina and Mallinckrodt 100-mesh silicic acid were used for column chromatographic cleaup and fractionation. Analytical standards of PCB and pesticides were obtained from the U.S. Environmental Protection Agency Pesticide Repository, Research Triangle Park, North Carolina.

RESULTS AND DISCUSSION

The relative quantities of OC fallout retained by pans sprayed or filled with liquid to the amounts found in a dry pan are given in Table 1 for the individual experiments at URI and USC. In almost every case the efficiency of the wet surfaces was higher over a 1-5 day sampling period. On the average, the wet pans retained 1.5 - 3 times more OC fallout than the dry pans, while the differences between the water, ethylene glycol-water, or glycerin-water surfaces were small (Fig. 1). Our results thus differ from those of McCLURE & LaGRANGE (1977), who reported that uncoated glass plates were "only slightly less efficient" than oiled plates.

TABLE 1

Comparative Fallout Collection Efficiencies of Dry and Wet Surfaces

Exposure time, hours	Surface[1]	Aroclor 1016	Aroclor 1254	Chlordane[2]	p,p'-DDT
Kingston, RI (1974-75)		Relative Fallout Collected (Dry Pan = 1.0)			
45	EG-W	--	1.3	--	1.9
55	EG-W	3.3	1.7	--	2.4
25	EG-W	--	1.6	--	2.8
22	EG-W	--	4.0	--	2.3
48	EG-W	3.1	2.5	--	2.0
Columbia, SC (1976-77)					
72	W	0.6	0.4	1.0	0.5
	G-W	0.7	0.6	1.0	0.4
116	W	3.0	2.6	2.3	5.6
	G-W	3.3	3.8	2.5	6.6
45	W	--	1.6	2.9	2.1
	G-W	--	1.3	0.8	1.5
27	W	--	3.5	--	--
	G-W	--	1.3	--	--
48	W	1.3	2.2	1.0	6.3
	G-W	1.4	3.4	0.5	5.4
48	W	2.5	1.3	1.0	1.1
	G-W	1.6	1.2	2.9	1.9
24	W	--	1.0	1.8	1.7
	G-W	--	1.1	1.8	--

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[1] Surfaces: W and EG-W = pans filled with distilled water and 20% ethylene glycol-water; G-W = pans sprayed with 50% glycerin-water.

[2] cis- + trans-chlordane

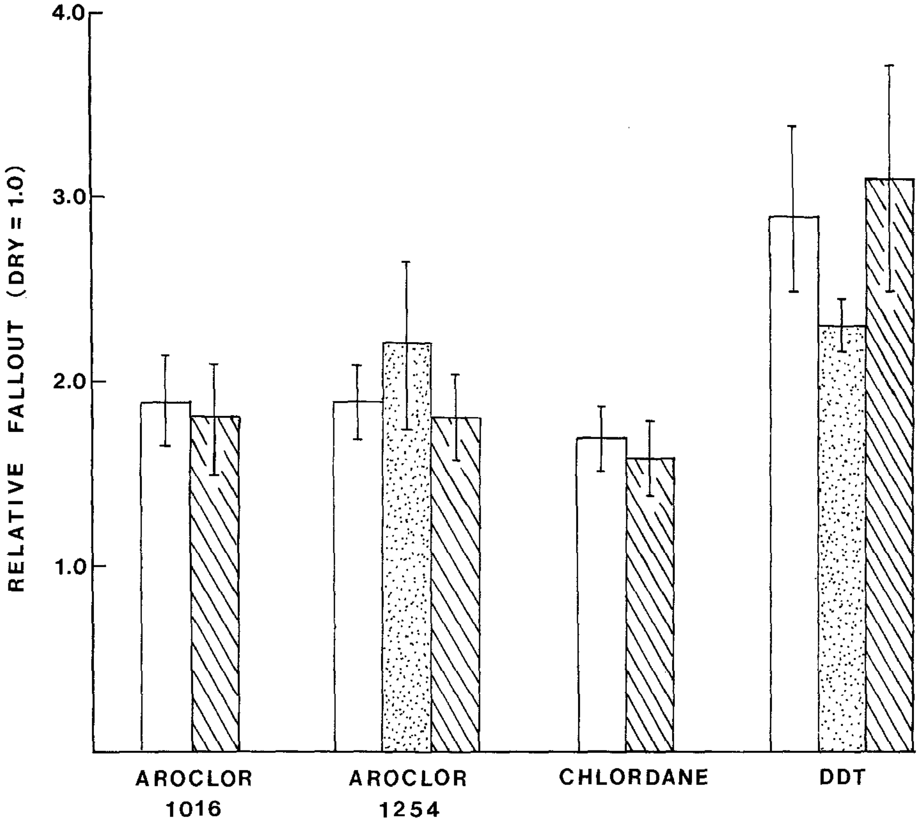

Fig. 1: Average values for the relative quantities of CHC fallout retained by wet *vs*. dry surfaces. Vertical lines represent standard deviations of the means.

water-filled pan	☐
ethylene glycol-water filled pan	░
glycerin-water sprayed pan	▨

TABLE 2

Replicate Collections of CHC Fallout

Location	Dates	Surface[2]	Area, m^2	Flux, 10^{-9} g/m^2-day			
				Aroclor 1016	Aroclor 1254	Chlordane[1]	p,p'-DDT
Kingston, RI	2/12-14/74	Dry	0.074	--	55	--	16
			0.074	--	40	--	18
"	2/14-16/74	Dry	0.074	94	224	--	65
			0.074	106	189	--	73
"	2/18-19/74	Dry	0.074	--	169	--	42
			0.074	--	153	--	26
"	5/8-10/75	Dry	0.074	43	79	--	14
			0.074	--	--	--	22
			0.140	44	81	--	27
Columbia, SC	4/8-11/77	G-W	0.29	37	41	4.1	4
			0.29	24	37	3.4	15
			0.29	37	40	3.0	13
"	5/9-11/77	G-W	0.29	<33	43	12	18
			0.29	<16	38	15	15
			0.29	<43	62	23	16

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1. cis- + trans-chlordane
2. G-W = 50% glycerin-water spray

TABLE 3

Fallout Fluxes of CHC[1]

10^{-9} g/m^2-day

Location	Dates	Aroclor 1016	Aroclor 1254	Chlordane[2]	p,p'-DDT
Kingston, RI	2/12-14/74	--	61	--	32
"	2/14-16/74	325	360	--	165
"	2/18-19/74	--	259	--	96
"	2/27-28/74	--	245	--	107
"	5/8-10/75	135	196	--	43
	mean	230	224	--	89
Columbia, SC	12/17-20/76		66	7	5
"	2/4-9/77	119	273	25	83
"	2/9-11/77	--	229	14	64
"	2/22-23/77	--	48	14	49
"	2/24-26/77	59	144	14	23
"	3/7-9/77	91	203	11	18
"	3/9-10/77	--	61	20	11
"	4/8-11/77	34	41	3	11
"	5/9-11/77	<31	48	17	16
	mean	68	124	14	31

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1. wet surface collector
2. *cis*- + *trans*-chlordane

The reproducibility of duplicate or triplicate fallout collections made with dry and glycerin-water sprayed pans is shown in Table 2. Average reproducibilities, defined as (range x 100/mean) for duplicates and (s x 100/mean, where s = standard deviation) for triplicates, were: Aroclor 1016 = 12; Aroclor 1254 = 19; chlordane = 27; and p,p'-DDT = 28. Our analytical precision (coefficient of variation) for PCB, chlordane, and p,p'-DDT was 15%, 8% and 7%, respectively (BIDLEMAN et al. 1978).

Fallout fluxes in 10^{-9} g/sq.m-day for Kingston, RI and Columbia, SC are given in Table 3. These are similar to PCB and DDT fluxes in Sweden (SODERGREN 1972) and PCB fluxes in La Jolla, Calif. (McCLURE 1976). Average rates of DDT fallout equal to or a few times higher than these have been reported along the Southern California Bight. However fluxes 10-100 times higher were observed in the Los Angeles area, apparently the result of emissions from the Montrose Chemical Co. DDT manufacturing plant (YOUNG et al. 1976). Fallout rates of PCB and DDT in Iceland were about 1-2 orders of magnitude lower than our values (BENGTSON & SODERGREN 1974).

Our results indicated that glycerin-water sprayed pans have fallout collection characteristics similar to those of a water surface over a 1-5 day period. The sprayed pans are much easier to handle than shallow pans filled with liquid.

ACKNOWLEDGEMENTS

This work was supported by the National Science Foundation Office of the International Decade of Ocean Exploration, under Grant No. OCE-76-15629 A02. Contribution no. 263 of the Belle W. Baruch Institute.

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