Volatization of DDT and Related Materials from Dry and Irrigated Soils

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DDT enjoyed 18 years of unrestricted use in Arizona, 4 years of restricted use followed by a total agricultural ban resulting from a State moratorium imposed in 1969. During its years of restricted use, DDT was found in high levels on forage crops which were as much as one mile or more from any known site of application. Consequently many hay crops could not be sold to dairymen when residue analyses indicated these inordinate levels.

Earlier work by Ware (1968) and Ware et al. (1970) demonstrated that DDT was not translocated from soil to the above-ground portions of alfalfa. Similarly, research indicated that DDTR residues in alfalfa were not the result of contamination by blowing DDT-laden dust. Only one route remained for such universal contamination—relocation from soils to above-ground parts by volatility.

Several studies exist to support this theory. Nash and Beall (1970) demonstrated that soybean plant DDT residues were the result of vapor movement from contaminated soil surfaces. Seven-fold DDT residue was found in plants absorbing vaporized DDT from the soil surface than those absorbing it from the roots alone. Two-fold DDT residue was found in lower leaves as compared to upper leaves, both observations indicating the air movement of soil-surface DDT to plant leaves, particularly those leaves in close proximity to the source of vaporized DDT.

Cliath and Spencer (1972) demonstrated that p,p'-DDE has eight times the vapor pressure of p,p'-DDT at 30°C. Field measurements of atmospheric concentrations of DDT compounds over a field containing residual DDT indicated that 66% of the total was p,p'-DDE. They predicted that most of the p,p'-DDT present in well-aerated soils would be volatized as p,p'-DDE, and could be a major pathway for loss of DDT from soil.

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Hartley (1969) suggested that vaporization rates of various chemicals could be predicted from their relative vapor pressures and molecular weights. In order to do this it is only necessary to know the vapor pressure of the compound and the volatization rate for a model substance which is not too volatile. Using Hartley's method and data on volatization rates for anisole, the following rates of DDT volatization (lbs/acre) would be predicted at various temperatures and wind conditions:

Temperature °C	Wind Condition		
	Still	Slow Wind	Stronger Wind
20	0.37	1.25	2.0
30	1.8	6.0	9.2
40	8.4	29	44
50	29	98	152

These figures are for volatization from glass plates or other types of non-adsorbing surfaces. Volatization rates from soils, or other surfaces, would be considerably less, depending upon reduction in vapor pressure of the chemical due to adsorption on the soil.

Spencer (1970) has also calculated the predicted volatization losses of dieldrin, again using anisole as the model compound. The volatization rate of dieldrin at 25°C was predicted to be 10.7 lb/acre/year. Barlow and Hadaway (1958) measured the loss of dieldrin from glass plates at 25°C and found it to be 10 lb/acre/year during the first 24-week period. The close agreement between predicted and measured values for dieldrin vaporization indicates that Hartley's method gives good estimates of volatization rates of various pesticides from non-adsorbing surfaces.

Freed et al. (1972) reviewed the DDT-volatility question and concluded that when soil is introduced as a component of a volatizing system, the rate of vaporization is reduced substantially to less than one lb/acre/year at 30°C, depending on the nature of the soil, the temperature, and the moisture content. Hartley (1969) indicated that at 30°C DDT would be lost at a rate varying between 1.8 and 6.0 lb/acre/year from glass plate.

The following experiments were designed to determine how much DDT and other related compounds would be vaporized from miniature dry and irrigated soil units at different seasons of the year when applied topically or uniformly mixed into the soil.

MATERIALS AND METHODS

Three separate vaporization studies were conducted: I, 56 days' duration, August-October 1969; II, 60 days' duration, February-May 1970; and III, 154 days' duration, June-November 1970. In all experiments the test compound was incorporated in the substrate at 10 ppm, or applied to the substrate surface at 2.0 lb/acre. The materials used were analytical grade p,p'-DDT, o,p'-DDT, p,p'-DDD, and p,p'-DDE.

The experimental soil units consisted of a plastic petri dish, 100 mm x 15 mm, with four 1/2" holes spaced uniformly in the bottom to accommodate four cotton dental rolls which served as wicks. The dish was mounted atop a wide-mouth quart Mason jar, filled with water and secured with melted paraffin. This produced a vapor-tight system such that water loss occurred only through the wicks, then from the sand. The test substrate was local riverbed quartz sand, sieved to a range of 20 to 42 mesh, washed and autoclaved.

Two physical arrangements were involved. The first consisted of treating the prepared sand with an acetone solution to contain 10 ppm of one of the four compounds. The soil was mixed thoroughly as the acetone was evaporated. From this a series of the petri-dish units were each filled with 75 grams of the fortified sand.

The second system involved treating 75 gm of dry sand topically in the petri dish with 1400 μg of a material, equivalent to an application of 2.0 lb/acre. The insecticide was applied randomly to the surface in 70 one-microliter droplets of acetone.

One half of the sand treatments were left dry; and the other half wicked, with water evaporating continually from their surfaces. Distilled water was added to the jars as needed.

All samples were placed on the roof of the Agriculture Building, in 3/8" plywood, painted boxes 4'x2'x10" deep. The box lids were removed at 8:00 a.m. and returned at 5:00 p.m. daily, except weekends when they remained covered, to protect the samples from evening summer storms.

Air temperatures ranged during experiment I from 26^{o} to 41^{o}C; II, -2^{o} to 40^{o}C; and III, 2^{o} to 43^{o}C.

Each experiment was sampled at slightly different intervals, but usually biweekly. Soils were dried overnight in the laboratory and soxhleted using 41:59, hexane:acetone. Analyses were by electron capture gas chromatography without cleanup of the extracts.

RESULTS

The analytical results are displayed in Tables 1 through 5. Because Experiment I was the initial effort, several mistakes were made, which can be seen in Table 1, indicating that we were looking for losses by volatization and not metabolites. Experiment II is the most complete and thus the most reliable. Experiment III was aimed at examining volatization losses of DDT and DDE over the equivalent of one growing season.

Results of this nature are difficult to narrate, and for the sake of brevity they are presented as a series of simple statements.

1. Generally materials applied topically to soil surfaces escape more readily under warm-dry than cool-moist conditions, with the exception of DDE.

2. p,p'-DDT vaporizes and is converted to DDE on dry soil more readily than on wet soil.

3. p,p'-DDT is converted to DDD in or on wet and dry soils.

4. o,p'-DDT vaporizes from dry soil more readily than from wet soil.

5. o,p'-DDT is converted to DDE at a greater rate on, but not in, dry rather than wet soils.

6. o,p'-DDT vaporizes at a greater rate than p,p'-DDT under either condition.

7. o,p'-DDT leaves no detectable residues of DDD.

8. p,p'-DDE vaporizes at a greater rate from wet than from dry soils, with the exception seen in Experiment III.

9. Volatization of topical applications is in the order of o,p'-DDT > DDD > p,p'-DDT > DDE from dry soil, and o,p'-DDT > DDE > DDD > p,p'-DDT from wet soil.

From these data, it can be said that under Arizona conditions: (a) 88% of 2.0 lb DDT/acre applied to fallow soil in June would volatize in 5 months, while 71% of a similar application would volatize from an irrigated soil; (b) 67% of 3.0 lb DDT/acre incorporated in the upper 0.5 inch of a fallow field, and 50% in an irrigated field, would volatize within 5 months. In all instances much of the vaporized material would be DDE. Very little o,p'-DDT and almost no o,p'-DDE would be found in field soil samples due to their rapid loss by vaporization. DDE residues in or on soils are readily volatized at high temperatures and become a substantial portion of DDT and related substances collected in large volume air samples in agricultural areas having a history of DDT use.

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TABLE 1

Volatization of p,p'-DDT, o,p'-DDT, p,p'-DDD and p,p'-DDE from wet and dry sand treated topically (1400 μg) or containing 10 ppm (750 μg). Residue expressed as micrograms. (I, Aug.-Oct. 1969).

Day	10 PPM		Topical		
	Wet	Dry	Wet	Dry	
			p,p'-DDT		
0	767	767	974	974	
7	415	598	845	380	
14	407	574	836	384	
28	368	482	644	224	217 p,p'-DDE
42	413	434	622	---	177 "
56	377	328	605	---	105 "
			o,p'-DDT		
0	646	646	936	936	
7	459	554	---	---	
14	429	555	657	---	494 o,p'-DDE
28	348	230	---	---	460 "
42	293	297	445	---	432 "
56	247	221	419	---	409 "
			p,p'-DDD		
0	899	899	1252	1252	
7	728	829	1181	1038	
14	633	791	---	---	
28	600	---	1026	791	
42	533	660	1062	566	
56	533	679	1058	566	
			p,p'-DDE		
0	798	798	1073	1073	
7	483	683	609	661	
14	426	769	592	796	
28	372	698	614	---	
42	373	737	440	---	
56	311	764	412	463	

TABLE 2

Volatization of p,p'-DDT, o,p'-DDT, p,p'-DDD and p,p'-DDE from wet and dry sand containing 10 ppm (750 μg). Residue expressed as micrograms. (II, Feb.-May 1970).

Day	Wet			Dry		
	DDE	DDD	DDT	DDE	DDD	DDT
			p,p'-DDT			
0	--	--	770	--	--	700
7	18	59	442	17	57	614
14	14	51	444	20	48	553
28	14	47	411	41	57	460
42	6	14	487	60	46	377
60	8	13	457	82	10	354
			o,p'-DDT			
0	--	--	630	--	--	630
7	10	--	523	13	--	567
14	9	--	506	14	--	583
28	7	--	456	18	--	474
42	--	--	406	5	--	375
60	6	--	320	14	--	246
		--				
			p,p'-DDD			
	DDMU	DDD		DDMU	DDD	
0	--	717		--	717	
7	20	669		15	694	
14	23	689		21	685	
28	15	587		19	616	
42	15	590		21	545	
60	7	564		25	518	
			p,p'-DDE			
	DDE			DDE		
0	917			917		
7	704			667		
14	680			758		
28	590			650		
42	440			497		
60	340			432		

TABLE 3

Volatization of p,p'-DDT, o,p'-DDT, p,p'-DDD and p,p'-DDE from wet and dry sand treated topically (1400 μg). Residue expressed as micrograms (II, Feb.-May 1970).

Day	Wet			Dry		
	DDE	DDD	DDT	DDE	DDD	DDT
			p,p'-DDT			
0	--	--	1400	--	--	1400
7	20	103	1330	34	88	1243
14	--	--	--	49	91	1252
28	21	70	1150	58	84	1200
42	10	25	1050	137	83	827
60	9	22	1160	204	14	667
			o,p'-DDT			
0	--	--	1417	--	--	1417
7	11	--	1316	87	--	1139
14	55	--	1138	64	--	991
28	4	--	1051	33	--	838
42	--	--	894	79	--	300
60	23	--	498	35	--	178
			p,p'-DDD			
	DDMU	DDD		DDMU	DDD	
0	--	1243		--	1333	
7	25	1107		19	998	
14	31	1270		28	1140	
28	30	1130		23	1100	
42	22	1100		30	771	
60	27	1005		24	631	
			p,p'-DDE			
	DDE			DDE		
0	1200			1200		
7	1312			1130		
14	1162			1327		
28	914			1118		
42	808			830		
60	778			885		

TABLE 4

Volatization of p,p'-DDT and p,p'-DDE from wet and dry sand treated topically (1400 μg). Residue expressed as micrograms. (III, June-Nov. 1970).

Day	Wet		Dry	
	DDE	DDT	DDE	DDT
	p,p'-DDT			
0	0	1381	0	1381
14	--	--	274	259
28	0	1227	209	157
42	0	1226	144	134
56	0	1107	177	134
70	12	825	--	--
92	--	810	130	87
112	8	825	144	89
133	6	827	103	90
154	13	381	115	57
	p,p'-DDE			
0	1219		1219	
14	616		888	
28	320		612	
42	283		494	
56	303		335	
70	272		253	
92	280		--	
112	239		--	
133	239		175	
154	196		54	

TABLE 5

Volatization of p,p'-DDT and p,p'-DDE from wet and dry sand containing 10 ppm (750 μg). Residue expressed as micrograms. (III, June-Nov. 1970).

Day	Wet		Dry	
	DDE	DDT	DDE	DDT
		p,p'-DDT		
0	3	592	3	592
14	3	525	149	333
28	3	473	121	234
42	3	445	113	209
56	3	390	104	184
70	4	395	--	--
92	3	346	107	166
112	4	353	127	167
133	4	352	101	137
154	8	290	--	--
		p,p'-DDE		
0	617		617	
14	352		564	
28	119		365	
42	148		340	
56	130		350	
70	--		--	
92	95		286	
112	79		285	
133	88		225	
154	85		260	