<(N–H–N) ≃ 101°). Since the O(10) of a neighboring molecule is also close to N(11), 2.828 Å, a weak bifurcated hydrogen bond may be involved, as was found in the structure determination of Mesurol. No other significant short contacts are present; therefore, intermolecular interactions should have minimal effect on the molecular configuration found for the aldicarb molecule.

A crystal-structure investigation of methomyl is also underway as it has an LD_{50} value intermediate between aldicarb and Mesurol. A comparison of the three structures will be given when the molecular structure of methomyl is reported.

ACKNOWLEDGMENT

The authors wish to acknowledge K. Mano's help in the DTA measurement and would like to thank the Quality Assurance Section, U.S.E.P.A., Pesticides and Toxic Substances Laboratory, Research Triangle Park, N.C., for kindly supplying a sample of the title compound.

Supplementary Material Available: A listing of the observed and calculated structure factor amplitudes (3 pages). Ordering information is given on any current masthead page.

LITERATURE CITED

Baughman, R. G., Jacobson, R. A., *J. Agric. Food Chem.* **23**, 811 (1975).

Busing, W. R., Martin, K. O., Levy, H. A., "ORFLS; A Fortran Crystallographic Least Squares Program", U.S. Atomic Energy Commission Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

Carson, A., Donohue, J., *Acta Crystallogr., Sect. B* **24**, 405 (1969).

Gifkins, M., Jacobson, R. A., *J. Agric. Food Chem.* **24**, 232 (1976).

Hanson, H. P., Herman, F., Lea, J. D., Skillman, S., *Acta Crystallogr.* **17**, 1040 (1960).

Hubbard, C. A., Quicksall, C. O., Jacobson, R. A., "The Fast Fourier Algorithm and the Programs ALFF, ALFFDP, ALFFPROJ, ALFFT, and FRIEDEL", U.S. Atomic Energy Commission Report IS-2625, Iowa State University and Institute for Atomic Research, Ames, Iowa, 1971.

Jacobson, R. A., *J. Appl. Crystallogr.* **9**, 115 (1976).

Johnson, C. A., "OR TEP-II; A Fortran Thermal-Elliposid Plot Program for Crystal Structure Illustrations", U.S. Atomic Energy Commission Report ORNL-3794 (Second Revision with Supplemental Instructions), Oak Ridge National Laboratory, Oak Ridge, Tenn., 1971.

Kolbezen, M., Metcalf, R., Fukuto, T., *J. Agric. Food Chem.* **2**, 864 (1954).

Rohrbaugh, W. J., Meyers, E. K., Jacobson, R. A., *J. Agric. Food Chem.* **24**(4), 713 (1976).

Sakurai, T., "UNICS: The Universal Crystallographic Computing System (I)", The Crystallographic Society of Japan, Tokyo, 1967.

Sutton, L. E., Ed., "Table of Interatomic Distances and Configuration in Molecules and Ions", Supplement, The Chemical Society, Burlington House, W.1, London, 1965.

Takusagawa, F., Jacobson, R. A., *J. Agric. Food Chem.*, preceding paper in this issue (1977).

Williams, D. E., "LCR-2, A Fortran Lattice Constant Refinement Program", U.S. Atomic Energy Commission Report IS-1052, Iowa State University and Institute for Atomic Research, Ames, Iowa, 1964.

Received for review July 14, 1976. Accepted November 19, 1976. Prepared for the U.S. Energy Research and Development Administration under Contract No. W-7405-eng-82.

Toxaphene and 1,1,1-Trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT) Losses from Cotton in an Agroecosystem Chamber

Ralph G. Nash, M. Leroy Beall, Jr., and William G. Harris*

Toxaphene at the rate of 200 to 267 mg/m^2 (2 to 2.7 kg/ha) and DDT at 100 to 133 mg/m^2 (1 to 1.3 kg/ha) were applied to cotton plants at weekly intervals for 6 weeks in an enclosed chamber (agroecosystem) and the residues monitored for 90 days. Twenty-four percent of the toxaphene and 15% of the DDTR (*p,p'*-DDE, *p,p'*-DDD, *p,p'*-DDT, and *o,p'*-DDT) volatilized and 20 and 24%, respectively, was found in the surface 1-cm soil. Most of the insecticide residues volatilized within 24 h from 18.9, 7.3, and 0.4 mg/m^2 per day (189, 73, and 4 g/ha per day) on days 1, 3, and 56 for toxaphene and 6.5, 1.8, and 0.2 mg/m^2 per day (65, 18, and 2 g/ha per day) for DDTR. Volatilization losses were insignificant, <0.1 mg/m^2 per day (<1 g/ha per day), for both toxaphene and DDTR after 90 days. Volatilization losses for both insecticides seemed to follow log concentration with log time the first week and then log concentration with linear time thereafter. Calculated first-order equation half-lives for volatilization of toxaphene, *p,p'*-DDT, *o,p'*-DDT, and *p,p'*-DDE were 15.1, 18.8, 14.3, and 15.1 days, respectively. On dry cotton leaves, toxaphene residues ranged from about 4000 to 700 ppm (100 to 18 mg/m^2) from application to 56 days, and DDTR residues ranged from about 2000 to 380 ppm (50 to 10 mg/m^2), respectively, for the same period.

Toxaphene (chlorinated camphene, 67–69% chlorine) has been used commercially for over 25 years and is the most widely used insecticide in the United States; about 25.86×10^6 kg (57×10^6 lb) was used in agriculture in 1974 (von Rümker et al., 1974). Nearly 90% of the toxaphene produced is applied to cotton (*Gossypium hirsutum* L.) (von Rümker et al., 1974), and, before the 1973 restrictions were placed upon using DDT, about half as much DDT was also used on cotton (a commonly used toxaphene/DDT mixture was 2/1). Although rarely have the adverse effects of these compounds on the environment been demonstrated, their fate, especially that of toxaphene, in a cotton field should be known. Environmental research has been limited on toxaphene, presumably because of its complexity, since toxaphene is a complex mixture of at least 175 compounds (Holmstead et al., 1974).

Recently, model systems have been used to trace the fate and movement of pesticides in the environment, i.e. the small aquatic/terrestrial ecosystem models of Metcalf et

Agricultural Environmental Quality Institute, Agricultural Research Service, U.S. Department of Agriculture, Beltsville, Maryland 20705.

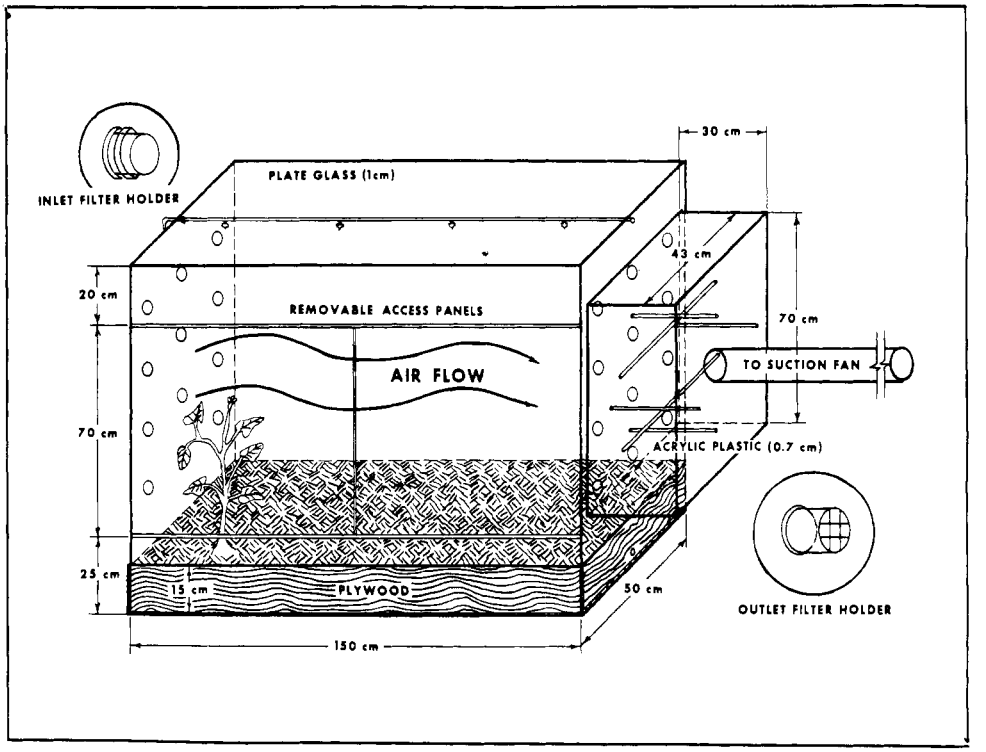

Figure 1. Diagram of agroecosystem chamber.

al. (1971), the aquatic ecosystems of Isensee et al. (1973), and the terrestrial ecosystems under development by the Environmental Protection Agency.

Volatilization of pesticides from a field has received limited research because of the complexity of trapping the residues from a given area or volume. Spencer et al. (1973), who reviewed the literature on pesticide volatilization, calculated that *p,p'*-DDT (1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane) and *o,p'*-DDT (1,1,1-trichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)ethane) losses were 14 and 106 g/ha per day, respectively, for day 2 at a 10-ppm soil incorporation rate. The results of Willis et al. (1971) and Cliath and Spencer (1972) indicated that immediately after applying DDT to soil, or tilling a soil containing DDT residues, large amounts were volatilized. Willis et al. (1971) measured 2.04 $\mu g/m^3$ DDT immediately after application and 0.1 $\mu g/m^3$ after 2 days. Cliath and Spencer (1972) measured 0.56 $\mu g/m^3$ DDTR for 39 h after tillage of a field containing DDT residues.

To account for total pesticide losses after treatment, we designed and constructed agroecosystem chambers, which allow us to monitor pesticide residues in or on plants, soil, water, and air from pesticide-treated plants or soil.

In preliminary experiments to test the efficiency of polyurethane foam filters as collectors of volatilized toxaphene and DDT and to ascertain their volatilization from glass surfaces (one experiment described by Beall et al., 1976), ^{14}C-labeled toxaphene and DDT were applied to fiberglass cloth and the amounts volatilized were monitored. The polyurethane foam filters and analyses were the same as described in the Experimental Section. The polyurethane plugs were collected 0.5, 2.5, 24, 72, 144, and 168 h after insecticide treatment of the fiberglass cloth. The amounts of toxaphene volatilized were 8.40, 4.46, 2.20, 0.43, 0.11, and 0.05%/h, respectively, and the amounts of DDT volatilized were 1.78, 2.32, 0.89, 0.31, 0.13, and 0.11%/h, respectively. Volatilization of both toxaphene and DDT from fiberglass cloth followed a log concentration with linear time equation more closely than a log concentration with log time equation. The volatilization half-lives were 25.1 h for toxaphene and 39.6 h for DDT. After 168 h, 6.13% of the toxaphene and 56.78% of the DDT still remained on the cloth. The residues accounted for were 97.24% for toxaphene and 99.90% for DDT. Consequently, we conclude that the polyurethane filters were efficient collectors of volatilized toxaphene and DDT.

This paper reports agroecosystem chamber results from two important insecticides, toxaphene and DDT, applied to cotton.

EXPERIMENTAL SECTION

Materials. *Agroecosystem Chamber.* Briefly, the system consists of a rectangular glass chamber (150 × 115 × 50 cm inside dimensions) (Figure 1) constructed of glass plates, 1-cm thick. After allowing for a 15-cm soil layer the chamber volume is 0.75 m^3 and the soil surface area is 0.75 m^2. At each chamber end, there are 12 5-cm diameter holes and 1 or 2 2.5-cm diameter holes. The large holes are for air intake and outlet. The small holes are for irrigation, drainage, or installation of monitoring wires at a later date. Inlet air is filtered through 0.3-cm sheet polyurethane foam, held in place with a removable plastic holder and sealed with an O ring. The outlet air is filtered through 5-cm diameter polyurethane foam by 5-cm depth plugs that are held in place with a removable glass thimble sealed with an O ring. (The polyurethane filters were preextracted 12 h with hexane–acetone (1:1) in a large floor Soxhlet.) Two sliding glass doors on one side of the chamber permit servicing.

Air is drawn through the agroecosystem chamber with a suction-fan motor (1/3 hp, 3450 rpm, 110 V, 6.6 A) connected to a large reinforced plastic box with 12 6-cm holes corresponding to the air outlet holes. This arrangement allows for an air pressure (about 12–13 cm of water) to be on the reinforced plastic box and only a very slight negative pressure (0.2–0.5 cm of water) inside the glass chambers. The plastic box is connected to the end of the agroecosystem chamber with caulking compound. The plastic box and suction fan are connected (50 cm apart) with one piece each of 11.3-cm i.d. rigid-plastic and

flexible pipe. A small hole, 23 cm from the box in the rigid pipe, is used to insert a sensor for a hot-wire anemometer to measure air flow. A mean velocity was obtained from 11 equal areas by taking 11 readings (10 equal annular areas and a central circle) at the intersections of the pipe diameter and the set of circles, which bisect the annuli and the central circle. Measurements are taken on each side of the cross-section at $[(2n - 1)/10]^{1/2}$ (n = 1, 2, 3 to 10/2) of the pipe radius from the center (Perry et al., 1963). However, we could only obtain nine measurements because the physical size of the anemometer probe prevented measuring the two outer cross-sectional areas. The two outer velocity measurements were assumed to be similar to the two lowest readings, because of an unusual flow path (Beall et al., 1976). Air velocity in the chambers was 0.35 km/h, which simulates calm winds. The mean air flow was 2.9 m^3/min (3.9 chamber air changes/min). Maximum chamber air temperatures ranged about 3 °C above external temperatures. The large volume of air pulled through the five chambers maintained conditions (air, soil temperature, relative humidity) essentially the same as those of the greenhouse.

Plants and Soil. Cotton (variety 4-42-77 glanded) was germinated and placed in potting soil, and five plants of the same size were transplanted in each chamber about 50 days after germination. The soil was a Galestown sandy loam with a pH value of 6.7, organic matter content of 5.2%, and 0.33 bar moisture tension at 15.6% soil water content. The soil was fertilized before transplanting the cotton by mixing 7.5 g (100 kg/ha) of N from a 10-10-10 NPK. Plants were surface irrigated or sprinkled as needed. Cotton grew rapidly and reached to the top of the chambers (1 m) within 50 days after they were transplanted. Consequently, all growth above 80 cm was removed to prevent moisture condensation on the chamber tops.

Glass Slides. Before the cotton was sprayed with insecticide, 12 glass slides (7.5 × 2.5 cm) were placed randomly on the soil surface in each chamber, and 18 slides on the insides of each chamber, where they were held in place with a small amount of caulking compound. All slides were collected immediately after treatment and after 1 and 6 days and replaced with clean slides. Each slide collection from each soil surface and chamber side was composited and considered a single sample.

Treatments. Beginning Aug 5, 1975, cotton plants in two chambers were each sprayed with commercial emulsifiable toxaphene and DDT (1.3% *p,p'*-DDE (1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethene), 1% *p,p'*-DDD (1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane, 82.0% *p,p'*-DDT, and 15.7% *o,p'*-DDT) per week at the rate of 267 and 133 mg of active ingredient (AI)/m^2 per week (2.7 and 1.3 kg/ha) the first two 6 weeks, then with 200 and 100 mg/m^2 per week of each insecticide for 4 more weeks. One of the five chambers was maintained as a control. Plants were sprayed with a thin-layer chromatography glass spray apparatus connected to compressed N_2 until (ca. 4 min) all 30 mL of insecticide solution was applied. Results from the two initial treatments, which were one-third greater than the last four, were adjusted to reflect equal treatment.

Sampling and Analyses. During the six treatment periods, sampling was conducted as described below. However, beginning week 7, all sampling (except leachate) was conducted once weekly for 3 weeks, then once every 2 weeks. The experiment was terminated on Nov 3, 1975 when the plants began to mature.

Plant and Soil. Several cotton leaves in each chamber were harvested immediately after treatment and after 6 days. Those from each chamber were composited, weighed, and chopped. Leaf surface area was measured on selected samples.

Ten 1-cm depth soil cores (2-cm i.d.) were taken immediately from each system after treatment and after 6 days. The cores were composited, mixed, and stored frozen. After the experiment, 15-cm cores were taken and divided into upper, middle, and lower 5-cm increments. Cores from each 5-cm increment were composited, mixed, and stored frozen.

Soil and plant samples were Soxhlet extracted 12 h with hexane–acetone–methanol (8:1:1) (Nash and Beall, 1971). Their extracts were concentrated to 10 mL by placing a three-ball Snyder column on the extract flask and heating. Two 25-mL portions of hexane were added successively to the extract and concentrated to <10 mL.

Soil extracts were diluted as necessary. The extracted plant and soil residue was air dried (65 °C, 2 h) and reweighed. All values are based on plant and soil dry weight or surface area.

Plant extracts were cleaned up by placing them on a 15-g Florisil (activated, 130 °C, overnight) column and eluting with 200 mL of ethyl ether–petroleum ether (15:85).

Glass Slides. The slides were extracted by rinsing each slide with petroleum ether (bp 30–60 °C). The composite extract was diluted or concentrated as necessary. Extracted glass areas were calculated by using one side of the slide only, which were assumed as representative samples of the total soil surface or sides of chamber. Chamber tops were not included as a contaminated area during the treatments, but were included as a contaminated area for all other sample collections.

Water. Water was applied to each chamber until water could be siphoned through a hole at the 5-cm height. Water was sampled on three dates, Sept 2 and 10 and Oct 6. Residues were prevented from washing down between the soil–glass interface by placing conduit tape around the chamber covering the soil–glass interface. Usually, the first 2 L of water siphoned off was analyzed. Each liter of water sample was extracted three times with 100 mL of petroleum ether and filtered through glass wool to break the emulsion. The 300-mL extract was back extracted three times with 200 mL of water, dried by passing through anhydrous Na_2SO_4, and concentrated with a Kurderna Danish apparatus. Values obtained are based on micrograms per liter of water.

Air. After the plants were treated, the polyurethane foam filters were placed into the 12 air-outlet holes, the chambers were closed, and the suction fans started. After 0.5 and 2.5 h, 1 and 3 days, and 6 days, the filters were collected and replaced with clean filters. The 12 filters from each system were composited and Soxhlet extracted 2 h (2 filters/Soxhlet) with petroleum ether (Beall et al., 1976). The extracts from six Soxhlets (1 sample) were combined and concentrated with a Kurderna-Danish apparatus. The concentrated extract was cleaned up by placing on an 0.8-g Florisil column (activated 130 °C overnight in disposable Pasteur pipet, capped with 0.5 cm Na_2SO_4, and connected to a short stem funnel with Teflon tubing) and eluting with 10 mL of 5% ethyl ether in 2,2,4-trimethylpentane. Dilutions of the clean extracts were made as necessary.

Gas–Liquid Chromatography. All samples were analyzed by gas–liquid chromatography. The detector was electron-capture ^{63}Ni; the column was 1.8 m × 4 mm i.d. glass packed with 15% QF-1 plus 10% DC-200 (1:1) on 80–100 mesh Chromosorb W (AW, DMCS); the gas used was CH_4–Ar (5:95) at 60 ml/min flow rate. Injection,

Table I. Insecticide Residues on Cotton Plants in Agroecosystem Chambers

Days after treatment	Compound, ppm						
	p,p'-DDE	*p,p'*-DDD	*p,p'*-DDT	*o,p'*-DDD	*o,p'*-DDT	DDTR	Toxaphene
0[a]	25	35	1340	9	205	1610 ± 310	4400 ± 870
6[a]	23	17	865	7	98	1010 ± 105	2680 ± 855
14[b]	36	41	1050	3	215	1340	1700
21	70	9	300	1	77	457	1460
28	22	15	720	2	79	838	1310
42	13	8	425	1	31	478	400
56	10	7	340	2	22	381	715

[a] Mean and standard deviation of first 6 weeks. [b] Days after last treatment.

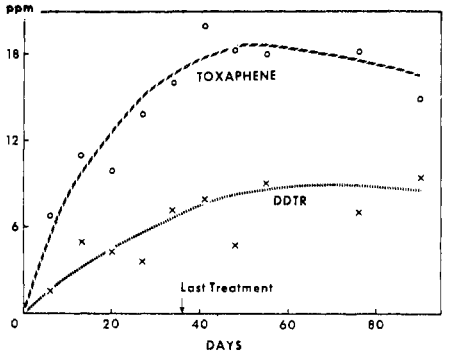

Figure 2. Toxaphene and DDTR residues in surface 1-cm soil of agroecosystem chambers.

column, and detector temperatures were 220, 220, and 300 °C, respectively. Relative retention times against standards were used for qualitative analyses. Peak heights were used to quantify DDT, and total integrated area (total area less solvent peak and agroecosystem control sample) was used to quantify toxaphene.

Standard deviations and regression equations were calculated where applicable.

RESULTS AND DISCUSSION

Plant Residues. The amounts of insecticide residues found on cotton plants are listed in Table I. These values varied indicating nonuniform spraying and insufficient sampling. There was no apparent accumulation on the plant leaves. Toxaphene leaf deposits on an area basis were 11.3 and 6.9 $\mu g/cm^2$ (113 and 69 mg/m^2) at 0 and 6 days, respectively, with a calculated half-life of 19.3 days. Correlation coefficients (r) were −0.9 for both log concentration with linear time and log concentrations with log time regression equations.

DDT leaf deposits on an area basis were 3.4 and 2.2 $\mu g/cm^2$ (34 and 22 mg/m^2) after 0 and 6 days, respectively, with a calculated half-life of 29 days. Correlation coefficients were −0.85 and −0.81 for log concentration with linear time and log concentration with log time, respectively.

Decker et al. (1950) measured toxaphene and DDT residues on fruit tree leaves for a period of time after a spray treatment. From their results, we determined regression equation half-lives. Log concentration with log time gave higher correlation coefficients (−0.97 vs. −0.89 and −0.99 vs. 0.97, respectively, for toxaphene and DDT) than log concentration with linear time. They harvested only treated leaves, whereas we harvested representative treated and untreated new leaves, which probably explains the different best-fit regression equations between the two experiments. Some of the decrease in leaf residues from our experiment could be attributed to dilution as a result of plant growth. Their calculated half-lives were 15.6 days for toxaphene and 15.3 days for DDT on fruit tree leaves.

Table II. Insecticide Residues in Soil Profile at End of Experiment with Agroecosystem Chambers

Depth, cm	Compound, ppm	
	DDTR	Toxaphene
0-1	9.47	14.9
0-5	2.49	4.56
5-10	0.09	0.48[a]
10-15	0.06	0.14[a]

[a] Values probably high, because method of determination gives high (50%) values at these concentrations.

Table III. Insecticide Residues in Water Leachate[a] from Agroecosystem Chambers

Date[b]	Compd, μg/L	
	DDTR	Toxaphene
Sept 2	2.19	24.9
Sept 10	6.24	19.9
Oct 6	1.97	9.7

[a] The leachate contained suspended material. [b] Treatments were on Aug 5, 12, 19, and 26 and Sept 2 and 9.

Table IV. Insecticide Residues (mg/m^2) on Soil and Side Surfaces[a] of Agroecosystem Chambers Containing Treated Cotton

Days after treatment	Toxaphene		DDTR	
	Soil	Sides	Soil	Sides
0[b]	22.5	15.3	7.08	3.83
1[b]	0.290	1.980	0.290	0.845
6[b]	0.185	1.280	0.090	0.325
14[c]	0.115	1.020	0.035	0.280
21	0.130	0.950	0.020	0.235
28	0.080	0.521	0.090	0.105
42	0.110	0.022	0.025	0.120
56	0.135	0.014	0.025	0.045

[a] Determined by placing glass microscope slides on the soil surface and chamber sides. [b] Mean of six treatments, except for 0 day for toxaphene sides, which is mean of five. [c] Days after last treatment.

Soil Residues. Soil surface insecticide residues accumulated in direct proportion to the amounts applied (Figure 2). No losses were observed after application was stopped, because of the short time period and variation of the data. Nearly all of the insecticide residues were concentrated on the soil surface (Table II). Residues below the surface were most likely carried down through the soil profile mechanically by silting in cracks during irrigation and sampling.

Water Residues. We found small but detectable amounts of insecticide residues in the leachate from the chambers (Table III). Again, residues may have been carried down through the soil profile in cracks and, subsequently, siphoned off.

Surface Residues. Insecticide residues, found on soil or chamber sides as a result of insecticide application, were

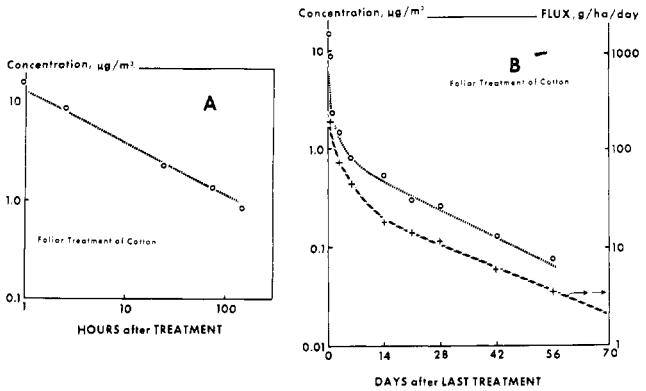

Figure 3. Toxaphene concentrations in air for 144 h (6) (A) and last 56 days (B) after application to cotton plants in agroecosystem chambers. A shows mean concentration of toxaphene in air after 6 weekly treatments and B shows air concentration after the 6th treatment. The curve (B) with the arrow refers to the vertical axis on the right.

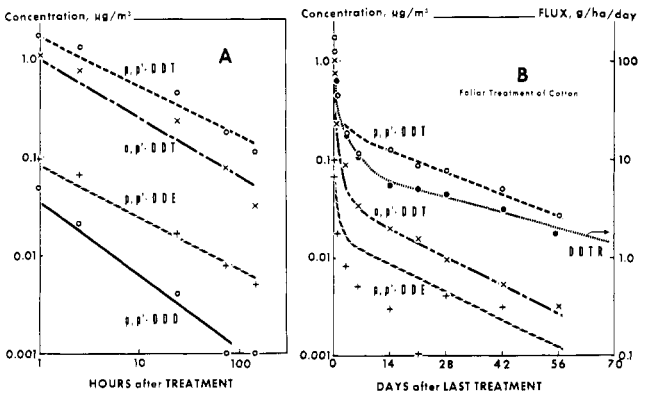

Figure 4. DDT concentrations in air for 144 h (6) (A) and last 56 days (B) after application to cotton plants in agroecosystem chambers. A shows mean concentration of DDTR in air after 6 weekly treatments and B shows air concentration after the 6th treatment. The DDTR curve (B) with arrows refers to the vertical axis on the right.

several times greater than those deposited by later vaporization from plant or soil surfaces and subsequent condensation on newly placed glass microscope slides (day 0 vs. all other days; Table IV). Less insecticide was deposited from vaporization on the slides placed on the soil surface than on the chamber sides.

After the first day, toxaphene residues on the soil slides remained fairly constant (0.1 to 0.3 mg/m^2) as did the DDTR (*p,p'*-DDE, *p,p'*-DDD, *p,p'*-DDT, and *o,p'*-DDT) residues. This probably reflected the concentration equilibrium with the soil and vapor residues.

Volatilization. Figures 3 and 4 show concentration and flux (based on absolute residue amounts trapped from air per given time and soil surface area) curves for toxaphene and DDT loss in air from the agroecosystem chambers. The 144-h (A-6 day) concentration curves are based on a mean of six treatments and two replications per treatment.

Both toxaphene and DDT seemed to volatilize at one rate for the first 6 days and then at a different rate. When we compared regression equations for log concentration with log time and log concentration with linear time for the first 6 days, correlation coefficients (*r*) were higher for the log concentration with log time equations. However, when we calculated best-fit equations for day 6 or days 14 to 56, a log concentration with linear time equation better described the data, except for *p,p'*-DDE and total DDT residues (DDTR), where log concentration with log time equations were better. For the individual compounds,

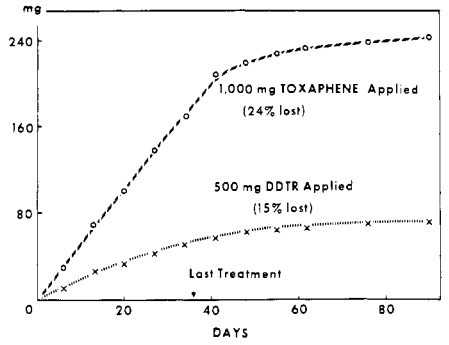

Figure 5. Accumulative volatilization losses of toxaphene and DDT to air after application to cotton plants in agroecosystem chambers.

Table V. Ratios of Amounts of *p,p'*-DDE and *o,p'*-DDT to *p,p'*-DDT in Air and on Plants in Agroecosystem Chambers

Days after treatment	*p,p'*-DDE/*p,p'*-DDT		*o,p'*-DDT/*p,p'*-DDT	
	Air	Plants	Air	Plants
0	0.016[a]	0.019	0.19	0.15
0.02[b]	0.05		0.42	
0.1	0.07		0.47	
1	0.05		0.43	
3	0.04		0.57	
6	0.03	0.03	0.35	0.11
14	0.02	0.03	0.16	0.21
21	0.03	0.23	0.17	0.26
28	0.05	0.03	0.12	0.11
42	0.08	0.03	0.09	0.07
56	0.11	0.03	0.09	0.06

[a] Treatment solution. [b] Days after last treatment.

except DDE, the data indicated that for about 1 week toxaphene and DDT volatilization losses followed a log concentration with log time and then log concentration with linear time. DDE did not follow the same loss vs. time curve because it is a degradation product, as well as a component of the applied insecticide, and, consequently, was being formed continuously while it was being volatilized.

Toxaphene was more volatile than DDT (Figures 3 and 4). Volatilization losses (Figure 5) for toxaphene were consistently more than twice those for DDT, though its application rate was only twice as large. At the end of the experiment, a total of 15% of the applied DDT and 24% of the total toxaphene had been volatilized.

We calculated concentration ratios of both *p,p'*-DDE and *o,p'*-DDT to *p,p*-DDT for the treatment solutions and in air and plants (Table V). The DDE/DDT concentration ratio in air was about three times greater than the treatment solution ratio, but, after 3 days, the extremely low DDE values made measurements difficult. Nevertheless, air concentrations of DDE remained nearly constant from day 6 to 56 (Figure 4), whereas that of DDT decreased logarithmically. This is probably indicative of the slow conversion of DDT to DDE. The air *o,p'*-DDT/*p,p'*-DDT ratio was twice that of the treatment solution for the first 6 days after treatment, then subsequently decreased, probably because of the greater percentage losses for *o,p'*-DDT than for *p,p'*-DDT.

DDE/DDT ratios for plants increased to 0.03 by day 6 and remained constant, except for day 21 when it was unusually high. Apparently, an equilibrium state of conversion of DDT to DDE and its subsequent loss had been reached. Likewise, the *o,p'*-DDT/*p,p'*-DDT plant ratios tended to indicate the more rapid loss of *o,p'*-DDT.

Our closed system contained plants which received most of the insecticide treatment. Soil insecticide residues in the agroecosystem chambers ranged from 1.6 to 8.0 ppm of soil, after 1 to 6 weeks. Plant insecticide residues (>381 ppm) (Table I) remained relatively constant, despite the repeated applications. Consequently, we must assume that the plant canopy had a major influence on insecticide volatility, and soil had a very minor influence. For day 1, total volatility losses were 6.5 (0.2, 2.1, and 4.2 mg/m^2 soil per day; 2, 21, and 42 g/ha per day, respectively, for *p,p'*-DDE, *o,p'*-DDT, and *p,p'*-DDT) (Figure 4). This loss value decreased rapidly with time to 1.8 and 0.2 mg/m^2 of soil per day (18 and 2 g/ha per day) after 3 and 56 days. For toxaphene, volatilization was 18.9, 7.3, and 0.4 mg/m^2 of soil per day (189, 73, and 4 g/ha per day) for days 1, 3, and 56 (Figure 3).

Spencer et al. (1973) calculated potential volatilization rates, which assumed that volatilization was proportional to the gross area of spray deposit, to indicate relative volatilization rates of several pesticides. They calculated that 10 μg/cm^2 (100 mg/m^2) of *p,p'*-DDT would take 70 days to volatilize from a fruit tree. Our results, with leaf deposits of 3.4 μg/cm^2 (34 mg/m^2) immediately after treatment and 2.2 μg/cm^2 (22 mg/m^2) after 6 days, indicated that 0.012 μg/cm^2 (0.12 mg/m^2) *p,p'*-DDT, though small, would still be volatilized if we project the curve to 70 days (Figure 4). If these losses were calculated from data collected when concentrations are log concentration with log time, they would be more rapid than that actually lost. Under actual field conditions the soils would contribute to volatilization also, but in our chambers the heavy cotton foliage probably intercepted most insecticide residues that volatilized from the soil.

We calculated that the half-life of *p,p'*-DDT in air was 18.8 days based on data beginning with day 14 after the last treatment. Consequently, after 90 days insignificant flux levels of 0.7 g/ha per day (0.07 mg/m^2 per day) DDT would be volatilized. After 29 h, DDT concentrations decreased to 0.3 μg/m^3, a value which Beyermann and Eckrich (1973) also found in their experimental air samples.

We calculated that the half-life of *o,p'*-DDT in air was 14.3 days. After 90 days, the flux level would be 0.05 g/ha per day (0.005 mg/m^2 per day). The half-life of *p,p'*-DDE, based on data beginning with day 6 after the last treatment, was 15.1 days. After 90 days the flux level would be 0.02 g/ha per day (0.002 mg/m^2 per day). This value is high compared with a system with no parent *p,p'*-DDT present to continuously degrade to *p,p'*-DDE.

If toxaphene volatilization losses (Figure 3) are projected to 90 days, 0.95 g/ha per day (0.095 mg/m^2 per day) would be lost. The calculated half-life for toxaphene in air was 15.1 days, slightly less than that for *p,p'*-DDT. Therefore, the time needed for toxaphene to reach insignificant levels would be similar to that of DDT, if toxaphene application rates were double those of DDT. This condition might be altered for both insecticides, and perhaps be more rapid under actual field conditions of plant maturation and defoliation to expedite cotton harvest.

For both insecticides (Table IV) deposited residues vaporized from the chamber sides (2 and 1 mg/m^2 levels for toxaphene and DDTR, respectively, at day 1 to <0.1 mg/m^2 after 56 days) reflected the lower levels of insecticide on the cotton leaves. The soil surface residues somewhat indicate the relative vapor concentration near the soil surface as compared with that on the chamber sides, thus relative volatility from soil vs. leaves. For example, the relatively constant toxaphene values for soil surfaces, after day 14, increased over those values for chamber sides after day 42. Thus, after day 42 most of the toxaphene was vaporized from the soil rather than from the plant surfaces. However, with DDT the soil surface values were never greater than the chamber side values, which indicated that with the slower vaporization of DDT, the ratio of soil to plant volatilization never becomes greater than one. Near the end of an experiment like ours, the soil could contribute a very significant amount to the total volatilization. However, the very thick cotton foliage probably intercepted most of the soil volatilized insecticide, thus decreasing most measurable amounts volatilizing from the soil.

Initially plants were surface irrigated; however, during the last 60 days, they were sprinkler irrigated with from 1 to 2.8 cm of water. Our results indicated that the simulated rainfall had no influence on toxaphene or DDT volatilization nor did our results indicate the rainfall decreased plant insecticide residues or increased the soil surface residues.

Estimated Balance Sheet. Unfortunately, since we did not determine total plant surface area or weight at the end of the experiment, we could not make a total balance sheet of insecticide residues. However, we could approximate total residues calculated. The amounts of toxaphene and DDTR volatilized during the experiment (90 days) were 240 and 75 mg, respectively. The amounts of residues found in the soil at the end of the experiment were 200 and 120 mg, respectively, for toxaphene and DDT. Thus, we could account for a total of 440 and 195 mg of toxaphene and DDTR applied, respectively, which leaves 560 and 305 mg of toxaphene and DDTR residues, respectively, unaccounted for. (Residues on the chamber sides were negligible.) At the end of the experiment, there were 0.72 and 0.38 mg/g (dry weight) toxaphene and DDTR on the cotton leaves, respectively. If 800 g (160 g/plant) of dry cotton leaves per chamber was harvested, the total residues could be accounted for on the cotton leaves. Our estimated value of 160 g of dry leaves/cotton plant is not unreasonable for the very large plants.

LITERATURE CITED

Beall, M. L., Jr., Nash, R. G., Kearney, P. C., Conference on Environmental Modeling and Simulations, Cincinnati, Ohio, April 20–22, 1976.
Beyermann, K., Eckrich, W., *Z. Anal. Chem.* **265**, 4 (1973).
Cliath, M. M., Spencer, W. F., *Environ. Sci. Technol.* **6**, 910 (1972).
Decker, G. C., Weinman, C. J., Bann, J. M., *J. Econ. Entomol.* **43**, 919 (1950).
Holmstead, R. L., Khalifa, S., Casida, J. E., *J. Agric. Food Chem.* **22**, 939 (1974).
Isensee, A. R., Kearney, P. C., Woolson, E. A., Jones, G. E., Williams, V. P., *Environ. Sci. Technol.* **7**, 841 (1973).
Metcalf, R. L., Sangha, G. K., Kapoor, I. P., *Environ. Sci. Technol.* **5**, 709 (1971).
Nash, R. G., Beall, M. L., Jr., *J. Assoc. Off. Anal. Chem.* **54**, 959 (1971).
Perry, R. H., Chilton, C. H., Kirkpatrick, S. D., Ed., "Chemical Engineers Handbook", 4th ed, McGraw-Hill, New York, N.Y., 1963, pp 5–7.
Spencer, W. F. Farmer, W. J., Claith, M. M., *Residue Rev.* **49**, 1 (1973).
von Rümker, R., Lawless, E. W., Meiners, A. F., Lawrence, K. A., Kelso, G. L., Horay, F., "United States Environmental Protection Agency and Council on Environmental Quality", Washington, D.C., EPA 540/1-74-001, 1974, Table I.
Willis, G. H., Parr, J. R., Smith S., *Pestic. Monit. J.* **4**, 204 (1971).

Received for review October 1, 1976. Accepted November 29, 1976. Mention of proprietary products does not imply endorsement or approval by the U.S. Department of Agriculture to the exclusion of other suitable products.