EVALUATION OF A TECHNIQUE FOR
MEASURING DRY AERIAL DEPOSITION RATES OF
DDT AND PCB RESIDUES*

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ABSTRACT - A rapid technique for the determination of dry aerial fallout fluxes of higher molecular weight chlorinated hydrocarbons by collecting particles on a mineral oil coated glass plate has been successfully adapted for collection of certain DDT and PCB residues over a one week period. However, the technique proved unsatisfactory for components more volatile than p,p'-DDE. Comparison of fallout fluxes measured by this collector with these measured by one that freezes fallout particles in a layer of ice provided relatively good agreement between mean values for total DDT and PCB 1254.

INTRODUCTION

Aerial transport and deposition appears to be one of the most important mechanisms by which chlorinated hydrocarbons are dispersed following release to the environment (Risebrough 1969; Nisbet and Sarofin 1972; Harvey and Steinhauler 1974; Bidlemann et al. 1976; Risebrough et al. 1976; Young and Heesen 1978). In this paper we discuss the advantages and limitations of a procedure for collecting and analyzing certain DDT and PCB residues carried to the earth's surface via dry fallout. This technique is a modification of a procedure first developed by McClure (1976) and McClure and Lagrange (1977). With it we have been able to quantify (Young et al. 1975; Young et al. 1976) the fallout rate of 1254 PCB, p,p'- and o,p'-DDT, p,p'-DDE, and p,p'-DDD. (Our analytical techniques do not satisfactorily measure the ortho isomers of DDE and DDD). However, the research has demonstrated that the approach is not valid for chlorinated hydrocarbons which are more volatile than p,p'-DDE.

SAMPLING PROCEDURE

The collection device for sampling dry aerial fallout is a cleaned piece of window glass (30.5 cm x 30.5 cm) covered with a thin layer of pharmaceutical mineral oil (Squibb brand) diluted by five parts pesticide-grade hexane. This mixture is applied with a TLC sprayer (Chromatosprayer, Applied Science, Inc., State College, PA), leaving approximately 0.2 ml of mineral oil on

the glass plate. The plate is then set on an elevated surface
(such as a roof top) away from obvious sources of contamination.
At the end of the sampling period, a cleaned piece of Teflon is
used to scrape the mineral oil (bearing fallout particles) from
the plate. The oil is transferred from the edge of the Teflon
strip to the inner rim of a centrifuge tube. After several
minutes of such scraping, the plate is resprayed with diluted
mineral oil and rescraped; this procedure is repeated for a third
scraping. Tests have indicated that this three-step process re-
covers more than 95% of the fallout material. Then, the sample
tube is covered with aluminum foil under a screw cap and re-
turned to the laboratory. Clean plates wrapped in aluminum foil
are similarly processed in the field to provide procedural blanks.
Procedural blanks are usually less than 5% of the total sample.

LABORATORY PROCEDURE

Aerial fallout samples are processed through a "clean-up
column" before being analyzed. A disposable 5 ml pipet (8 mm OD,
6 mm ID) serves for a column which is packed with specially pre-
pared and activated silica gel. MCB Silica Gel (SX-144-6)
100-200 mesh is washed with a 1:1 solution of methanol/benzene.
Three milliliters of solution are used per one gram of adsorbent.
After rinsing, the silica gel is dried in a Rotovapor and ac-
tivated at 180° C overnight and then stored under hexane. The
column is packed by inserting a plug of silane treated glass
wool, adding several mls of hexane and slurrying the silica gel
with a pipet. Using the markings on the 5 ml pipet as a guide,

adsorbent is added until the volume of the compacted bed is 1.7 ml $\pm$ 0.1 ml. A vibrator is held against the column briefly to compact the adsorbent.

The fallout samples come into the laboratory in centrifuge tubes containing up to one ml of mineral oil. The sides of the tube are washed down with enough hexane to bring the volume to 3 mls. The sample is then introduced into the column using a pipet to transfer it from the centrifuge tube. The initial elution is with 1.7 mls of hexane to remove the mineral oil from the column; this fraction is discarded. The column is then eluted first with 5.7 ml of 20% benzene/hexane, followed by 6 ml of benzene. The first fraction elutes the PCB and DDT compounds and the second fraction elutes the Dieldrin fraction. The sample is then ready for injection into the gas chromatograph. Standard recovery tests with the silica gel column indicate that the Aroclors, p,p'- and o,p'-DDT, p,p'-DDE, and Dieldrin have recovery efficiencies of 90 percent or better. The corresponding factor for p,p'-DDD is about 95 percent.

All glassware (including glass fallout plates) used for chlorinated hydrocarbon analysis is cleaned by soap and water washing. The glassware is then heated in a kiln at 540° C for four hours (to volatilize the interfering compounds from the glassware). All solvents used in the analysis are pesticide grade solvents or equivalent.

INSTRUMENTATION AND QUANTITATION

Samples are injected into a Tracor MT 220 gas chromatograph equipped with a ^{63}Ni detector. The glass column used is 1.8 m (6 ft) long, 6 mm OD, 2 mm ID, and is packed with mixed phase 1.5 percent OV-17 and 1.95 percent QF-1 on 80/100 mesh Gas-Chrom Q (prepared by Applied Science Labs, Inc., State College, PA). The carrier gas is prepurified nitrogen with a flow rate of 60 ml/min detector purge and 20 ml/min through the column. The injector, column, and detector temperatures are 225, 200, and 285°C, respectively. The components are identified by retention time and quantitated by comparison of the peak heights of the standards to the peak heights of the samples.

COLLECTION EFFICIENCY

McClure and Lagrange (1977) originally used this procedure for sampling over a relatively short period (generally less than two days). For our studies it was desired to sample over a longer period, generally about one week. Thus, it was necessary to determine the efficiency of collection of the system under these conditions. In April 1974, an eight day experiment was conducted on the roof of a private home in Redondo Beach (a residential suburb of Los Angeles) approximately 2 km from the Pacific Ocean.

In this test, fourteen sampling plates were arranged on a flat portion of the roof and coated with the mineral oil and

hexane mixture. Three of the plates were sampled daily for the eight day period (the plates were resprayed after sampling for the next day's sample). A second set of three plates was sampled and resprayed every other day. A third set of four plates was sampled on the fourth and eighth day, and a fourth set of four plates was sampled on the eighth day only. The forty-eight samples were processed according to the above described procedure and analyzed for p,p'-DDT, o,p'-DDT, p,p'-DDE, p,p'-DDD, and PCB residues most closely resembling Aroclor 1254. Average values for the total quantity of each of these compounds accumulated over the eight days are given as a function of collection frequency in Table 1.   In addition, the mean quantity of each chlorinated hydrocarbon, and the coefficients of variation (CV) for each set of samples, were computed. Averages of these values (except those for the eight day set) were then taken (Table 2). These results show that, in general, the longer the sampling period, the better the precision of the aerial fallout data, probably because of the increased sample size. The CV's for total DDT and 1254 PCB in the eight day collections (similar to our usual one week sampling interval) are 8 and 20 percent, respectively.

The data presented in Table 1 indicate that collection efficiency decreases with duration of plate exposure. To determine if this loss of efficiency is a linear process that can be corrected using linear recovery factors, we calculated corresponding regression lines and their correlation coefficients (Table 3).

Most of the results were statistically significant at greater than the 95 percent confidence level; p,p'-DDE and p,p'-DDD results were significant at greater than the 90 percent level. Because our fallout samplers are generally exposed for one week before the sample is collected, the collection efficiency factor for a given constituent was taken as the ratio of the best-fit cumulative value for a seven-day exposure to the extrapolated value for a zero-day exposure. Standard seven-day collection efficiencies (and their 95 percent confidence intervals) calculated from these data are listed in Table 4. In our fallout surveys we normalize our blank-corrected results to standard weeks (Monday through Sunday) and divide by 7 to obtain an estimated average daily flux at a given station for that week. The flux values then are corrected by these efficiency factors. These results suggest that the more volatile components have poorer collection efficiencies. We have previously measured the partitioning of these chlorinated hydrocarbons in the atmosphere between the particulate and vapor phase in many locations (Heesen and Johnson, 1976).

Two other contaminants of interest, Dieldrin and PCB residues most closely resembling Aroclor 1242, were found to have very poor linearity in the eight day efficiency experiment. To investigate this problem further, 0.1 mg of each material was added to 10 ml of a 17 percent solution (by volume) of mineral oil in hexane. The two mixtures were placed on two separate fallout sampling plates and allowed to stand for a period of four days on the laboratory roof. The recovery factor for the

Dieldrin spike was 26 percent. The results of the Aroclor 1242 spike are illustrated in Figure 1. It should be noted that Aroclor 1242 is a mixture of chlorinated biphenyl compounds. We suspect the low recovery of Aroclor 1242 is due to the higher volatility of this mixture; Aroclor 1242 has an average vapor pressure that is 4×10^3 times higher than DDT (Mackay and Leinonen, 1975). The linear relationship in Figure 1 also supports this explanation. However, the low Aroclor 1242 recovery also may in part be due to photolysis. Similarly, the low recovery of the Dieldrin may be due to photolysis of the Dieldrin to "photo-dieldrin" (Crosby, 1976).

In another experiment, a one gallon glass jug was lightly sprayed with a 17 percent mixture of mineral oil in hexane. A mixture of Aroclor 1242 and Aroclor 1254 in hexane was added to the bottom of the sprayed jug and the hexane was allowed to evaporate. The jug was sealed with an aluminum foil lined cap and placed on the laboratory roof for a period of six days. The jug was then cut about 5 cm above the bottom and each section was processed and analyzed. The results of this experiment are illustrated in Figure 2. The Aroclor 1242 peaks in general correspond to the early peaks (before 70 mm) and the Aroclor 1254 peaks are represented by the later peaks (after 70 mm).

The results illustrated in Figure 2 show that the compounds with the longer retention times (which are relatively non-volatile) remained in the bottom of the jug and that the compounds with the shorter retention times (which are relatively volatile) migrated from the mineral oil to the top of the jug. This illustrates the inverse relationship between collection efficiency of the

oiled plate system and volatility of the compounds of interest. In an effort to improve the sampling efficiency, we substituted the mineral oil collection media with several other materials (glycerin, silicon oil, and water in a Pyrex dish). However, none of these substitutes proved to be as effective as the mineral oil. To further test the collection efficiency of the oiled plate system, we designed another type of sampler which retained the fallout components by freezing them upon deposition. A clean aluminum baking dish (30 cm x 23 cm x 7 cm) was constrained by a spring to rest on top of a 25 kg block of dry ice (which was housed in an insulated plywood box to reduce the rate of sublimation). A layer of ice, caused by condensation and freezing of atmospheric moisture, was observed to form in the aluminum pan shortly after it was placed on top of the dry ice block. This ice remained frozen in the pan until the sample was thawed and extracted. The dry ice usually lasted two to three days, depending on weather conditions; this limited the duration of the collection period accordingly.

To compare the efficiencies of the cooled pan and oiled plate deposition collectors, we deployed them together for two or three day periods on six separate occasions. The ratios (and their standard deviations) of the quantities of total DDT and 1254 PCB collected by these two very different systems is summarized in Table 5. The data utilized to obtain the ratios shown were first corrected for procedural blanks; the oiled plate data (used as the normalizer) were then corrected by our previously determined time dependent collection efficiency factors.

CONCLUSION

The relatively close agreement obtained for total DDT and 1254 PCB using the two samplers indicates that these deposition collection systems probably yield reliable values for the aerial fallout rate of these chlorinated hydrocarbons. In view of the greater ease and economy of deploying the oiled plate system, and the fact that it can be exposed for up to a week with satisfactory collection efficiencies, we believe it is the preferable system for conducting aerial deposition surveys of DDT residues and 1254 PCB on a regional scale.

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TABLE CAPTIONS

Table 1.   Cumulative average quantities (ng) of chlorinated
           hydrocarbons measured over an eight day period during
           1974 on four sets of collection plates sampled at
           different frequencies at Redondo Beach, CA.

Table 2.   Average means (ng) and average coefficients of
           variation for chlorinated hydrocarbon concentrations
           in aerial fallout samples collected at Redondo Beach,
           1974.

Table 3.   Correlation coefficients for eight day collection
           series of chlorinated hydrocarbons in dry aerial
           fallout.

Table 4.   Dry aerial fallout seven day collection efficiencies
           with 95 percent confidence intervals.

Table 5.   Ratios of fallout rates measured by the dry ice
           cooled pan and oiled plate collectors (dry ice pan/
           oiled plate).

Table 1. Cumulative average quantities (ng) of chlorinated hydrocarbons measured over an eight day period during 1974 on four sets of collection plates sampled at different frequencies at Redondo Beach, CA.

Collection Frequency	3-5 Apr.	3-7 Apr.	3-9 Apr.	3-11 Apr.
p,p'-DDT				
1-day	190	300	384	540
2-day	158	263	345	509
4-day	–	235	–	454
8-day	–	–	–	312
o,p'-DDT				
1-day	52	90	121	181
2-day	46	81	114	172
4-day	–	68	–	166
8-day	–	–	–	110
p,p'-DDE				
1-day	29	64	91	134
2-day	17	48	63	94
4-day	–	37	–	74
8-day	–	–	–	39
p,p'-DDD				
1-day	28	62	104	180
2-day	23	46	81	157
4-day	–	51	–	163
8-day	–	–	–	104
1254 PCB				
1-day	60	140	218	401
2-day	46	90	161	352
4-day	–	104	–	327
8-day	–	–	–	195

Table 2. Average means (ng) and average coefficients
of variation for chlorinated hydrocarbons
measured in aerial fallout samples
collected at Redondo Beach, 1974.

	p,p'-DDT	o,p'-DDT	p,p'-DDE	p,p'-DDD	Total DDT	1254 PCB
1-day samples						
Mean	66	15	16	22	126	42
CV	24%	22%	15%	24%	17%	34%
2-day samples						
Mean	126	43	23	39	231	80
CV	16%	13%	15%	12%	11%	29%
4-day samples						
Mean	226	83	37	81	425	155
CV	6%	13%	14%	17%	6%	15%
8-day samples						
Mean	311	109	39	103	561	187
CV	4%	24%	31%	13%	8%	20%

Table 3. Correlation coefficients for eight day collection series of chlorinated hydrocarbons in dry aerial fallout.

Constituent	Correlation Coefficient*
p,p'-DDT	-0.99
o,p'-DDT	-0.97
p,p'-DDE	-0.94
p,p'-DDD	-0.94
1254 PCB	-0.98

* For the two degrees of freedom applicable here, correlation coefficients of $\pm$ 0.95 and $\pm$ 0.99 correspond to the 95 and 99 percent confidence limits, respectively.

Table 4. Dry aerial fallout seven day collection
efficiencies with 95 percent confidence
intervals.

Fallout Constituent	Collection Efficiency (%)	Confidence Interval
p,p'-DDT	60	46-64
o,p'-DDT	64	50-82
p,p'-DDE	36	11-81
p,p'-DDD	63	42-92
1254 PCB	54	43-66

Table 5. Ratios of fallout rates measured by the dry
ice cooled pan and oiled plate collectors
(dry ice pan/oiled plates).

Test No.	Total DDT	1254 PCB
1	1.00	0.98
2	0.56	0.47
3	0.84	0.76
4	0.81	0.41
5	1.11	1.72
6	1.29	0.68
Mean $\pm$ SD	0.94 $\pm$ 0.26	0.84 $\pm$ 0.48

FIGURE CAPTIONS

Figure 1. Recovery of Aroclor 1242 standard components from
an oiled glass plate after a four day exposure (chro-
matogram recording speed 10 mm/sec).

Figure 2. Recovery of Aroclor 1242 and 1254 standard components
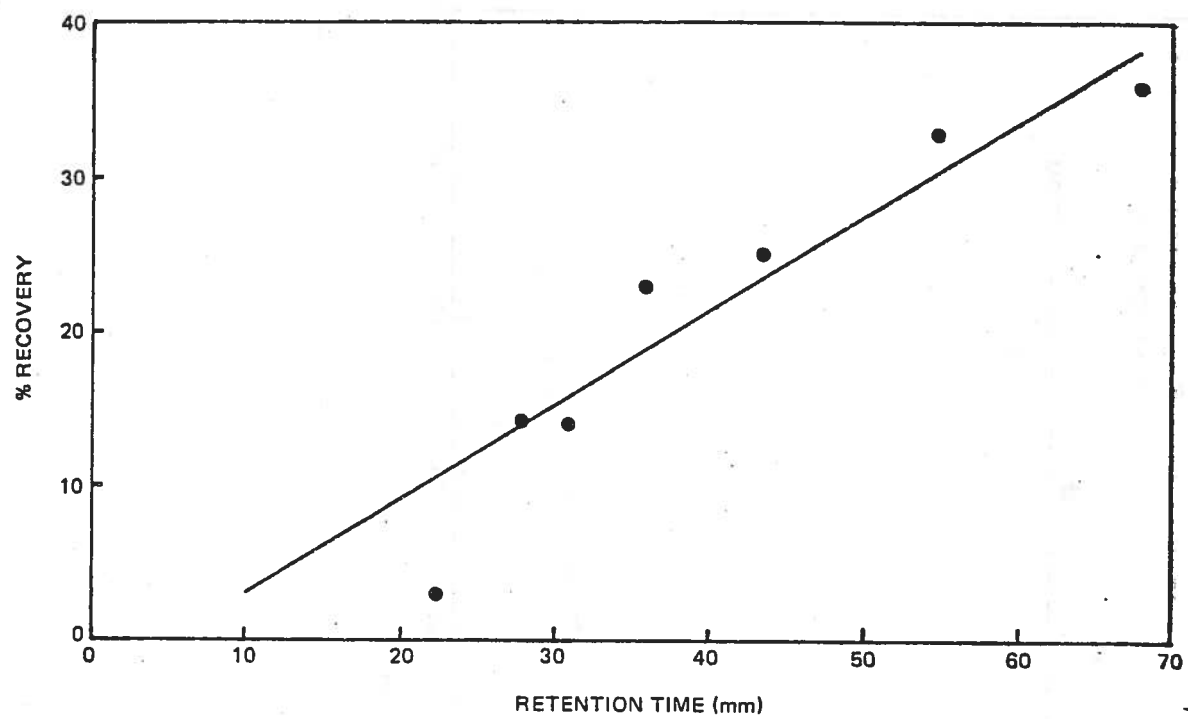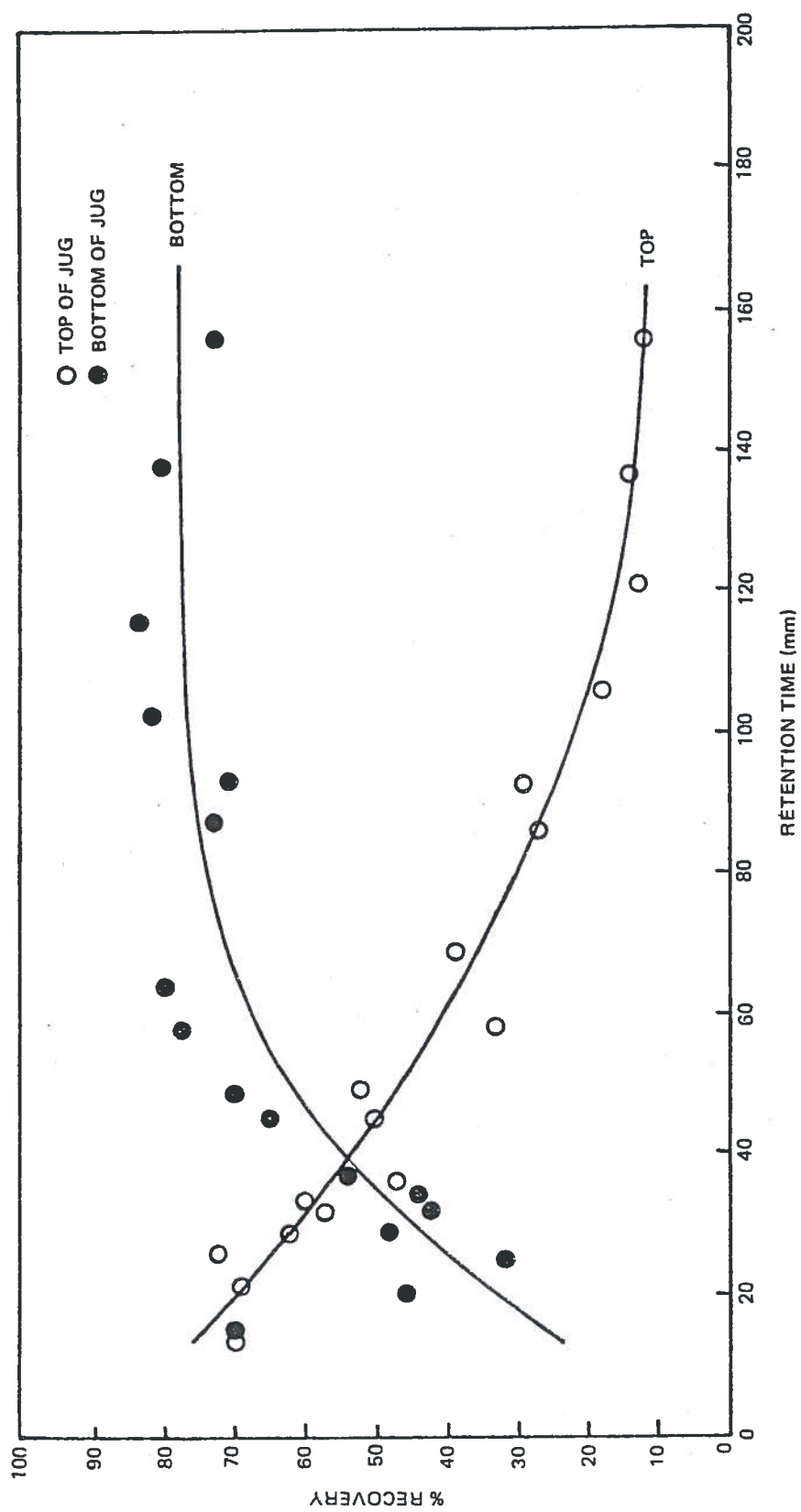from an oiled and sealed glass jug after a six day
exposure.

Figure 1.

Figure 2.