Endrin Decomposition on Air-dried Soils

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Gunther and Blinn (1), Gunther (2), Beynon and Elgar (3), and others have stressed that even organochlorine pesticide-containing samples should be stored at low enough temperatures to assure that any residues present do not decompose further while awaiting extraction; storage for longer than a few days should be at -10°C., or below, in closed containers.

Since soil samples from the field may vary widely in moisture contents, it is customary to report soil analytical results on an air-dried basis. The current practice is to store the soil samples in plastic bags at 0°C., or below, to air-dry by a variety of techniques, and to sieve the soils prior to extraction. For the detection and determination of endrin residues

Bulletin of Environmental Contamination & Toxicology,
Vol. 4, No. 5, 1969, published by Springer-Verlag New York Inc.

in soil this practice of air-drying and sieving soils prior to extraction can result in erroneous results due to loss of endrin through isomerization.

Fowkes *et al*. (4) studied the clay-catalyzed decomposition of endrin using clays dried at 90° to 110°C.; Benesi *et al*. (5) showed that this decomposition of endrin was promoted by the acid sites of the clay. Bowman *et al*. (6) observed that endrin applied to soils previously dried at 45°C. then placed in a gravity, convection-type oven at 45°C. disappeared (or was converted to other compounds) within 24 hours from all soils except one high in organic matter content.

This paper presents data to show that endrin applied to air-dried soils at room temperature, or below, can decompose by isomerization to an aldehyde (4,5,6,7,8,8-hexachlorohexahydro-4,7-methano-3,5,6=methenoindan-1-carboxaldehyde) and a ketone [1,8,9,10,11,11-hexachloropentacyclo $(6.2.1.^{3,6}0.^{2,7}0.^{4,10})$ dodecan-5-one].

Materials and Procedure

Soils. All soils in this study were used in the air-dried condition (room temperatures). The 15 soils used were selected from a large number of soils collected throughout southern California. Selection was based upon results of preliminary experiments which indicated that endrin would be more likely to undergo isomerization on soils with pH values less than 7. The soils selected therefore had pH values between 5.3 and 6.8 and represented the following four soil types: loamy sand, sandy loam, silty loam, and loam.

Procedure. Ten-gram samples of the soils were weighed into 2 oz., screw-capped bottles, treated by pipetting 2.0 ml. of 25.0 μg./ml. of endrin in *n*-hexane onto the soil, capped using aluminum foil liners, and stored either at room temperature (25°C.) or in the refrigerator (3°C.). At the various sampling times 1.0 ml. of water was added to each soil to quench the isomerization reaction and the samples were extracted twice with 25-ml. portions of 4:1 *n*-hexane-acetone by shaking each time for one hour on a reciprocating shaker. The combined double extracts were washed free of acetone with 100 ml. of water, dried by passing through anhydrous sodium sulfate into a 50-ml. volumetric flask, and diluted to volume with *n*-hexane.

Gas Chromatography. All dried extracts were analyzed with an Aerograph A600-B gas chromatograph equipped with an electron-capture detector. A 2'x1/8" aluminum column packed with 7.5% QF-1 and 5% DC-200 on 80/100 mesh Gas Chrom Q was used at temperatures of 175° to 180°C.; this column readily separated analytical samples of endrin, the aldehyde, and the ketone.

Results and Discussion

The gas chromatograms for the endrin-treated soil extracts exhibited decreases in peak heights and areas for the endrin peak with concomitant increases for the aldehyde and ketone peaks as the endrin decomposed on the soil. Phillips et al. (7) have shown that endrin is isomerized in a gas chromatograph at 230°C. to the aldehyde and ketone. Under the experimental conditions used in this study (175° to 180°C.), gas chromatograms for endrin standards showed two minor peaks (a maximum of less than 13% of the endrin peak height) with retention times corresponding to those for the aldehyde and ketone. To ensure that endrin was being converted on the soils and not in the gas chromatograph, endrin standards and soil extracts fortified with endrin were run at random among the other samples.

Ten different air-dried soils were treated with 5 p.p.m. of endrin each and extracted and analyzed after standing at 25°C. for 45 hours. Gas chromatograms for 7 of the 10 soil extracts exhibited peaks for the aldehyde and ketone but none for endrin, indicating that endrin on these soils had completely isomerized within this short period; the remaining three soil extracts showed endrin losses between zero and 50%.

Five additional air-dried soils were then treated with 5 p.p.m. of endrin each and extracted and analyzed after standing at 25°C. for 12 hours. Endrin losses from these soils ranged between 10 and 80%.

Losses of endrin from Madera sandy loam and Aiken silty loam at 25°C. and from Huerohuero sandy loam at both 3° and 25°C. were then measured at various times after treatment with 5 p.p.m. of endrin. The results presented in Table 1 are averages for 3 replicates at each sampling time and are corrected for average recovery values (71 ± 5% for Aiken, 72 ± 7% for Huerohuero, and 74 ± 4% for Madera). Also included are results obtained for soil samples which were moistened with water prior to treatment with endrin.

Table 1

Endrin decomposition on Madera sandy loam, Aiken silty loam, and Huerohuero sandy loam soils

Madera Sandy Loam, 25°C.		Aiken Silty Loam, 25°C.	
Hours after treatment	% endrin remaining	Hours after treatment	% endrin remaining
24	78 ± 6	24	63 ± 2
48	62 ± 2	48	49 ± 2
72	51 ± 4	72	39 ± 4
96	38 ± 7	96	30 ± 4
144	29 ± 3	96[a/]	102 ± 4
144[a/]	104 ± 2	--	--

Huerohuero Sandy Loam

25°C.		3°C.	
Hours after treatment	% endrin remaining	Hours after treatment	% endrin remaining
4	54 ± 4	24	82 ± 11
8	35 ± 7	48	64 ± 6
12	15 ± 2	72	50 ± 4
16	11 ± 1	96	35 ± 2
16[a/]	107 ± 9	--	--

a/ Soil moistened with 2 ml. of water before endrin treatment

The data show that the rate of endrin decomposition on air-dried soils at 25°C. can vary widely from soil to soil. Endrin on Huerohuero sandy loam decomposed rapidly at 25°C., and even at 3°C. the rate of decomposition on this soil was comparable to that for the Madera sandy loam and Aiken silty loam soils at 25°C. Results obtained for the soil samples moistened before endrin treatment show that moisture prevented the decomposition of endrin at 25°C., within the time period involved in this study.

In view of these findings it is obvious that precautions must be taken in handling soil samples for endrin residue analysis. It appears that storage and extraction of moist soils should prevent major endrin losses through isomerization. However, it is recommended that soils being analyzed for endrin residues be checked to see that no losses of endrin during storage and extraction occur.

Acknowledgment

The able technical assistance of Mrs. A. Eula Ryan is acknowledged. This work was supported in part by grants from the Shell Chemical Co. and by W-45 Regional Research.

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