Persistence of Endosulfan in Soils

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The persistence (at >0.05 ppm) of total endosulfan residues under natural conditions of wet and dry cultivation was studied. When the initial dose of application was the same, the residues persisted for about 120 days in wet soils and 100 days in dry soils. There was a difference in the persistence of the pesticide in three dry soils that received low, normal, and high initial doses, and the residue persisted for 60, 100, and 160 days, respectively. Except in the dry soil that received the high dose, in all other soils endosulfan sulfate was the principal metabolite. In the former, endosulfan alcohol and endosulfan ether were the principal metabolites for the first 50 days, after which endosulfan sulfate appeared.

The use of endosulfan (Thiodan, 6,7,8,9,10,-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin 3-oxide), a broad-spectrum nonsystemic insecticide, has been on the increase in India during the recent past consequent to the ban on endrin and the decline in the use of other organochlorine pesticides due to their longer persistence and higher toxicity to mammals. Technical endosulfan contains two isomers, viz., endosulfan A and endosulfan B in a 4:1 ratio, respectively (Lindquist and Dahm, 1957). The various metabolites of endosulfan that have been reported are endosulfan alcohol, endosulfan ether, endosulfan sulfate, endosulfan α-hydroxy ether, and endosulfan lactone (Maier-Bode, 1968). The available information (Lindquist and Dahm, 1957; Barnes and Ware, 1965) indicates that endosulfan A is more toxic and endosulfan B less toxic than the technical material and that endosulfan sulfate is as toxic as technical endosulfan. Further, endosulfan alcohol and endosulfan ether were reported to be nontoxic.

Endosulfan is less toxic to mammals when compared with other organochlorines (for rats, acute oral LD_{50} is 100 mg/kg body weight and acute dermal LD_{50} is 681 mg/kg body weight), but it is highly toxic to fish (Maier-Bode, 1968; Van Dyk and Greeff, 1977). Several instances of pollution of the aquatic environment with residues of endosulfan, due either to accidental contamination (Sievers et al., 1972) or to runoff from arable soils (Gorbasch et al., 1971; Van Dyk and Greeff, 1977; Rao et al., 1979), have been reported. Yet, little information on the persistence of endosulfan residues in soils is available.

Byers et al. (1965), in a study where the pesticide was applied to coastal Bermuda grass as 5% granules, twice at a rate of 2 lb/acre, reported the finding of 0.2246 ppm of endosulfan residue 96 days after the last treatment. Maier-Bode (1968), quoting earlier work, noted that no residues could be detected (the sensitivity of the method was 0.03 ppm) in arable soils after 101 days. Van Dyk and Van Der Linde (1976) reported that under laboratory conditions, endosulfan A was as persistent as endosulfan B and that their concentration fell to less than 10 ppb in 130 days in three types of soils, under covered and uncovered conditions (the initial concentration of the residue varied between 2.9 and 3.8 ppm in different soils). They concluded that "The data did not clearly indicate the persistence time of endosulfan." The report of Stewart and Cairns (1974) that when technical endosulfan was incorporated into soil at a rate of 6.7 kg/ha, 50% of both endosulfan A and endosulfan B was degraded in 60 and 800 days, respectively, is quite at variance with all other reports on the persistence of endosulfan in soils.

Thus, the information available so far does not give a clear picture of the persistence of endosulfan in soils. Furthermore, there have been no data from this country on this aspect.

The present work reports the study of persistence of endosulfan residues in wet and dry soils under natural conditions that prevail in Guntur District, South India (16° 23′ N, 80° 33′ E), and the nature of metabolites formed after application of high and low initial doses.

MATERIALS AND METHODS

Design of the Experiment. No attempt was made to either regulate or alter the local farming practices. One paddy field, representing flooded soil conditions, and three dry fields were selected; cotton was being grown in two of the dry fields and brinjal in the third of the dry fields. The crops are mainly dependent on rains. The paddy field and one dry field (designated as plot I) were sprayed with 250 mL of 35% endosulfan emulsifiable concentrate (EC) per acre (87.5 g of active ingredient). The other two dry fields, designated as plots II and III, were sprayed at a rate of 1 L (350 g of active ingredient) and 125 mL (41.88 g of active ingredient) of 35% EC per acre, respectively, to represent a higher and lower dose than the normal dose applied on plot I. It was observed that as the crop was not dense at the time of spraying, large quantities of pesticide reached the soil. The dry soils were of loamy clay type (pH 7.8, conductivity = 0.24 mmho, available organic carbon = 0.2–0.5%, mean moisture content = 12.0 ± 3.5%) whereas the wet soil was of clay type (pH 8.4, conductivity = 0.15 mmho, available organic carbon = 0.2–0.5%).

From each plot, soil samples (500 g in weight) were collected from three randomly selected blocks out of 12 blocks/plot. From each block, three subsamples (again randomly selected by using random tables) were selected. The three subsamples were mixed, and one sample was drawn by quartering. Each result is an average of the extraction of three such samples.

For a study of the maximum vertical movement of endosulfan residues, a 7-in. deep cylindrical core was taken and the core was divided into seven samples, each of 1-in. thickness. Three such 7-in. deep cylindrical core samples were collected in plot I on the 100th day after spraying.

The soil from the wet field was collected in a cloth, excess water was drained out, and the moist soil was extracted.

While sampling, no attempt was made to remove the plant debris in the sample and only stones were removed.

Extraction and Cleanup. The soil sample from the dry fields was ground and sieved. A sample of 500 g was

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Table I. R_f Values of Isomers and Metabolites of Endosulfan on Silica Gel Plates (250-μm Thick)

compd	R_f value in: 4% acetone in heptane, room temp	4% acetone in heptane, 18 °C	heptane–benzene (1:1), room temp (30 ± 2 °C)
endosulfan A	0.79	0.63	0.90
endosulfan ether	0.43	0.31	0.72
endosulfan B	0.21	0.15	0.58
endosulfan sulfate	0.13	0.08	0.50
endosulfan α-hydroxy ether	0.10	0.03	0.23
endosulfan alcohol	0.04	0.01	0.15
endosulfan lactone	0.00	0.00	0.04

extracted with 1000 mL of 10% acetone in distilled hexane in a Soxhlet extractor for 16 h. The moisture content of the sample was kept above 5% to ensure better recovery (Williams, 1968).

The extract was washed with water to remove acetone and dried by passing it through a column of anhydrous sodium sulfate. The dried extract was concentrated to about 30 mL in a Kuderna-Danish evaporator. The residues from hexane were partitioned into acetonitrile by serial extraction and from aqueous acetonitrile back into hexane. Additional cleanup was achieved with Nuchar C-190N (Kathpal and Dewan, 1975). The cleaned-up extract was concentrated to 1 mL, first with a Kuderna-Danish evaporator and then with a modified micro-Snyder column as described in *Pesticide Analytical Manual* (1977).

As the extraction of wet soil with Soxhlet posed certain difficulties, another method was used. Soil was extracted with acetonitrile in a wrist-action shaker for 2 h. The solvent/soil ratio was 2:1. The aqueous acetonitrile was filtered from the slurry under partial vacuum, and the slurry was repeatedly washed with fresh quantities of the solvent. Seven hundred milliliters of 2% sodium sulfate solution was added to acetonitrile, and the residues were serially partitioned from the aqueous acetonitrile into hexane. The hexane extract was cleaned up with Nuchar and was concentrated as described above.

The validity of various fortification procedures was reviewed by Chiba (1969). The work of Pionke et al. (1968) showed that neither the moisture content at the time of fortification nor the solvent used for fortification influenced the quantitative recovery of the pesticides from soils. Further, their work showed that recoveries were quantitative up to 30 days after fortification.

In the present study technical endosulfan in hexane solution was added to untreated soils. The soils were kept under laboratory conditions for 24 h and extracted as explained above. The fortification was done at three levels: 0.5, 1, and 2 ppm. For each level of fortification, three replicates were used. Untreated dry soil gave an average recovery of 91% (SD of ±3.0%) at the 0.5-ppm level, 86% (SD of ±3.2%) at the 1-ppm level, and 84% (SD of ±2.8%) at the 2-ppm level (the average recovery at the three levels was 87%). Fortified wet soil samples gave an average recovery of 96% (SD of ±2.4%) at the 0.5-ppm level, 96% (SD of ±2.9%) at the 1-ppm level, and 93% (SD of ±3.0%) at the 2-ppm level (the average recovery at the three levels of fortification was 95%).

Thin-Layer Chromatography. Silver nitrate impregnated silica gel (silica gel was prewashed to remove traces of chlorides) plates (20 × 20 cm, 250 μm thick) were spotted with the extract, technical endosulfan, and products of degradation prepared according to the suggested methods (Lindquist and Dahm, 1957; Barnes and Ware, 1965). The plates were developed in 4% acetone in heptane, and the spots were made visible by exposing the plates to UV light. Cochromatography was performed by using 1:1 benzene–heptane. The sensitivity of this method was 0.5 μg. The R_f values of the isomers and metabolites of endosulfan are given in Table I.

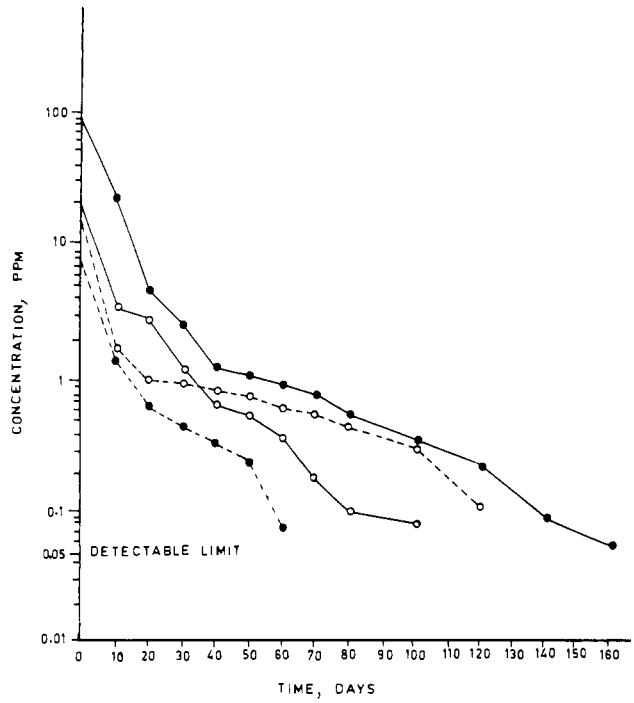

Figure 1. Persistence of endosulfan in soils. Dry soils: (O—O) plot I; (●—●) plot II; (●--●) plot III. (O--O) Wet soil.

Table II. Level of Pesticide Present, Expressed as Percentage of Initial Deposit

	initial deposit, ppm	days after application: 20	40	60	80	100
wet soil	17.6	5.1	4.2	3.2	2.9	1.8
dry soils						
plot I	19.7	12.8	3.1	1.8	0.5	0.4
plot II	89.6	5.3	1.4	1.1	0.6	0.4
plot III	8.0	7.1	3.9	0.9		

Colorimetric Analysis. The method of Maitlen et al. (1963) was followed. They observed that captan, chlordane, heptachlor, and ovex caused some interference in the method, but 45 other pesticides did not interfere. Both of the isomers of endosulfan respond to this colorimetric procedure. The method is applicable in the range of 5–100 μg. None of the interfering pesticides were ever used in the fields under study. The values herein reported were corrected for values of untreated samples as well as the recovery values obtained after fortification of the untreated sample.

RESULTS AND DISCUSSION

Persistence. Figure 1 shows the persistence of endosulfan A and B. There was a rapid fall in the residue levels in all soils. The percentage loss of residues is shown in Table II. In the initial phases, the percentage loss of residues in wet soils was more when compared with that of dry soils. This seems to be due to volatilization as in dry soils plus transportation of residues from the wet soil through runoff. While there was a marked difference in the concentration of residues initially, after 30 days the total quantity of the pesticide and the rate of degradation

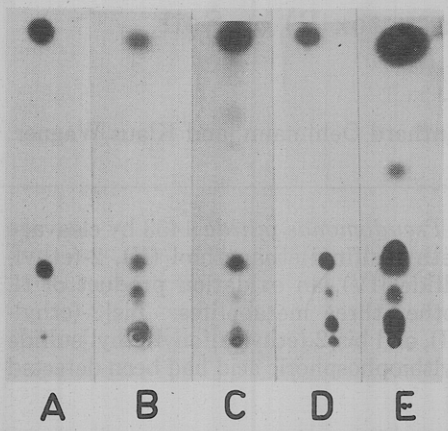

Figure 2. Thin-layer chromatograms showing the residues and metabolites of endosulfan in different soils on the 50th day after spraying. (A) Technical endosulfan; (B) residues in wet soil; (C) residues in dry soil (plot I); (D) residues in dry soil (plot II); (E) isomers of endosulfan and its metabolites in descending order are endosulfan A, endosulfan ether, endosulfan B, endosulfan sulfate, endosulfan α-hydroxy ether, endosulfan alcohol, and endosulfan lactone.

were only slightly different from those values in wet and dry soils that received the same initial dose.

The results further show that the time of persistence of residues is dependent on the initial concentration of residues. There is clearly longer persistence in dry soils that received a higher initial dose. The rate of breakdown was slow in the soil that received a higher initial dose than the other two dry soils, a conclusion also reached by Edwards (1966).

Nature of Metabolites. Figure 2 shows the nature of the metabolites formed in different soils on the 50th day after spraying. The principal metabolite in the plot that received a higher initial dose was endosulfan alcohol followed by endosulfan ether in the first 50 days; endosulfan sulfate appeared only thereafter. In all other plots, endosulfan sulfate was the principal metabolite and it appeared within 5 days after spraying in both the dry soils that received moderate and low initial doses and after 15 days in the wet soil. In the wet soil, besides endosulfan sulfate, endosulfan alcohol was also formed. Further, our work, based on thin-layer chromatograms, also showed that in any field endosulfan A tends to decrease in concentration at a faster rate than endosulfan B. However, the former persisted in traces as long as the latter could be detected in the soil. It was also found that the amount of endosulfan sulfate formed in wet soils was more than that in the dry soil that received the same initial dose.

The work of Roy et al. (1977) showed that soon after spraying endosulfan, there was a reduction in the microflora of paddy fields, which were revived 20 days later. Martens (1976) reported that the majority of soil fungi formed endosulfan sulfate whereas active bacteria formed endosulfan alcohol. The inhibition of the formation of endosulfan sulfate in plot number II for the first 50 days seems to indicate that the soil fungi are inhibited to a greater extent in soils with a higher initial dose than in soils with a moderate and low initial dose.

Vertical Distribution. Soils pose specific problems in sampling techniques as the distribution of pesticides in soils varies with time and depth. Wheatly and Hardman (1960) showed that analytical errors caused by sampling at depths differing as little as 1 cm are significant. The present work showed that by the 100th day 95% of endosulfan along with endosulfan sulfate was present in the top 3 in. only (the reported rainfall during this period was 620 mm). While no endosulfan suulfate was found in 3–4-in. soil cores, traces of endosulfan A and endosulfan B were present. There was no penetration of endosulfan or its metabolites beyond 4-in. depth.

CONCLUSIONS

(1) Unlike other organochlorine pesticides [reported to persist between 3 and 10 years, see Edwards (1973)], the persistence of endosulfan in soils is very short. (2) The reduction in the concentration of residues was initially more in wet soils compared with dry soils that received the same amount of pesticide. (3) In dry soils the duration of persistence was directly related to the initial dose of application, the persistence being longer at higher initial doses. (4) Endosulfan sulfate was the principal metabolite in all soils except the dry soil that received a higher initial dose. In the latter, for the first 50 days endosulfan alcohol and endosulfan ether were the principal metabolites and endosulfan sulfate appeared after the 50th day. (5) The rate of degradation of endosulfan A is more than that of endosulfan B in all the soils studied. However, traces of endosulfan A persisted as long as endosulfan B persisted in the soil.

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