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Persistence of the Insecticide Dimethoate in Three Different Soils under Laboratory Conditions

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Dimethoate, (O,O-dimethyl-S-(N-methylcarbamoylmethyl)-phosphorodithioate) has been used as a systemic insecticide in plants for several years (Hewitt et al. 1958, Santi and De-Pietri-Tonelli 1959). The oxygen analogue of dimethoate (dimethoxon, omethoate, O,O-dimethyl-S-(N-methylcarbamoylmethyl)-phosphorothiolate), which is the metabolite of toxicological interest owing to its increased AChE inhibition properties, and other metabolites have been demonstrated in different plants after root and foliar application (Dauterman et al. 1960; Grimmer et al. 1968; Singh and Yadav 1981). The hydrolytic half-life of the more hydrophilic thiolophosphate omethoate was found to be smaller than that of the dithiophosphate dimethoate (32,5 and 122d, pH 6 and 25°C in vitro, Grimmer et al. 1968), but the biological half-life in plants will be determined by the special enzymatic cleavage of certain moieties of the organophosphates. Thus, in tomato plants biological half-lives of 9,2 and 3,2 d have been determined for omethoate and dimethoate (Grimmer et al. 1968), but following repeated application of dimethoate to peaches and apples the residues of dimethoate exceeded 1 ppm, while those of omethoate were always below 0.2 ppm (Ferreira et al. 1987).

Foliar application provides potential for contamination of soil by dimethoate and its metabolites as a result of the runoff of sprays or as a result of shredding and cultivation of treated foliage. The present studies have been undertaken to investigate the persistence of dimethoate in 3 different soils without leaching at 10 and 20°C, and the residues of dimethoate and omethoate were analyzed versus time until 36d.

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MATERIALS AND METHODS

^{14}C-OCH_3-Dimethoate was synthesized following the method of Dedek and Grahl (1973) by reaction of ^{14}C-CH_3OH with P_4S_{10} and N-methylchloracetamide with a purity of 99% (rel. to ^{14}C) and a specific activity of 2,15 x 10^6 dpm/µg = 820 GBq/mmol.

Soil persistence studies were performed according to the BBA (1980) (Biologische Bundesanstalt Braunschweig, FRG). The investigations were carried out with three standardized soils, which were supplied by the VEB Chemiekombinat Bitterfeld from the Landwirtschaftliche Untersuchungs- und Forschungsanstalt in Speyer (FRG), a humus rich sandy soil (soil 1), a clay loam soil (soil 2), and a heavy clay soil (soil 3).

Table 1. Properties of the used soils

soil	organic carbon [%]	ps * [%]	pH values	water capacity [weight %]
1	0.25 - 0.75	10	5.5 - 7.5	26.5
2	2.0 - 3.0	10-20	5.5 - 7.5	43.9
3	0.5 - 1.5	20-30	5.5 - 7.5	38.6

% of soil removed by flowing water (fraction = 0,02 mm) soil 1 = humus rich sandy soil; soil 2 = clay loam soil; soil 3 = heavy clay soil

For the application the radioactive dimethoate (1 mg/ml benzene) was diluted with inactive dimethoate (1 mg/ml acetone). For the experiments 50g of the different soils were put in 300 ml Erlenmeyer flasks and held over night in rooms with constant temperature (10°C and 20°C) with 90 % of the calculated water capacity. The flasks were closed with wad stoppers. Always duplicate analyses were carried out. After 24 h 150µg of dimethoate, corresponding to 3 ppm, total radioactivity 1.61 x 10^7 dpm, were added to the flasks with soil 1 and 2 including the 10 % rest of water. For soil 3 200µg dimethoate (4 ppm, total radioactivity 3.14 x 10^7 dpm) were added. The closed flasks were held in rooms with constant temperature for 31 up to 36 days. At the times mentioned in the Fig. 1 and 2 the concentrations of dimethoate and omethoate were estimated. The recovery rates for dimethoate for the different soils were determined by adding a corresponding amount of dimethoate to a soil sample and extraction for 15 minutes.

For extraction of dimethoate and metabolites the different samples were shaken with 70 ml of a mixture of ethanol-water 2:1 for 30 minutes with a shaking machine. After setting down the mixtures were filtered through a middle hard grade paper. Corresponding to the different soils it was washed exhaustively with ethanol-water 2:1 and again filtered (ca. 200-250 ml). In 100 µl of the solution the total radioactivity was measured. Afterwards the samples were evaporated to 2 till 3 ml in a rotary evaporator and chromatographed. For TLC PSC-plates with silica gel 60 HF_{254} (0.25 mm with a 3 cm concentration zone) were used (Merck, Darmstadt, FRG). The plates were developed with the solvent system acetone-water 5:1. The TLC-plates were analysed for radioactive zones with an Automatic Linear Analyzer LB 2832 (Berthold, Wildbad, FRG).

The peaks were identified by cochromatography with authentic reference substances or by detection with a solution of 0.5 g $PdCl_2$ in 100 ml water and addition of some drops 25 % HCl.

(R_F dimethoate 0.91) (R_F omethoate 0.77)

Table 2. Persistence of dimethoate in clay loam soil at 10°C, applied amount 3ppm (150 µg = 1.61 x 10^7dpm per 50g of soil)

exp. time	extracted radioactivity		extracted amount dimethoate	omethoate	more polar compounds
[d]	[dpmx10^7]	[%]	[µg]	[µg]	[µg]
0	1.570	100.00	146,3*	0	0
3	1.465	93.31	136.5	0	0
6	1.270	80.89	116.0	2.2	0
10	1.080	68.79	98.0	2.4	0
13	0.990	63.06	90.5	1.7	0
17	0.900	57.32	75.6	4.7	2.3
21	0.703	44.78	50.6	4.4	7.0
28	0.480	30.57	26.5	3.0	10.3
32	0.422	26.88	16.1	2.7	14.0

* day 0 sample = 97,5% recovery

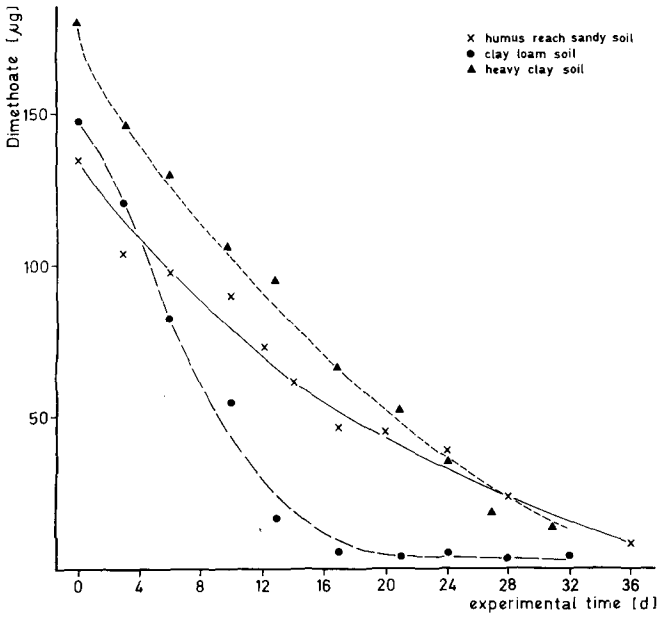

Figure 1. Degradation of dimethoate in three different soils at 20°C and at the maximum water capacity

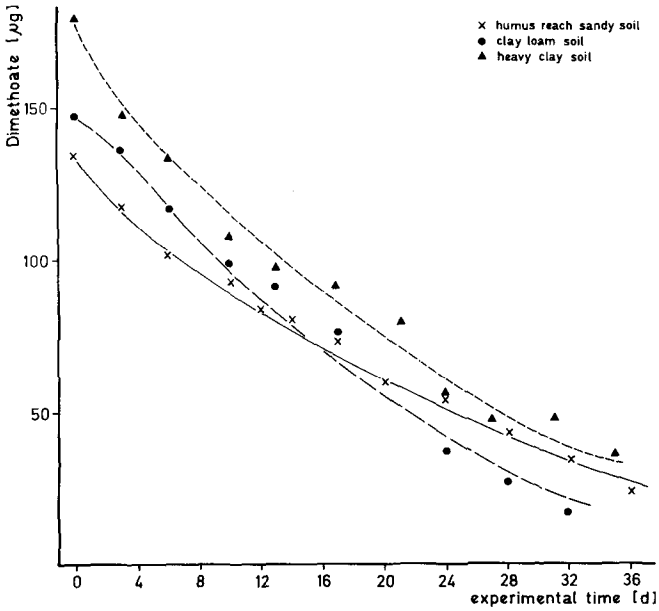

Figure 2. Degradation of dimethoate in three different soils at 10°C and at the maximum water capacity

Table 3. Persistence of dimethoate in clay loam soil at 20°C, applied amount 3ppm (150/ug = 1.61 x 10^7dpm per 50g of soil)

exp. time	extracted radioactivity		extracted amount dimethoate	omethoate	more polar compounds
[d]	[dpmx10^7]	[%]	[/ug]	[/ug]	[/ug]
0	1.570	100	146.3*	0	0
3	1.432	91.21	120.3	0	0
6	1.032	65.73	81.5	6.4	5.4
10	0.680	43.31	54.6	3.8	3.3
13	0.438	27.90	16.8	9.1	11.8
17	0.347	22.10	5.1	3.7	15.9
21	0.229	14.59	3.4	1.8	11.0
24	0.205	13.06	4.8	1.7	8.6
28	0.203	12.93	2.4	2.6	9.4
32	0.163	10.38	3.0	1.8	7.0

* day 0 sample = 97,5% recovery

RESULTS AND DISCUSSION

The results of the investigations on the persistence of dimethoate in three different soils at 10°C and at 20°C and at the maximum water capacity are summarized in Fig.1 and 2. Tab. 2 and 3 show exemplarily the residues of the dimethoate and of the omethoate and the amounts of dimethoate, which changed into more polar products, in the clay loam soil at 10 °C and at 20 °C. Adequate values are in our hand also for the other soils.

In the clay loam soil (Fig. 1 and 2) a fast decrease of the amount of the dimethoate occurs after a retardation phase of one to two days. Such retardation phase could not be observed in the other two soils used. If the degradation curve of the agent shows a retardation phase, this may be taken as an indication of a microbial decomposition. This agrees with the higher amount of organic carbon in the clay loam soil, which therefore is assumed to contain a higher amount of the microorganisms, in contrast to the other two soils. The degradation curves of the dimethoate in the heavy clay soil at 20°C and also at 10°C are similar to the degradation curves of the dimethoate in the humus rich sandy soil at the same temperatures. The decrease of the dimethoate in these both soils is weaker than in the clay loam soil.

Table 4 The half time values of the dimethoate in three different soils at 10°C and at 20°C

soil	temp. [°C]	t 1/2 [d]	r^2	rate constant
1	20	9.7 (5.8-13.5)	0.930	0.0717
1	10	15.3 (12.8-17.8)	0.969	0.0453
2	20	4.8 (0 - 9.6)	0.905	0.1455
2	10	10.3 (6.8-13.8)	0.949	0.0670
3	20	8.5 (4.8-12.2)	0.943	0.0816
3	10	15.8 (13.5-18.2)	0.977	0.0437

soil 1 = humus rich sandy soil; soil 2 = clay loam soil; soil 3 = heavy clay soil; r^2 = a rate for the precission of the regression

Assuming that the decrease of the dimethoate in the soils follows predominantly a reaction of the first order, the half time values can be calculated using the linear regression analysis on the natural logarithm of the amount of extracted dimethoate as a function of time (Goedicke and Endlich 1985). The half time values of dimethoate in the three soils and the rate constants of the dimethoate decrease are given in Tab. 4. In the humus rich sandy soil and also in the heavy loam soil the half time values of dimethoate are 9 days at 20°C and 15 days at 10°C, but in the clay loam soil the analogous values are 5 days at 20°C and 10 days at 10°C. This means, that the content of dimethoate decreases more fastly in the clay loam soil with the higher amount of organic carbon. Generally its rate of decrease is evidently lower in the three soils at 10°C than at 20°C.

The observed half time value for the clay loam soil from 5 days is in agreement with that from Bohn (1964) for sandy loam soil from 4 days in field measurements during drought conditions and a mean temperature of 22°C. He used about the double amount of dimethoate. On influence of moderate rainfall the disappearance of dimethoate is more rapid with a half time value of 2.5 days. The dimethoate did not migrate beyond 7.5 cm from the surface of the soil following multiple applications of the insecticide. The rate constant of the disappearance of dimethoate did not change at multiple applications.

The observed concentrations of omethoate, the main metabolite of dimethoate, are generally very low, because probably the transformation of this substance is relatively fast. After 6 days 2 to 3 µg of omethoate are observed in all three soils. The highest amount of omethoate (7 to 9 µg) was extracted from the soil after about two weeks. After this time the amount of omethoate

decreases and varies between 3 and 1/ug till the end of the experiment. There is no difference in the amount of omethoate between the three soils neither at 20°C nor at 10 °C.

Small amounts of the more polar compounds with unknown structures are observed in the humus rich sandy soil and in the heavy loam soil. The amounts are less than 5% of the applied dimethoate. But in the clay loam soil at 20 °C about 5% of the applied dimethoate are observed from 6^{th} day after application as transformed to more polar compounds. This amount increases to 15% until to 17^{th} day and then decreases to 7% till to 32^{nd} day. At 10°C 2% of the applied dimethoate react to more polar compounds. Until to the end of the experiments this amount increases up to 14%.

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