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Persistence of 4-Chloro-2-methylphenoxyacetic Acid in Soil

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MCPA (4-chloro-2-methylphenoxyacetic acid) is one of the most effective systemic foliar herbicides for the selective control of weeds, and the vast amounts that are used annually are degraded ultimately to yield non-toxic products. Different mechanisms have been proposed to explain how a soil microbial population develops the capacity to degrade a pesticide (AUDUS 1960, HAMAKER 1972). The metabolic pathway of MCPA has been studied by GAUNT (1962), GAMAR & GAUNT (1971), and GAUNT & EVANS (1971).

There are different reports concerning the persistence of MCPA, 2,4-D (2,4-dichlorophenoxyacetic acid) and/or 2,4,5-T(2,4,5-trichlorophenoxyacetic acid) in grassland, brushlands, forests and soil (PLUMB et al. 1977, NORRIS 1971, 1975, BURGER et al. 1962, AUDUS 1964), and the rate of degradation is variable from acid to neutral soil (THORSTENSON 1975), and again different moisture and temperature conditions (SATTAR & PAASIVIRTA 1980a,b). MCPA is widely used in Finland (TIITTANEN & BLOMQVIST 1979, 1981) for the control of weeds in the grass fields and brush control in the forests, and also extensively used in Sweden (AAMISEPP 1976). There is no literature about the persistence of MCPA in a typical soil from Jyväskylä. Therefore, the present study has been undertaken to determine the residues of MCPA to a typical agricultural soil in Finland.

EXPERIMENTAL

One sandy clay soil (pH 5.2, organic matter 6.3%, sand 50.2%, silt 32.5%, clay 18.1%, field capacity 18.2%) was collected from Mattila, Jyväskylä at a depth of 0-15 cm (mixture of five composite soil samples), dried at 23 ± 2°C, ground to pass through a 10-mesh sieve and then used for the experiment. Each 200 g soil was treated with 10, 100, 500 and 2000 ppm of MCPA-Na salt (Kemira Co., Finland) at field capacity moisture. The soil was incubated for 32 weeks at 23 ± 2°C, and soil samples were collected immediately after treatment and after 2, 4, 8, 16 and 32 weeks of incubation. Soils were dried at room temperature after sample collection.

Five and ten g soil from each sample were extracted after air-drying with diethylether-acetone-hexane-heptane (2:1:1:1) by adding 2,6-dimethoxyphenol (internal standard) in a Griffin flask shaker. The soil extract residues were derivatized with pentafluorobenzyl bromide (1% solution in acetone) in the presence of potassium

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carbonate and acetone. Finally, the water-toluene cleanup procedure was applied to the crude derivative sample. The extraction, derivatization and cleanup was applied following the method of SATTAR & PAASIVIRTA (1978, 1980a,b). A gas chromatograph with ^{3}H ECD was used. A 25 m long glass capillary column with 0.3 mm an external diameter and coated with SE-30 silicone phase was used. Temperature was 210°C for injector and detector. A programmed run was used, 120 to 200°C with 6°C/min. Nitrogen was used as carrier gas at 1 mL/min.

RESULTS AND DISCUSSION

The recovery yield of MCPA after the different periods of incubation is presented in Table 1 and result is the average of 4 analyses. Table 1 shows that the residues of MCPA decreased gradually with an increase of incubation time which was similar for four levels of MCPA application. The degradation rate was slightly slower with higher concentration of MCPA. At 0-day incubation the recovery was almost 100% with all treatments, but after 2 weeks of incubation, it had decreased to 40%, and after 8 weeks to 60% (average rate). The dissipation was up to as much as 98% for the samples incubated for 32 weeks.

Table 1. Residues of MCPA (ppm) in Soil with Different Periods of Incubation.

Incubation time (weeks)	Fortification (ppm)			
	10	100	500	2000
0	9.85	98.5	496	1990
2	5.76	58.3	298	1210
4	4.44	45.1	236	986
8	1.70	20.2	107	444
16	0.72	7.9	45	205
32	0.08	1.5	12.7	65.6

Table 2 shows the per cent of MCPA residues remaining in soil with different periods of incubation. At 0-day, the overall recovery yield was 98.9% which decreased gradually due to degradation, and after 32 weeks the yield recovered was 2.0%. The overall degradation rate (Table 2) has been observed with a linear regression as follows:

Linear regression: $y = ax + b$

where a is the slope of the line and b is the y-intercept

The results have been fitted to the linear regression line in Fig. 1 by observing the residues remaining in soil (%), log versus incubation time. The linear regression shows the similar expression with different levels of MCPA (Table 3).

The examples of the different chromatograms have been presented in Fig. 2 (A-D), 4-chloro-o-cresol (2) and 5-chloro-3-methylcatechol (3) are the metabolites of MCPA (1), and here the metabolites 2 and 3 have also been identified by gas chromatographic peaks (Fig. 2D)

Table 2. Per Cent MCPA Residues Remaining in Soil with Different Periods of Incubation.

Incubation time (weeks)	Fortification (ppm)			
	10	100	500	2000
0	98.5	98.5	99.1	99.5
2	57.6	58.3	59.5	60.7
4	44.4	45.1	47.1	49.3
8	17.0	20.2	21.4	22.2
16	7.2	7.9	9.0	10.3
32	0.8	1.5	2.5	3.3

Table 3. The Slope (a), y-Intercept (b), and Correlation Coefficient (r) of the Linear Regression by Plotting the Residues (%) of MCPA Against Incubation Days.

MCPA applied (ppm)	b	a	r
10	62.7	-2.43	-0.790
100	63.7	-2.43	-0.800
500	62.3	-2.29	-0.768
2000	66.1	-2.44	-0.809
Overall average	64.4	-2.44	-0.801

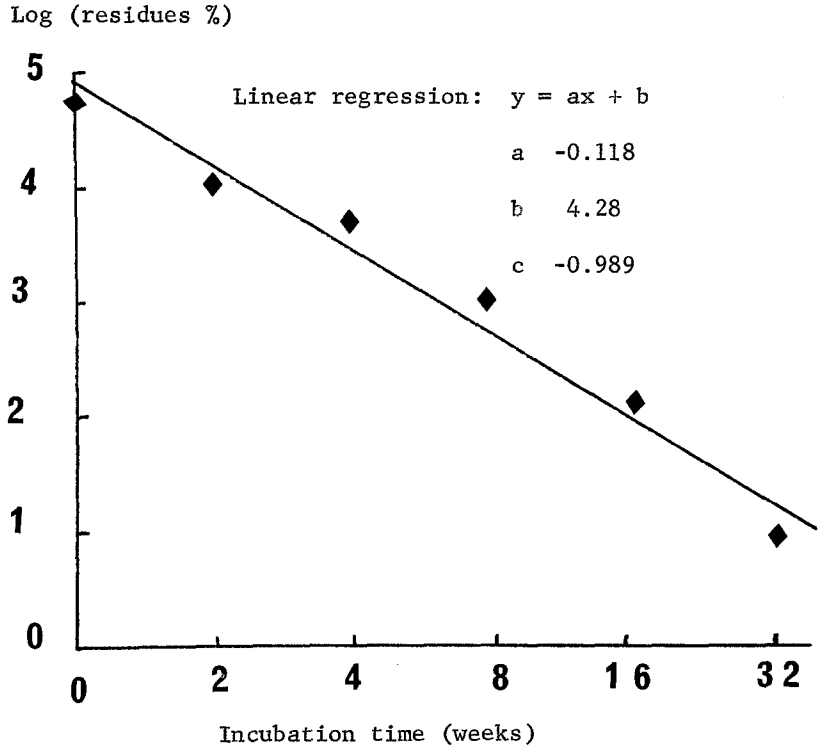

Fig. 1. Logarithms of the Measured MCPA Residues (average %) Remaining in Soil with Different Periods of Incubation and Corresponding Linear Regression Line.

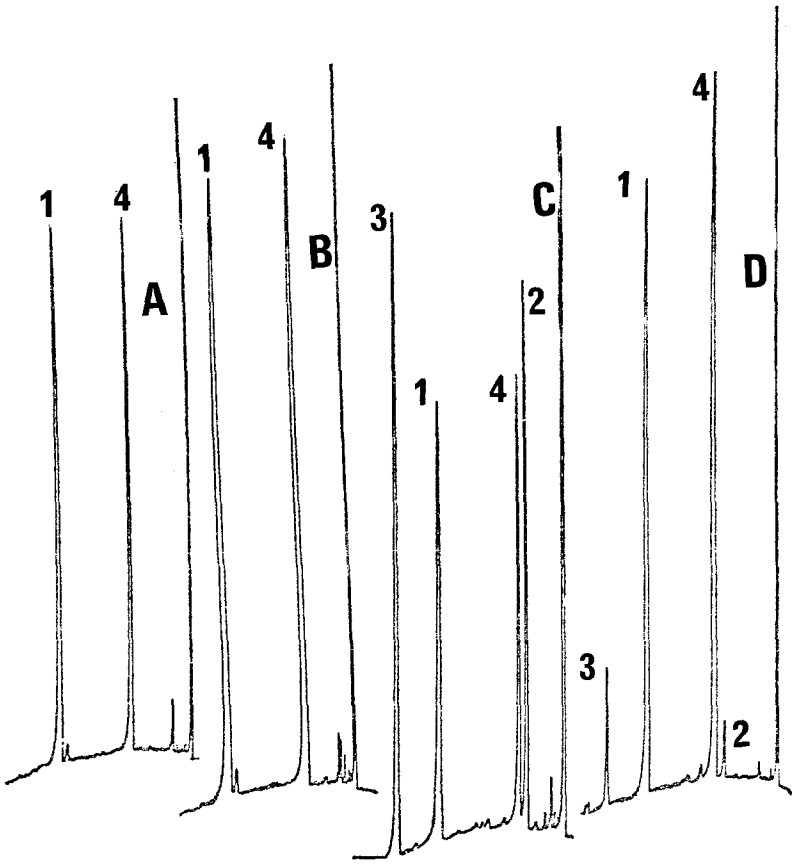

Fig. 2. Examples of the Different Gas Chromatograms (A-D) of MCPA (1), 4-chloro-o-cresol (2), 5-chloro-3-methylcatechol (3) and 2,6-dimethoxyphenol (Internal Standard, 4). (A) Model Compound Mixture. (B) At 0-Day Incubated Soil Sample. (C) Model Compound Mixture. (D) Soil Sample after 4 Weeks of Incubation.

compared to the respective standard peaks in Fig. 2C. The metabolites have also been verified by a mass spectrometry (SATTAR & PAASIVIRTA 1980a). The residue levels down to ppb were measured in MCPA and the results verified by mass fragmentography (PAUKKU & PAASIVIRTA 1980, SATTAR et al. 1981).

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