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Fate of ^{14}C-Nitrofen in Soils

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Nitrofen (2, 4-dichlorophenyl-p-nitrophenylether) is a selective pre- and post-emergence herbicide for the control of annual grasses and various broad leaved weeds in cereal grains and vegetables. Microorganisms play an important role in the degradation of nitrofen (Lee et al, 1980 and 1982; Oh et al, 1981). We had found that the degradation of nitrofen was rapid in a rice-fish model ecosystem (Kale and Raghu, 1989). The purpose of present study was to follow the degradation of nitrofen as affected by flooding and green manure amendment under semi-tropical conditions and the results are presented here.

MATERIALS AND METHODS

Vertisol soil (pH - 7.2 Org. carbon - 1.26% Nitrogen - 0.46%.) collected from Trombay (Bombay) experimental field was used. Ten gram soil samples were taken in test tubes and maintained either under moist (60% WHC) or flooded (3cm water above the soil surface) conditions. In case of sterilized soil samples, sterilization was done by autoclaving (Kale and Raghu, 1982). Cotton plugs were used as stoppers. For green manure amendment, leaves of Glyricidia sepium (Jacq) Walp. Syn. G. maculata (H. B. K.) were puddled into the soil at the rate of 28 t/ha after 7 days of flooding. The pesticide was added after another 7 days. Duplicate samples were used for each treatment and these studies were conducted over a period of 30 days. Uniformly labelled ^{14}C-nitrofen (sp. activity 14.2 µci/mg) was added to every tube except the control tubes at the rate of 2.5ppm. The tubes were incubated at 30°C and the samples were analysed after 10, 20 and 30 days.

Soil samples were extracted twice by shaking with 100 ml acetone on a rotary shaker (100rpm) for 1 hour followed by filtration through Buchner funnel. The aliquots of the extracts were counted in liquid scintillation counter (Packard Tricarb 3255). The

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Table 1. Total ^{14}C-activity recovered from sterilized, unsterilized and green manure amended soils treated with ^{14}C-nitrofen.

		Sterilized			Unsterilized			Green manure amended		
	Day	E	B	T	E	B	T	E	B	T
Moist	10	96.8 ±2.3	6.4 ±0.2	103.2	83.1 ±0.24	18.8 ±0.5	101.9	65.9 ±1.2	30.6 ±1.7	96.5
	20	90.7 ±3.7	9.8 ±0.1	100.5	89.5 ±2.8	14.1 ±1.5	103.6	58.1 ±0.8	22.9 ±1.2	81.0
	30	92.0 ±3.5	10.6 ±0.6	102.6	77.7 ±2.7	15.6 ±0.8	93.3	54.1 ±1.1	7.0 ±0.5	61.1
Flooded	10	97.9 ±3.6	2.9 ±0.1	100.8	60.9 ±1.6	21.4 ±0.3	82.3	52.1	24.0	76.1
	20	102.7 ±4.3	6.0 ±0.3	108.7	49.1 ±1.7	26.1 ±0.6	75.2	39.5 ±3.2	45.1 ±2.0	84.6
	30	97.2 ±2.2	6.8 ±0.7	104.0	38.5 ±1.5	55.8 ±1.2	94.3	32.3 ±2.3	21.7 ±1.2	54.0

E - Extractable residues B - Bound residues T - Total residues.

acetone extracts were partitioned with 25 ml petroleum ether and 600 ml 2% sodium sulphate solution. The petroleum ether extracts were subjected to thin layer chromatography (aluminum oxide plates of 0.25mm thickness) using the solvent system hexane:dichloromethane (1:1). The radioactivity in various extracts was estimated by using a liquid scintillation counter. The cotton plugs were subjected to Soxhlet extraction using acetone to determine any volatile fraction. Non-extractable or bound residues were determined by combustion of 50mg of powdered soil samples in a Biological Material Oxidizer (R.J.Harvey, NJ., USA). The $^{14}CO_2$ evolved was trapped in Oxysolve-C cocktail (Zinsser Analytic, UK) and estimated by liquid scintillation counting. Quench corrections were made using channel ratio method.

RESULTS AND DISCUSSION

In sterilized moist soil, nitrofen did not undergo any degradation (Table 1) and TLC runs of the extractable residues showed that most of all the activity was in the form of parent compound (Table 2). In unsterilized unamended moist soil also, the herbicide did not show any appreciable degradation. At the end of 30 days the extractable residues were 77.7% and bound residues were 15.6% (Table 1). No significant amount of aminonitrofen was detected.

Table 2. Distribution pattern of nitrofen and amino-nitrofen (% of applied activity) in sterilized, unsterilized and green manure amended moist soils.

Treatment	Day	Nitrofen	Amino nitrofen	Origin	Rest
Unamended sterilized	10	97.4	1.7	5.2	1.1
	20	96.4	2.1	1.5	0.8
	30	94.3	1.8	4.4	1.6
Unamended unsterilized	10	80.2	1.4	8.2	1.3
	20	91.3	4.7	1.7	0.9
	30	74.5	0.7	1.6	0.9
Green manure amended unsterilized	10	45.0	1.5	5.6	5.5
	20	51.5	1.2	2.4	2.6
	30	49.5	0.7	1.7	2.2

Table 3. Distribution pattern of nitrofen and amino-nitrofen (% of applied activity) in sterilized, unsterilized and green manure amended flooded soils.

Treatment	Day	Nitrofen	Amino nitrofen	Origin	Rest
Unamended sterilized	10	88.1	0.7	3.2	5.9
	20	99.5	0.9	0.9	1.5
	30	93.9	0.7	1.5	1.0
Unamended unsterilized	10	16.2	8.1	11.8	17.1
	20	12.9	5.0	20.6	10.6
	30	7.9	8.6	7.2	14.8
Green manure amended unsterilized	10	5.7	9.0	21.0	9.9
	20	8.7	5.3	9.4	16.0
	30	4.3	16.2	6.2	5.5

In unsterilized unamended flooded soils, there was faster degradation of the herbicide even at 10 day incubation as compared to that in moist soil (Table 1). The extractable residues rapidly decreased from 60.9% at 10 days to 38.5% at 30 days while bound residues increased from 21.4% to 55.8% during the same period. In contrast, in moist soil under similar conditions the proportion of bound residues remained fairly constant (14-19%) throughout the period of incubation. TLC of the soil extracts of unamended flooded soil showed that nitrofen rapidly decreased even at 10 days (Table 3). At 10 days 16.2% of the applied activity was in the form of nitrofen and it subsequently decreased to 7.9% at 30 days. Solvent extraction of cotton plugs did not show any radioactivity suggesting the absence of any volatiles. Flooding has been shown to enhance the degradation of nitrofen [Niki and Kuwatsuka (1976), Oh et al (1981), Qian et al (1982) and Oyamada and Kuwatsuka (1988)].

Green manure amendment decreased the persistence of nitrofen in moist soil (Table 1). The extractable activity decreased from 65.9% at 10 days to 54.1% at 30 days while bound activity also decreased from 30.6% to 7.0%. In flooded soil, green manure amendment decreased the extractable residues considerably at the end of 30 days (Table 1). It is seen than less than 10% of it remained as parent compound at the end of 10 days and aminonitrofen was the major degradation product in

extractable residues (Table 3). Lee et al (1980) in their studies found that aminonitrofen was a major metabolite. Green manure amendment to flooded soils is known to decrease the persistence of HCH isomers (Ferreira and Raghu 1981) and DDT (Mitra and Raghu 1988).

These results suggest that nitrofen undergoes faster degradation in flooded than in moist soils and the degradation is further enhanced by the addition of green manure.

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