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Mineralization, Volatilization, and Degradation of Carbofuran in Soil Samples from Kenya

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Carbofuran (2,3-dihydro-2, 2-dimethyl-7-benzofuranyl-N-methylcarbamate) is an effective systemic and contact insecticide and nematicide used against a wide range of agricultural pests (Aquino and Pathak, 1976; Caro et al, 1973). Though carbofuran is less persistent than the organochlorine pesticides, it is acutely more toxic to animals. It is very water soluble and tends to disappear faster from flooded soils by microbial degradation, volatilization and leaching (Venkateswarlu et al, 1977; El-Zorgani, 1976; Lalah and Wandiga, 1993). In Kenya, carbofuran is extensively used against rice pests in paddy fields and because of its high acute toxicity to fish and mammals (LD_{50} 11 mg/kg in rats), the fate of its residues in terms of their persistence, mobility and dissipation pathways is of great concern (Lalah, 1993; Plimmer, 1988). It is applied at the rate of 0.5 - 4 kg a.i./ha for the control of soil dwelling, foliar feeding insects and mites at the seed furrow in rice paddy fields. Approximately 97% of all the rice in Kenya is produced by irrigation schemes covering 9000 hectares Lalah and Wandiga, 1993). With the increasing population, efforts are being made to intensify rice production and to increase this acreage. This will result in an increase in the use of carbofuran at least in the near future. Laboratory studies on its adsorption and desorption confirm that carbofuran adsorbs strongly to this soil and that its adsorption is influenced by the organic matter and clay content of the soil (Lalah and Wandiga, 1993). However, due to its high water solubility, it leaches extensively in this soil both under laboratory and field conditions (upto 33% found in the leachate after 48 hours of test). A number of different metabolites have been identified from the soil confirming the great microbial and chemical activity on carbofuran in the soil. The aim of this experiment was to follow the rate of mineralization, volatilisation and degradation of carbofuran in the Ahero soil sample under laboratory conditions.

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MATERIALS AND METHODS

Ring labelled ^{14}C-carbofuran (carbofuran/benzofuranyl-ring 2C-14); specific activity of 86.5 µCi and radiochemical purity of 99% by TLC was obtained from IAEA, Vienna. Non-labelled standards i.e. carbofuran, 3-hydroxycarbofuran, 3-ketocarbofuran, carbofuran-7-phenol, 3-hydroxycarbofuran-7-phenol were obtained from the Department of Toxicology, NCSU, USA. Solvents, dichloromethane, ethylacetate and benzene were all of residue grade. A Harvey cocktail for $^{14}CO_2$ absorption was obtained from the Department of Toxicology, NCSU, USA. Paper lined standard glass tanks, precoated silica gel SIL G/UV 254 plates were used to identify the metabolites which were viewed at 254 nm. A Berthold LB2832 Automatic TLC Linear Analyzer was used to locate the radioactive spots. A Perkin Elmer 1000TR liquid scintillation spectrometer was used for radioassay and the bound residues were combusted in a Harvey OX- 600 Biological Oxidizer. Biometer flasks (250 mL) were obtained from Bellco Glass, Inc., New Jersey.

The soil sample used in this study was collected from the Kano Plains of Kenya. It was a lowland heavy sandy soil type. The composition of the soil was as follows: pH 7.0; sand 38%; clay 37%; silt 25%; organic matter 1.08%; moisture content 5.3%. The soil was air dried in the laboratory, ground with mortar and pestle and sieved through a 2 mm mesh. Approximately 25 g samples of soil were weighed and then transferred into 250 mL Bellco biometer flasks placed in the laboratory. One set of the soil samples in the flasks were flooded by adding 20 mL portions of water. The other set of samples were left non-flooded. A mixture of 5.12 mg of radiolabelled and non-labelled carbofuran was added to each set of the soil samples and stirred to obtain a homogeneous sample. The biometer flasks were left undisturbed in the laboratory for 33 days. Some 20 mL of 1M KOH was used to trap the $^{14}CO_2$ produced while the organic volatiles were trapped by polyurethane plugs placed at the passage between the soil sample and the KOH trap. Sampling was done by taking two flasks (one non-flooded and the other one flooded) and analysing for extractable and bound residues, the polyurethane plug extracted to obtain the organic volatiles and $^{14}CO_2$ trapped in 1 M KOH. Sampling was after 4, 7, 20 and 33 days. The extractable residues from polyurethane plugs and the soil samples were determined by Soxhlet extraction with dichloromethane (150 mL) for 8 hours. Aliquots of the extracts were counted to determine the residues and a sample of the extracted soil was combusted to determine the bound residues. A sample (1 mL) of water from the flooded soil sample was also taken for counting. The results are summarised in the following tables.

RESULTS AND DISCUSSION

The following tables, 1, 2 and 3 summarize the results of the experiment. Tables 1 and 2 show the extent of mineralisation and volatilisation of carbofuran in the two sets of soil samples while table 3 shows the percentage residues determined in the different components of the soil samples both under flooded and non-flooded conditions.

Table 1. $^{14}CO_2$ production in the soil samples.

Incubation period (days)	Flooded soil mg carb. equiv.	(%)	Non-flooded soil mg carb. equiv.	(%)
4	0.04	0.73	0.07	1.33
7	0.06	1.53	0.11	2.21
20	0.10	2.85	0.22	4.26
33	0.38	13.77	0.56	11.04

Note: carb. denotes carbofuran
equiv. denotes equivalent.

Table 2 ^{14}C-Organic volatiles trapped from the soil samples

Incubation period (days)	Flooded soil mg carb. equiv.	(%)	Non-flooded soil mg carb. equiv.	(%)
4	0.07	1.4	0.09	1.8
7	1.27	24.8	0.33	6.4
20	2.00	39.1	0.84	16.4
33	2.57	50.3	0.65	12.8

Table 3 The percent dissipation of carbofuran in flooded and non-flooded soils

Period	bound		extracts		Water		$^{14}CO_2$		Vol	
(days)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
4	18	5.2	42	94	39	-	0.7	1.3	1.4	1.8
7	6.1	9.7	36	88	32	-	1.2	2.3	25	6.4
20	9.9	6.1	23	89	26	-	1.7	4.9	39	16
33	2.5	0.8	17	87	24	-	6.8	12	50	13

Note: (a) represents flooded soil, (b) represents non-flooded soil, Vol. represents organic volatiles. 100% represents the amount of chemical added to the soil sample initially i.e. 5.12 mg mixture of ^{14}C-carbofuran and non-labelled carbofuran.

TLC analysis was done on the soil sample extracts. The plates were developed in benzene + ethyl acetate (8+2 by volume) and viewed under UV lamp. From analysis of soil extracts using TLC techniques, the following metabolites (table 4) were identified and quantified. The metabolites were identified by co-chromatography with known standards and confirmed on a TLC scanner. By cutting out the radioactive spots on the TLC plates, the identified metabolites were quantified by counting and expressed as a percentage of the total counts in the samples spotted before development. The results are summarized in the following table 4.

Table 4 Percent metabolites identified in non-flooded soil sample extracts.

Incubation period (days)	Carbofuran		Carbofuran-7-phenol		3-Keto carbofuran-7-phenol	
	(a)	(b)	(a)	(b)	(a)	(b)
4	99.5	99.6	0.27	0.19	0.25	0.18
7	99.1	99.6	0.72	0.19	0.22	0.21
20	88.7	97.5	10.30	2.16	1.03	0.30
33	63.1	94.9	35.46	3.14	1.42	1.93

(a) and (b) represent flooded and non-flooded soils, respectively.

The amount of $^{14}CO_2$ produced as a percentage of total residues i.e. the rate of mineralization, was found to be slightly more rapid in non-flooded soil than in flooded soil samples. However, the rate of volatilization of carbofuran was much more rapid under flooded soil than under non-flooded soil conditions. This can be explained because carbofuran is very water-soluble and is therefore lost rapidly by co-evaporation with the water on the surface of the soil. This was also found to be the case in studies carried out under field conditions where rapid disappearance of carbofuran was recorded during the first 18 days after pesticide application (Lalah, 1993). The rate of formation of bound residues was higher in flooded soils than in non-flooded soils, constituting upto 18.5% in flooded soils and 5.23% in non-flooded soil samples after 4 days. However, the levels of bound residues were lower than those found in the same type of soils under field conditions. A large proportion of carbofuran residues were detected in the water phase of the flooded soils, 38.7% after 4 days and 23.7% after 33 days. The Soxhlet extractable residues still contained the greatest portion of recovered residues in both flooded and non-flooded soils. The main metabolites identified in both soils were carbofuran, carbofuran-7-phenol and 3-ketocarbofuran-7-phenol. The TLC results confirmed more degradation of carbofuran under flooded soil conditions. This was also found to be the case in the field studies.

These results confirm that carbofuran is more rapidly metabolised under flooded soils than under non-flooded soils. The major dissipation pathway is volatilization which is greatly influenced by the high solubility of carbofuran in flooded water.

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