Bull. Environ. Contam. Toxicol. (1996) 56:575-583

Bulletin of Environmental Contamination and Toxicology

Adsorption/Desorption and Mobility of Carbofuran in Soil Samples from Kenya

J. O. Lalah, S. O. Wandiga

Department of Chemistry, College of Biological and Physical Sciences, University of Nairobi, P.O. Box 30197, Nairobi, Kenya

Received: 10 October 1994/Accepted: 9 October 1995

Carbofuran (2,3-dihydro-2-2-dimethyl-7-benzofuranyl-N-methylcarbamate) is a very effective systemic and contact insecticide and nematicide used against a wide range of agricultural pests (Aquino and Pathak, 1976; Caro et al., 1973). Though less persistent than most organochlorine pesticides, carbofuran is more toxic to animals, it is very soluble in water and tends to degrade faster under flooded soil conditions (Caro et al., 1973; Venkateswarlu et al., 1977; El-Zorgani et al., 1980). The adsorption and desorption characteristics which determine the movement of pesticides through the soil profile, their bioavailabiltiy, microbial degradability and persistence depend upon the soil properties such as organic matter content, clay content and the physical/chemical properties of the pesticide i.e. size, shape, solubility in water, pK values and polarity (Wondimagegnehu and Foy, 1986; Calderbank, 1989). In Kenya, carbofuran is used extensively against rice pests in paddy fields and because of its acute toxicity the fate of its residues in terms of their persistence and mobility is of great concern (Anonymous, 1985; Plimmer, 1980). The aim of this study was to investigate the adsorption/desorption and mobility of carbofuran in samples of soil collected from the Ahero and Chiromo areas of Kenya.

MATERIALS AND METHODS

The two soils used in this study were collected from two different agricultural regions of Kenya i.e. the lowland heavy, sandy soils of the Kano Plains at Ahero and the red, silt loam soils from Chiromo in Nairobi. A third soil was a standard sandy soil obtained from the Institute of Ecological Chemistry, GSF, Munich. The composition and physical characteristics of the three soils are presented in Table 1. The soil samples were air-dried in the laboratory, ground with mortar and pestle and sieved through a 2 mm mesh.

Correspondence to: J. O. Lalah

Labelled ^{14}C-carbofuran (2,3-^{14}C-dimethyl-2,3-dihydro/3-^{14}C/benzofuran-7-yl-methylcarbamate); specific activity: 728.3 MBq/mmol and radiochemical purity of 97% by TLC was obtained from the Institute of Isotopes, Budapest, Hungary. Non-labelled standards of carbofuran, 3-hydroxycarbofuran, 3-ketocarbofuran and 3-ketocarbofuran phenol were kindly supplied by the Institute of Ecological Chemistry, GSF, Munich. Anhydrous calcium chloride, residue grade dichloromethane, acetone, n-hexane and methanol and HPLC methanol, acetonitrile, and water were used including Hydroluma cocktail for scintillation counting. Precoated TLC plates Silica Gel SIL G/UV 254 were used for TLC analysis.

Glass centrifuge tubes (100 ml), overhead shaker, and a 1200 rpm centrifuge were used in the adsorption/desorption studies. A low pressure rotating pump and glass columns (size: diameter 4.6 cm; height 27 cm) were used in the leaching experiments. Other apparatus used include a rotary evaporator, a Soxhlet apparatus and a nitrogen evaporator for concentrating the sample extracts. Equipment used were a Berthold BF 8000 Liquid Scintillation Spectrometer, a Packard 306 Automatic Sample Oxidizer, a Berthhold UV lamp at 254 nm, a Berthold Automatic Linear analyzer Scanne and a Hewlett Packard HPLC with ODS column fitted to a Berthold Two Channel UV-radioactive detector LB510 and an automatic fraction collector.

For the adsorption and desorption studies, the procedure followed was that developed by the European Economic Community (EEC 1988). Five grams of dry soil were weighed into 100 ml glass centrifuge tube and 25 ml of 0.01 M $CaCl_2$ solution containing a mixture of non-labelled carbofuran and ^{14}C-carbofuran was added. A blank centrifuge tube containing only 5 grams of soil and 25 ml 0.01 M $CaCl_2$ solution and two control tubes containing only 0.01 M $CaCl_2$ solution and radiolabelled carbofuran were also prepared. For the other tubes, tests were conducted in duplicate. The experiments were done at 5 ppm (0.025 mg cold carbofuran and 0.0045 µCi ^{14}C-carbofuran), 1 ppm (0.005 mg cold carbofuran and 0.0009 µCi ^{14}C-carbofuran) and 0.2 ppm (0.001 mg cold carbofuran and 0.00018 µCi ^{14}C-carbofuran) each in 25 ml of 0.01 M $CaCl_2$ solution. Samples were shaken on an overhead shaker at room temperature (about 25°C) for 22 hours, a period of time which was found to be sufficient to attain equilibrium. Samples were shaken and centrifuged at 1200 rpm for 10 minutes after 0, 2, 4 and 22 hours respectively. Then 2 ml aliquot of supernatant was removed and added to 15 ml Hydroluma cocktail for counting. The difference between the amounts of ^{14}C-residues found in the standard solution and the supernatant was taken to be the amount adsorbed by the soil.

Desorption was determined on the same samples used for the adsorption test by removing a known volume of the supernatant (75%) from the tube after 22 hours and then replacing it with equal amounts of pesticide free 0.01 M $CaCl_2$ solution. Two desorption extractions were made simultaneously. Each time the tubes and the contents were shaken and centrifuged as described above and 2 ml aliquot removed and counted after 0,2,4,6 and 22 hours of shaking.

In the leaching experiments, soil samples were packed in glass columns (diameter: 4.6 cm) to a height of 27 cm with a glass wool plug at the bottom (Wondimagegnehu and Foy, 1986). Each soil column was saturated with 0.01 M $CaCl_2$ by passing the solution through it upwards by capillarity for 12 hours. The column was then allowed to drain free overnight with 0.01 M $CaCl_2$ solution passing through it at a predetermined rate. The dry mass of soil in each column was 550 grams. Approximately 5.01 mg of ^{14}C-carbofuran (244,200 dpm) was placed on top of the soil column and washed with 0.01 M $CaCl_2$ solution at the rate of 7 ml per hour for 48 hours. The volume of the leachate was measured and analyzed for radioactivity. The soil column was carefully removed and divided into O-5 cm, 5-10 cm, 10-15 cm, 15-20 cm, 20-25 cm and 25-27 cm sections for analysis of ^{14}C-residues. The volume of the leachate was analyzed by adding 2 ml aliquots to a cocktail for liquid scintillation counting. The metabolites in the leachate were analyzed by taking 100 ml acidifying with a few drops of 0.25 M HCL and extracting 3 times with 50 ml CH_2Cl_2. The extracts were combined and reduced to dryness in a rotary evaporator at about 20°C and then redissolved in 10 ml of methanol for TLC and HPLC. An aliquot of the extracts was spotted on precoated silica gel plates and developed in n-hexane:acetone (60:40 v/v). The plates were visualized under the UV lamp at 254 nm and the presence of ^{14}C-carbofuran in the extract was further confirmed in a TLC scanner. The metabolites were also analyzed by a Hewlett Packard HPLC with an ODS column (a Beckman stainless steel 250 * 4.6 mm, 5nm), solvent: acetonitrile/water (7:3 v/v), flow rate: 1.2 ml/min; injection volume: 10 µL. To determine the carbofuran residues in soil, the soil samples from each section of the column were air-dried in the laboratory and 25 grams weighed and Soxhlet extracted with 150 ml of dichloromethane and an aliquot taken for counting. The extracted soil was air-dried and combusted to determine the bound residues. The dichloromethane extract was reduced to dryness, redissolved in methanol and analyzed by TLC and HPLC as outlined above.

RESULTS AND DISCUSSION

Table 1 shows the results of the physical characteristics of the soil samples used for the adsorption/desorption and mobility tests of carbofuran in soil. Before the experiments were run, several preliminary tests were performed on standard sandy soil samples obtained from the Institute of Ecological Chemistry, GSF, Munich.

Table 1. The Physical characteristics of the soils used

Soil	pH	Sand	Clay	Silt	*OC	Moisture
Ahero	7.0	38	37	25	1.08	5.3
Chiromo	6.1	30	42	28	1.22	6.5
GSF Sandy	6.0	97	5.1	3.2	0.7	0.69

Note: * OC denotes organic carbon.

Tables 2,3 and 4 show the results of the adsorption and desorption of carbofuran in Chiromo and Ahero soils. The amount of carbofuran adsorbed to Ahero soil was slightly higher than the amount absorbed to Chiromo soils. In Ahero soil samples the amount of the pesticide adsorbed (as % of applied pesticide) also increased when the concentration of pesticide applied was lowered i.e. 32.3% with 5 ppm, 33.2% with 1 ppm and 36.8% with 0.2 ppm of carbofuran applied to the soil. The results show that adsorption depends on both clay and organic matter contents of the soil. As evidently shown, more carbofuran was adsorbed onto Ahero soil and Chiromo soil although it was more difficult to remove the adsorbed pesticide from the Chiromo soil than from the Ahero soil. There was stronger adsorption of carbofuran onto Chiromo soil and of the total amount of pesticide adsorbed onto Ahero soil, up to 70% was desorbed while only about 39% of the total pesticide adsorbed onto Chiromo soil was removed within the 6 hours of the desorption test. It was also observed that the adsorption of carbofuran onto Ahero soil to attain equilibrium was more rapid than onto Chiromo soil.

Table 2. The Adsorption (as % of applied pesticide)

Time (hours)	Ahero soil			Chiromo soil		
	0.2ppm	1ppm	5ppm	0.2ppm	1ppm	5ppm
0	0	0	0	0	0	0
2	36.6	28.5	29.5	19.5	20.3	19.6
4	32.8	29.9	29.8	25.7	24.7	28.1
22	36.8	33.2	32.3	32.3	31.9	31.9

Table 3. The adsorption of pesticide (µg/g of soil)

Time (hours)	Ahero Soil			Chiromo soil		
	0.2 ppm	lppm	5ppm	0.2ppm	lppm	5ppm
0	0	0	0	0	0	0
2	0.07	0.29	1.48	0.04	0.20	0.98
4	0.07	0.30	1.49	0.50	0.25	1.41
22	0.07	0.33	1.62	0.06	0.32	1.60

Table 4 The Desorption (as % of adsorbed pesticide) at 5 ppm concentration

Time (hours)	Ahero Soil		Chiromo Soil	
	%desorp.	µg pestic	%desorp.	µg pestic
0	30.8	2.49	13.3	1.06
2	29.1	1.55	13.3	0.91
4	22.9	0.87	10.2	0.61
22	20.3	0.58	9.8	0.56
Total adsorbed		8.08		7.98
Total desorbed		5.49		3.14
Desorp: % of total adsorbed		70%		39%

Note: Desorp. denotes desorption.
pestic. denotes pesticide.

Table 5 shows the soil column leaching profile of carbofuran in the three soils. The distribution of carbofuran in sections of the soil columns is shown as the total radioactivity (extractable plus bound residues) in the sections as a percentage of the total radioactivity applied to the column at the beginning of the experiment. The experiment lasted 48 hours. These percentages are expressed as µg of carbofuran equivalents based on total recovered activity in each section of the column and the specific activity of carbofuran used. The results show very rapid vertical movement of ^{14}C-carbofuran and metabolites down the soil columns. After 48 hours, 33% of total radioactivity was recovered in the leachate from the Ahero soil, 29% in the Chiromo soil and 60% in the sandy soil leachate. This again suggests a stronger adsorption of carbofuran (due to higher clay and organic matter contents) in the chiromo soil than the other soils. Sandy soil had very little clay and organic matter compared to the other soils and as expected there was more extensive leaching of carbofuran in this soil.

Table 5. Leaching of carbofuran in the soils after 48 hours

Section of column	Ahero soil		Chiromo soil		Sandy soil	
	mg carb equiv.	% tot	mg carb equiv	% tot	mg carb equiv	% tot
0-5 cm	0.2	3.95	0.28	5.6	0.03	0.52
0-03 cm	0.14	2.78	0.56	10.5	0.02	0.34
10-15 cm	0.30	6.01	0.53	10.5	0.02	0.38
15-20 cm	0.63	12.5	0.62	12.2	0.03	0.65
20-25 cm	0.79	15.8	0.67	13.3	0.11	0.24
25-27 cm	0.98	19.5	0.23	4.38	0.20	4.02
Leachate	1.65	33.0	1.63	29.0	3.01	60.0

Note: 550 gm of soil sample in the column was treated with 5.01 mg ^{14}C-carbofuran. The same amount of soil and chemical was used for the three types of soil.
Carb denotes carbofuran.
tot. denotes total.
equiv. denotes equivalent.

Tables 6, 7 and 8 show some of the metabolites that were identified by HPLC. The identification was based on cochromatography with authentic standards and the presence of ^{14}C-carbofuran equivalents was also confirmed by TLC scanning after developing in n-hexane: acetone (60:40 v/v). The HPLC was with an ODS column, solvent system; acetonitrile/water (70/30 v/v); flow rate 1.2 ml/min; injection volume: 10 µL. The absorbance was at 205.4, 215.4, and 280.6 nm. The ratios of each metabolite against the total number of metabolites identified in each section of the column are given in the tables.

The results show a very rapid vertical movement of carbofuran residues down the soil columns. Some 33% of total radioactivity was recovered in the leachate from the Ahero soil while 29% and 60% were recovered from the Chiromo and GSF sandy soil columns, respectively. The effect of microorganisms on the degradation of carbofuran in the soil columns is the formation of more metabolites and these seem to bind more to the Chiromo soil sample. Also many of these metabolites were present in the leachate in trace amounts indicating that most of them had eluted from the soil columns.

Table 6. Carbofuran metabolites present in the Ahero soil column. (as % of total number of metabolites)

Section of Column	% Metabolite				
	(a)	(b)	(c)	(d)	(e)
0-5 cm	44.6	44.6	10.8	-	-
5-10 cm	26.7	-		52.2	21.1
10-15 cm	42.4	-		-	57.6
15-10 cm	31.3	-		68.7	-
25-27 cm	6.3	-		63.5	30.0
Leachate	32.8	-		55.6	11.6

Note : (a) represents carbofuran,
(b) represents 3-hydrocarbofuran,
(c) represents 3-ketocarbofuran
(d) represents 3-hydroxycarbofuran phenol,
(e) represents 3-ketocarbofuran phenol

Table 7. Carbofuran metabolites present in the Chiromo soil column. (as % of total number of metabolites)

Section of Column	% Metabolite				
	(a)	(b)	(c)	(d)	(e)
0-5 cm	27.6	-	36.3	-	36.1
5-10 cm	29.4	6.2	17.3	-	47.1
10-15 cm	43.9	28.9	-	-	27.1
15-10 cm	69.5	-	-	-	30.5
20-25 cm	52.3	20.6	-	-	27.2
25-27 cm	43.1	-	41.1	5.9	15.7
Leachate	92.2	4.03	0.67	-	3.16

Table 8. Carbofuran metabolites present in the GSF Sandy soil column. (as % of total number of metabolites)

Section of Column	% Metabolite				
	(a)	(b)	(c)	(d)	(e)
0-5 cm	6.8	88.8	-	-	4.4
5-10 cm	-	-	-	-	-
10-15 cm	-	-	-	-	-
15-10 cm	37.8	62.2	-	-	-
20-25 cm	52.3	-	-	-	-
25-27 cm	-	-	-	-	-
Leachate	52.3	-	3.0	3.3	41.4

In the Ahero soil column, the main compounds along the column and were carbofuran, 3-hydroxycarbofuran phenol and 3- ketocarbofuran were found only in the top 5 cm of the soil column. In the Chiromo soil column all the metabolites carbofuran, 3-hydroycarbofuran, 3-ketocarbofuran and 3-ketocarbofuran phenol were found spread out along the entire soil column. However, in the leachate mainly carbofuran was found. In the GSF Sandy soil column, the main metabolites were carbofuran, 3-hyrdoxycarbofuran and 3-ketocarbofuran phenol.

The adsorption of carbofuran to both the Ahero and Chiromo soils was high (32.3% and 31.9% at 5 ppm, respectively). However, there was less adsorption in the sandy soil. These results suggest that the adsorption of carbofuran in the Kenyan soils was mainly influenced by the amount of clay and organic matter in the two soil samples. However, 70% of the adsorbed pesticide was removed by desorption after 22 hours in the Ahero soil and 39% desorbed from the Chiromo soil. The data from the adsorption of carbofuran to both the Ahero and the Chiromo soils fitted well into the Freundlich adsorption isotherm equation which relates the amount of pesticide adsorbed to its concentration in solution at equilibrium expressed as $X = K_F C^{1/n}$, where X= amount of pesticide adsorbed per gram of soil, C= equilibrium concentration of the pesticide per ml of the 0.0lM $CaCl_2$ solution and K_F and l/n are the Freundlich constants. The Freundlich constants of carbofuran in the two soils were found to be K_F =15.49 µg/g and l/n ≈ 1.0 µg/ml for the Ahero soil and K_F=15.14 µg/g. and l/n≈l.0 µg/ml for the Chiromo soil.

These results confirm that the physical/biochemical characteristics of the soil greatly influence the rate of adsorption and leaching of carbofuran and therefore, apart form the climate factors, affect its disappearance and degradation in the soil environment.

Acknowledgements. The authors thank the German Academic Exchange Service (DAAD) and the Institute of Ecological Chemistry (GSF) in Munich, Germany for the financial and technical assistance.

REFERENCES

Annonymous: Annual reports 1983 - 1985; National Irrigation Board of Kenya, Ministry of Agriculture (1985). Republic of Kenya.

Aquino GB, Pathak MD (1976) Enhanced absorption and persistence of carbofuran zone application under flooded conditions. J. Econ. Entomol. 69:686-690.

Calderbank A (1989) Physicochemical processes affecting pesticides in soil. Rev. Environ. Contam. Toxicol. 108: 29-192.

Caro JH, Freman HP, Glotfelty DE, Turner BC and Edwards WM (1973) Dissipation of soil incorporated carbofuran in the field. J. Agric. Food Chem. 21:1010-1015.
EEC DIRECTIVE 79/831. Protocol for a ring - test exercise: Adsorption - Desorption in soils Annex 5, Dec, 1988.
Plimmer JR (1988) Movement of pesticides from the site of application: Pesticides, Food and Environmental Implications. Proceedings of a symposium, Neuherberg, 24-27th Nov. (1987). IAEA, Vienna, 1988.
Venkateswarlu K, Siddarame Gowda TK and Sethunathan N (1977) Persistence and biodegradation of carbofuran in flooded soils. J. Agric Food Chem. 25:533-535.
Wondimagegnehu Foy CL (1986) Adsorption desorption and mobility of chlorsulfuron in soils. J. Agric. Food Chem. 34:89-92.