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Distribution and Dissipation of Carbofuran in a Paddy Field in the Kano Plains of 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

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Carbofuran (2,3-dihydro-dimethyl-7-benzofuranyl methylcarbamate) is a systemic and contact insecticide and acaricide which has a broad spectrum of activity against many agricultural pests (Aquino and Pathak, 1976). It is very effective in the control of major rice pests i.e. the green leafhoppers, brown planthoppers, stemborers and whorl maggots (Aquino and Pathak, 1972;Venkateswarlu et al., 1977). Although less persistent, carbofuran is more toxic to animals than most organochlorines (LD_{50} 11 mg/kg in rats, dogs and chickens) (Caro et al., 1973). It has been studied in a number of countries with regard to its fate in different environments. Studies conducted in India and China (Jinhe et al., 1989; Panda et al., 1988) have shown that carbofuran degrades non-enzymatically and by microorganisms under sub-tropical conditions. The degradation occurs by hydroxylation at the benzylic carbon to give 3-hydroxycarbofuran and 3-ketocarbofuran under upland conditions and via hydrolysis to form phenols i.e. carbofuran phenol, 3-hydroxycarbofuran phenol, and 3-ketocarbofuran phenol under flooded conditions (Jinhe et al., 1980; Vollner et al., 1980; Jinhe et al., 1989). A significant part of this pesticide remains in the form of bound residues in the soil, rice plants and fish tissues (El-Zorgani et al., 1980; Jinhe et al., 1980, Vollner et al., 1980; Jinhe et al., 1989).It is hydrolysed both in flooded and non-flooded soils but slightly more rapidly under flooded conditions and it shows increased persistence when incorporated into non-flooded soils as a result of reduced losses by volatilization and photochemical degradation (Vollner et al., 1980; Panda et al., 1988). The persistence increases with the depth of soil incorporation of the insecticide.

In Kenya, carbofuran (in the form of 5% technical Furadan granules) 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.

Correspondence to: J. O. Lalah

Approximately 97% of all rice grown in Kenya is produced by irrigation schemes covering 9000 hectares (Annonymous, 1985). 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. Carbofuran residues and its toxic carbamate metabolites are therefore of great concern in terms of their persistence, mobility and toxicity to fish and mammals (Plimmer, 1988; MacRae, 1989). This study follows the dissipation, metabolism and distribution of carbofuran in flooded and non-flooded soils of the Kano plains of Kenya under field conditions.

MATERIALS AND METHODS

Ring labelled ^{14}C-carbofuran (carbofuran/benzofuranyl-ring 2(-14); specific activity: 11.9 μCi/mmol and radiochemical purity of 99% by TLC was purchased from the International Isotopes, Munich. Non-labelled standards: carbofuran, 3-hydroxycarborfuran, 3-ketocarbofuran, carbofuran phenol, 3-ketocarbofuran phenol and 3-hydroxycarbofuran phenol were kindly supplied by the Institute of Ecological Chemistry, GSF, Munich while 5% technical Furadan granules were purchased from Rhone Poulenc, Nairobi. Distilled methanol, dichloromethane, acetone and toluene were obtained from suppliers in Nairobi. HPLC grade methanol, benzene, ethyl acetate and water were used. Crystalline 2,5-diphenyl oxazole (PPO)and POPOP both for use in liquid scintillation cocktail were purchased from Sigma Chemical Company, UK. A Harvey cocktail for $^{14}CO_2$ absorption was purchased from J.H. Harvey Inst. Corp., USA.

PVC pipes (diameter: 3.7 cm and length: 20 m) were purchased and cut into 55 cm long cylindrical tubes to be inserted into the soil of the paddy field. A mortar and pestle for soil sample homogenization was used and all samples of soil and pesticide residue extracts awaiting analysis were stored at 4 °C. Paper lined standard glass tanks, precoated silica gel SIL G/UV 254 plates and a Spectroline UV lamp was used for TLC analysis. An oven was used for the determination of moisture content while a Soxhlet apparatus and a rotary evaporator were used for extraction and concentration of the soil sample extracts. A Berthold LB 2832 Automatic TLC Linear Analyzer was used to locate the radioactive spots. A Tricarb 1000 TR Perkin Elmer Liquid Scintillation Spectrometer was used for radioassay and the bound residues were cornbusted in an OX-600 Harvey Biological Oxidizer. The experimental site was located at Ahero, 350 km west of Nairobi (Lat. 0°-12'S; long. 24°-50'E; Alt. 3854 ft). The field work was implemented in collaboration with the Ahero Rice Research Station, National Irrigation Board. The weather conditions which include the relative humidity, air temperatures, rainfall and windspeed of this location were recorded by the Department of Meteorology, Nairobi during the experimental period. A soil sample collected from the experimental site gave the following properties: pH 7.0; sand 38%; clay 37%; silt 25%; organic carbon 1.08% (Ref. Bayerische Hauptversuchsanstalt fur Landwirtschaft der Technische Universitat, Munich, Germany). The field study began in January, 1993 and lasted 111 days. A small plot measuring 18 metres by 6 metres was chosen within the irrigation scheme where rice had not been previously cultivated. The plot was prepared by tractor and then by hand to remove all weeds and stones as is usually done for rice cultivation. The plot was then subdivided into three equal parts (each 6 by 6 metres). Two parts were completely drained to give non-flooded conditions while one part was flooded with water to the level usually used in rice cultivation. The plots were then left undisturbed for one week after which 36 hard PVC cylinders as described previously were driven into the soil with three centimetres left protruding above the soil surface to prevent run-off water. The tubes were left undisturbed for one week before applying the pesticide.

The plots were divided into A, B, and C. In plot A (flooded paddy soil) and plot B (non-flooded soil), each cylinder received 1.7 µCi of ^{14}C-carbofuran and 11.7 mg of non-labelled standard carbofuran equivalent to 20 ppm. In plot C (non-flooded soil), each cylinder received 1.7 µCi of ^{14}C-carbofuran and 0.4 grams of 5% technical Furadan granules equivalent to 20 ppm. The labelled and non-labelled chemicals were mixed in 8.5 mL of methanol in a vial prior to application. The chemicals were applied to the surface of the soil and covered with a thin layer of soil. The first two cylinders from the three plots were carefully removed and wrapped in plastic paper bags soon after pesticide application for determination of the initial residues. The other cylinders were sampled in duplicate at various time intervals upto 111 days.

The soil samples were carefully removed from the PVC cylinders by cutting each pipe laterally into sections of O-10 cm, 10-20 cm, 20-30 cm, 30-40 cm and 40-50 cm. The soil from each section was separated, mixed and approximately 10 grams taken for analysis to determine the distribution of carbofuran along the soil column. The sample was placed in a 250 mL conical flask and 50 mL acetone was added, strirred and left to settle and then the acetone decanted. This was done twice and then the extracts were combined and filtered to remove any remaining soil particles. From the acetone extract, 2 mL were taken and counted. The extracted soil samples were left in the flasks to dry, reweighed and 1.5 grams taken for combustion in an OX-600 Harvey Biological Oxidizer for 4 minutes. The $^{14}CO_2$ produced was absorbed in a Harvey cocktail and counted. All analyses were done in duplicate. The remaining soil samples from each section of the pipe were combined, air-dried in the laboratory and then ground in a mortar and pestle and thoroughly mixed. Approximately 50 grams of the soil sample (in duplicate) were extracted in a Soxhlet apparatus using 150 mL dichloromethane for 4 hours and the extractable residues were determined by counting 1 mL of the extract. Non-extractable (bound) residues were determined by cornbusting 1.5 grams of extracted soil and counting the $^{14}CO_2$ trapped in the Harvey cocktail.

RESULTS AND DISCUSSION

Tables 1, 2 and 3 show the results of the dissipation of ^{14}C-carbofuran from the flooded and non-flooded soils over a period of 111 days. Table 4 shows the vertical distribution of carbofuran residues in the PVC cylinders with time under field conditions. These are also illustrated in figures 3, 4 and 5. The daily readings of the weather conditions at West Kano Scheme were taken by the Department of Meteorology in Nairobi and are presented in the following figures 1 and 2.

Table 1. The dissipation of ^{14}C-carbofuran/non-formulated carbofuran in flooded soil.

Days after treatment	Extractable µg/g	%	Bound µg/g	%	Total µg/g	%
0	11.2	57.0	1.8	9.0	13.0	66.0
18	4.6	23.3	5.8	29.3	10.4	52.6
25	4.3	21.9	3.4	17.4	7.7	39.3
40	1.8	10.4	8.1	40.9	9.9	50.3
54	1.4	9.4	2.3	17.8	3.7	27.8
111	1.2	7.4	2.2	12.8	3.4	20.2

The recovery of carbofuran residues from the soil samples was low because the amount of pesticide lost in the water as a result of co-evaporation during the air drying process was not taken into account. This was particularly true in the case of the flooded soil samples. In terms of the extractable residues, there was rapid dissipation of carbofuran from 11.21 ppm to 4.58 ppm after 18 days in flooded soil. The rate of dissipation slows down from this time to the end of the experiment. The trend shows a biphasic pattern with fast disappearance upto 18 days followed by a slower rate of dissipation. The bound residue level was high at 9% of the total residues recovered on zero day because the samples had to be carried from Ahero to Nairobi overnight and had to be

Table 2. The dissipation of ^{14}C-carbofuran/non-formulated carbofuran in non-flooded soil.

Days after treatment	Extractable μg/g	%	Bound μg/g	%	Total μg/g	%
0	14.2	84.5	1.8	10.4	16.0	94.9
18	10.0	59.4	8.9	52.7	9.4	55.9
25	3.6	22.2	5.9	36.9	9.4	59.1
40	-	-	7.4	46.2	-	-
54	-	-	7.3	45.6	-	-
111	2.9	18.4	2.6	17.8	12.3	36.2

Table 3. The dissipation of ^{14}C-carbofuran/5% technical Furadan in non-flooded soil.

Days after treatment	Extractable μg/g	%	Bound μg/g	%	Total μg/g	%
0	11.8	56.5	2.0	9.6	13.8	66.3
18	5.1	24.2	6.5	31.3	11.6	55.5
25	3.3	15.7	10.0	48.1	13.3	63.8
40	0.8	4.0	6.5	31.3	7.4	35.3
111	1.4	6.7	7.2	34.8	8.7	41.5

Note: Mass of dry soil in the cylinders were as follows:-
Plot A: 1017 grams
Plot B: 1191 grams
Plot C: 961 grams

Table 4. The vertical distribution of carbofuran residues in the PVC cylinders with time under field conditions/as percent of the total recovered residues.

Days after treatment	40			54			111		
Plot	A	B	C	A	B	C	A	B	C
Section:									
0-10 cm	79.2	51.3	50.8	76.3	72.0	70.0	28.3	52.2	49.6
10-20 cm	6.3	31.4	22.2	9.21	14.2	-	24.8	11.6	19.2
20-30 cm	5.7	6.8	11.4	11.3	10.0	15.4	17.0	28.8	17.4
30-40 cm	5.2	5.1	8.5	1.8	2.6	7.0	15.2	5.0	8.7
40-50 cm	3.6	5.4	7.0	1.4	1.0	6.7	14.7	2.4	5.0

air-dried before the analysis. In flooded soil the bound residue level went upto about 29.3% of the recovered pesticide residues after 18 days and was just over 40% after 40 days. This agrees with the findings of the adsorption tests which suggested that the formation of the bound residues was very rapid in this type of the

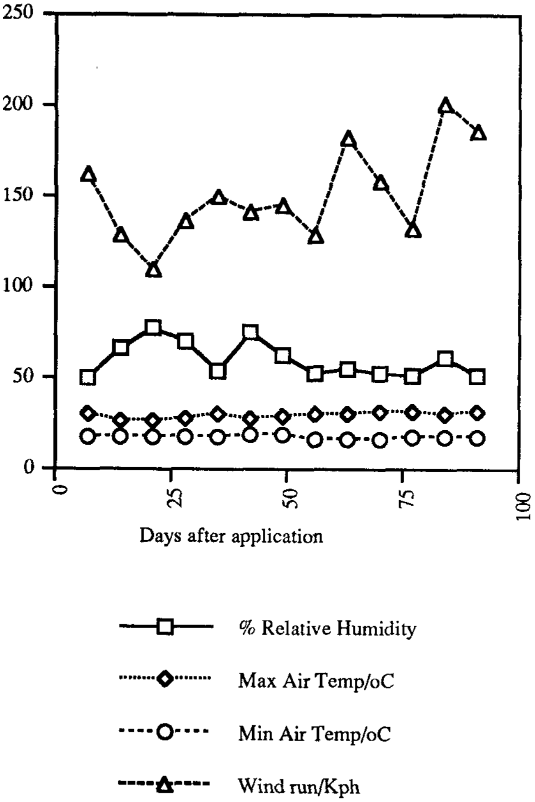

Fig. 1. The Average weekly weather data at Ahero

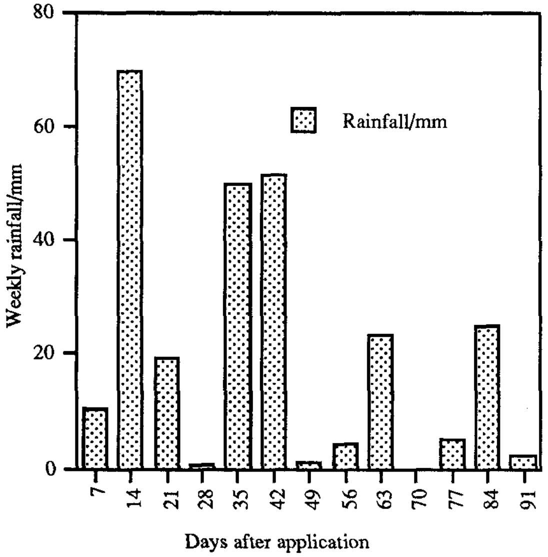

Fig. 2. The total weekly rainfall at Ahero

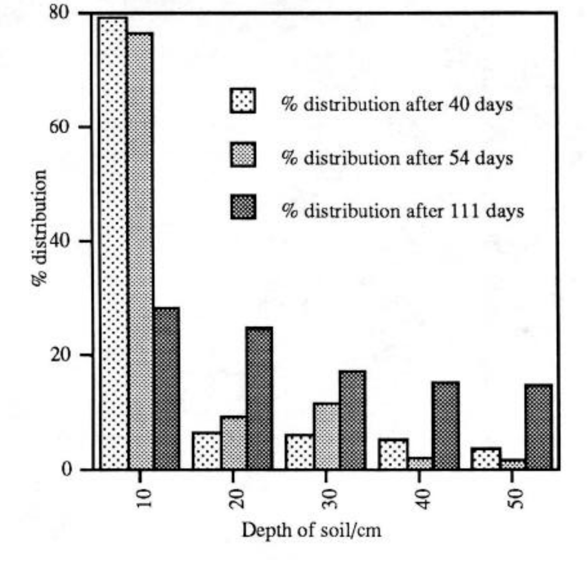

Fig. 3. Plot A. The Distribution of cabofuran with soil depth

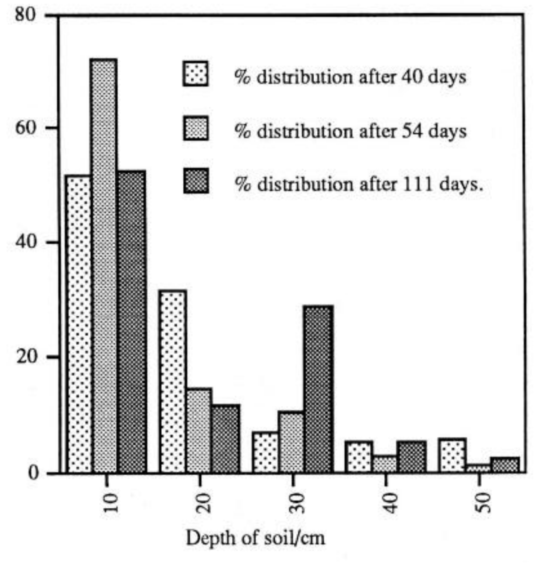

Fig. 4. Plot B. The Distribution of carbofuran with soil depth

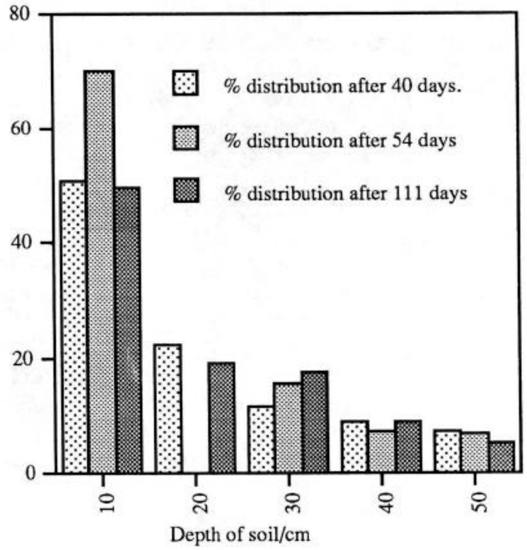

Fig. 5. Plot C. The Distribution of Carbofuran with soil depth.

soil. Other researchers have also reported high levels of bound residues in sub-tropical soils (Jinhe, 1984). Over 50% of the total residues disappeared within 25 days of the experiment. There is therefore no potential risks to fish and other organisms in this soil due to direct poisoning of carbofuran after this period.

The dissipation of carbofuran from non-flooded soil treated with standard carbofuran showed a slightly different trend from that treated with 5% technical Furadan although the extractable residue levels showed a similar dissipation pattern- a rapid first phase followed by a slower second phase after 18 days. However, there was slightly more persistence of standard carbofuran in non-flooded soil but still a loss of over 50% of the total residues occurred after 25 days. The bound residues were also higher upto 59% after 54 days. The dissipation of carbofuran from flooded soil was more rapid than that in non-flooded soils with levels approaching 40% in less than 25 days and falling below 20% after 111 days in terms of total residues. In flooded soil most of the carbofuran residues were found in the top 10 cm of the soil even after 111 days. This is a potential danger to fish due to surface water contamination. In fact, most of the pesticide tended to stay in the water above the soil surface, since carbofuran is very water soluble. About 18% of the residues were in the 40-50 cm section of the soil column after 111 days. However, in non-flooded soils there was definite movement of the pesticide (most in the 20-30 cm section) vertically downwards. These results show that there is very little risk of ground water contamination with carbofuran in this type of soil.

The maximum and minimum air temperature at Ahero was fairly constant in the range 26-30 °C (max) and 14-18 °C(min). This is typical of this region. However, there was a distinct difference in the % relative humidity and the amount of rainfall recorded, being higher between 0-18 days. These climatic factors coupled with soil microbial characteristics played a major role in the rapid dissipation and degradation of carbofuran from the soil and also in the formation of bound residues.

In conclusion, carbofuran can be considered to be non-persistent in this tropical soil which concurs with the findings of previous studies conducted in other tropical countries. High temperatures, high % relative humidity and rainfall and different soil microbial properties stimulated the disappearance of this pesticide from the soil. The dissipation was more rapid under flooded conditions than under non-flooded conditions and carbofuran existed in the soil mostly in bound form 2-3 weeks after application. In flooded soil, most of the residues were found in the top 10 cm layer of soil presenting great danger to fish and other organisms. Contaminated water may find its way into the nearby canals and the River Nyando which passes through this area during the first 3 weeks of pesticide application.

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