

Persistence of Carbofuran in Malaysian Waters

¹G.H.N. Farahani, ²Zuriati Zakaria, ³Aini Kuntom and ²B.S. Ismail

¹Department of Chemistry, Faculty of Science,
Islamic Azad University-Shahrekord Branch, 166 Shahrekord, Iran

²Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 UKM, Bangi, Selangor, Malaysia

³MPOB, No.6, Persiaran Institusi, Bandar Baru Bangi, 43000 Kajang, Selangor, Malaysia

Abstract: The stability of carbofuran was investigated in river, sea and ground waters of Malaysia. The water samples collected were from pollution-free areas in Malaysia and all samples were spiked with carbofuran at 1 µg/mL. The concentrations of carbofuran residue in the samples were measured under light and dark conditions at various intervals and their half-lives determined. It was found that the half-lives in unfiltered and filtered river water exposed to sunlight and filtered river water kept in the dark were 5, 6.6 and 8.6 days respectively. For sea water exposed to sunlight and kept in the dark, the half-lives of carbofuran were 3.28 and 12.98 days respectively. The residue of carbofuran was monitored in ground water and it was observed that the concentration of carbofuran was reduced to 65% of the initial concentration after 67 days. It was observed that the dissipation of carbofuran through oxidation and adsorption on solid suspended materials was insignificant. This study showed that photolysis and hydrolysis are the main pathways for the dissipation of carbofuran in water and that the pH of the water is one of the main factors influencing its degradation.

Key words: Carbofuran • Insecticide • Dissipation • Half-life • River • Sea and ground water

INTRODUCTION

Cultivation of plants for economical purposes is a constant struggle against losses from pests such as weeds, insects and diseases. The most frequently used method to combat pests is the application of pesticides, namely insecticides, herbicides, fungicides, etc. and these products have contributed significantly to agricultural productivity. A consequence of the extensive use of these chemicals is the problem of pesticide pollution of the surrounding water bodies and this problem has increased over the past decade [1]. Pesticides are mobilized from agricultural fields and plantations to surface run-offs [2]. The amount lost from fields and transported to surface waters depends on several factors such as soil characteristics, topography, weather, agricultural practices as well as the chemical and environmental properties of the individual pesticides [3, 4]. The combined effect of these factors on the temporal and spatial magnitude of pesticide concentrations and fluxes in large integrating river systems is largely unknown [5]. Chemical reactions and physical displacements influence the persistence of chemicals in the soil, but with different environmental

implications. Chemicals, which are sufficiently resistant to degradation and are adequately soluble to be transported in water, may reach the sea in significant amounts. Water run-off and river transport are the main processes involved in the land-sea transfer of chemicals [4, 6].

The proven persistence and toxicity of organochlorine pesticides justifies their replacement by other more easily degradable, polar, labile and less persistent pesticides, such as N-methyl carbamates. The carbamates are a family of compounds with general structures ($R_1OCONR_2R_3$) that are derived from carbamic acid with the introduction of different substituents. Their great success in agricultural production activities has led to a continual increase in their usage, nevertheless their acute toxicity is of great concern, therefore it is necessary to determine the fate of these carbamate pesticides [7].

Fresh water is considered the most precious of all natural resources. In the rural areas, ground water is often the only source of water supply with acceptable quality for human consumption, without treatment, but ground water can get contaminated by domestic, industrial and agricultural wastes, including fertilizers and pesticides. Several studies have demonstrated a positive correlation between concentrations of pesticides and nitrates,

suggesting that these contaminants are linked through land use practices [8, 9].

Photolysis and hydrolysis are two main degradation pathways of carbofuran in the environment. Different techniques have been used to study the oxidation of carbofuran, one of which includes UV irradiation in the presence of ozone or Fenton's reagent [1], the latter being the most effective degradation system. Photodegradation of pesticides in fresh water has been widely studied [10-20]. The photolysis of *N*-methylcarbamate insecticides in fresh water has also been the subject of several studies [13, 21-23], with a few carried out in sea water [24]. Studies were conducted on the hydrolysis of *N*-methylcarbamates [25-26] in fresh water, but again, only limited studies were undertaken on pesticides in marine environments. Seiber *et al.* [27] and Raha and Asit [28] observed that oxidation and volatilization are generally considered insignificant dissipation pathways for carbofuran in water.

Carbofuran (2,3-dihydro-2,2-dimethyl benzofuran-7-yl-*N*-methyl carbamate) is a broad spectrum systemic acaricide, insecticide and nematicide and is included in the general group of carbamate derivative pesticides (Fig. 1) [1]. In Malaysia, the pesticide is used in the rice fields for the control of rodents and in the oil palm plantations for the control of the rhinoceros beetle. Thus, data on the dissipation of this pesticide in river water is important to ensure that its use does not cause any adverse impact on the environment.

The aim of this study is (i) to monitor the degradation of carbofuran spiked into different types of water, (ii) to consider the potential pathways of degradation of carbofuran and (iii) to determine the half-life of carbofuran in different types of water.

MATERIALS AND METHODS

Experimental Procedures: Acetonitrile, dichloromethane (HPLC grade), anhydrous sodium sulfate (99.50%) from Fisher Scientific and carbofuran pestanal (99.9%) from Sigma-Aldrich Laborchemikalien were used. Filter paper 45 μm from Whatman and deionised water purified with a Mili-Q system from Millipore (Milford, MA, USA) were also used. Standard stock solution (1000 mg/L) was prepared by dissolving 50 mg of carbofuran in 50 mL acetonitrile and storing it at -20°C . Working standard solutions were prepared by dilution of the relevant aliquots from the stock solution with acetonitrile.

Extracted residues were analyzed using a HPLC H/P Agilent 1100 fitted with a LC Column (ZORBAX 300SB- C_{18} (4.6 \times 250 mm), 5 μm thickness). The injection volume was 20 μL . The mobile phase was acetonitrile:water (50:50 v/v)

with a flow rate of 1 mL/min. The ultraviolet absorption was measured at 280 nm and the peak area was used for quantification.

Sample Preparation: Clean and clear river water samples were collected in October 2004 from a small river (Sungai Gombak), north-east of Kuala Lumpur. One portion of the river water was filtered whilst the other three portions were spiked with carbofuran at 1 $\mu\text{g}/\text{mL}$. The water samples were treated as follows; i) 24 screw capped translucent bottles each containing 50 mL river water were exposed to sunlight, ii) 24 screw capped translucent bottles each containing 50 mL filtered river water were exposed to sunlight, iii) 24 screw capped amber bottles each containing 50 mL filtered river water were used to simulate the dark. Sea water was collected in December 2004 from around the Pangkor Island situated in the Straits of Malacca. The sea water (not filtered) was spiked (as described), poured into amber bottles (simulating the dark) and placed outdoors. The ground water samples were collected from a well in Kampong Abu Bakar Baginda in Bandar Baru Bangi, located about 25 km south of Kuala Lumpur city. 39 screw capped amber bottles each containing 50 mL ground water spiked with carbofuran (at 1 $\mu\text{g}/\text{mL}$) were placed outdoors to simulate the dark. The presence of residues of carbofuran were monitored up to 67 days as follows:- 25, 23 and 67 days in river, sea and ground water respectively. After filling each bottle with 50 mL of the water sample, 35.7% of space inside the bottle was occupied by water and the rest with air and finally each of the bottles was tightly sealed with a screw cap. Table 1 shows the physicochemical properties of the water samples from the 3 different water sources.

Method: All the samples were kept outdoors at ambient temperature and translucent bottles were used to ensure the samples were exposed to sunlight. For elimination of sunlight, amber bottles were used in the experiment. Sampling was done according to the time schedule and temperature at the sampling time ranged from $26 \pm 1^{\circ}\text{C}$ (minimal temperature) to $33 \pm 1^{\circ}\text{C}$ (maximal temperature). Temperatures inside the bottles were difficult to estimate throughout the duration of the experiment as they varied with the sunlight distribution (diurnally and nocturnally) and sunlight intensity during the day.

Extraction was carried out with 5 mL dichloromethane after which the mixture was shaken for 2 min. A separating funnel was used to separate the aqueous and organic phases. The procedure was repeated 3 times. All extracts were combined and dried using the sodium sulfate cartridge; the solvent was evaporated using a vacuum

Table 1: Characteristics of river, sea and well water

Sample name	Turbidity (FTU)	S.S.M (mg/L)	Sulfate (mg/L)	COD (mg/L)	*Con ($\mu\text{s}/\text{cm}$)	PH	TDS (mg/L)	T($^{\circ}\text{C}$)
RW**	11	0	1	10	20.7	6.52	8	-
seawater	4	0	2550	226	15.31	7.40	8620	29
GW***	0	0	22	0	155.6	5.70	74	-

*Conductivity **River water ***Ground water

rotary evaporator and replaced with acetonitrile. Finally the volume of each samples was adjusted to 10 mL by dilution with acetonitrile in a volumetric flask. Extracts were analyzed by HPLC under the conditions mentioned above. All the experiments were carried out in triplicate.

Recovery Study: The EPA method 632 with slight modifications was used to extract and analyze carbofuran from the water matrix. Extraction was carried out on 50 mL deionised water spiked with carbofuran at 1 $\mu\text{g}/\text{mL}$ followed by analysis as described above. Analytical grade carbofuran (0.05 g) was dissolved in acetonitrile and diluted to 50 mL to make up the standard stock solution of 1000 $\mu\text{g}/\text{mL}$. A high performance liquid chromatograph was calibrated using 6 working standard solutions of carbofuran: (5, 10, 15, 20, 25 and 50 $\mu\text{g}/\text{mL}$), which were prepared by appropriate dilutions of the 1000 $\mu\text{g}/\text{mL}$ standard stock solution prepared with acetonitrile.

RESULTS AND DISCUSSION

Recovery Study: The EPA method 632 (for determination of carbamate and urea pesticides in municipal and industrial waste water) with a slight modification was used for extraction and analysis of carbofuran from the different water matrixes (river, sea and ground water). The EPA gave the results of a recovery study done (using this method), complete with statistical analysis. In the method reported, reagent water and wastewater from pesticide manufacturing industries were spiked at 37 and 148 $\mu\text{g}/\text{L}$ respectively and the experiments were replicated seven times. The recovery percentages obtained were 87.8 and 99.3% with standard deviation of 2.7 and 1.4% respectively. The method detection limit (MDL) reported for this method was 3.2 $\mu\text{g}/\text{L}$. In the present study the recovery and relative standard deviation (RSD) obtained were 97.7% and 0.24% respectively. From the calibration curve of the HPLC, the correlation coefficient (r^2) obtained was 0.9995. The calibration status of the HPLC was frequently checked prior to analyzing samples. For the purpose of calibration of the HPLC, it was sufficient to inject two standard solutions of carbofuran at 0.5 and 1 $\mu\text{g}/\text{mL}$ prior to the analysis of each set of samples in the

study. All the samples were injected into the HPLC twice and the average of the peak area was used for quantitation.

Monitoring of Carbofuran Dissipation in River, Sea and Ground Water:

A Laboratory scale study to consider the stability of carbofuran was conducted from the 21st of October to the 15th of November 2004. According to the time schedule (0, 1, 2, 4, 6, 11, 18, 25 days), sampling and extraction activities were carried out to monitor the presence of carbofuran residue in the three river water samples kept under different conditions (river water and filtered river water exposed to sunlight and filtered river water in the dark). External standard solutions were used to calculate the concentration in the samples. Table 2 shows the residues of carbofuran in all the samples: river water exposed to sunlight (RWES), filtered river water exposed to sunlight (FRWES) and filtered river water in the dark (FRWD). It was observed that the rate of degradation of carbofuran in the first 11 days was more compared to that after 11 days in filtered river water in the dark. For river water and filtered river water exposed to the sun light, it was observed that the rate of degradation of carbofuran was faster in first 6 days than that from day 6 to day 25. It was found that the rate of degradation of carbofuran under the three different conditions for river water was as follows: RWS>FRWS>FRWD (Fig. 1).

Sea water was used in the study of the stability of carbofuran under two different situations in the laboratory. i) sea water exposed to sunlight and ii) sea water in the dark. Residues of carbofuran in sea water were determined according to the specified time schedule (0, 0.33, 1, 2, 4, 6, 9, 16 and 23 DAT) (Table 3). A similar trend was observed for the rate degradation of carbofuran in sea water exposed to the sunlight. Whereby in the first 6 days the degradation rates was faster than that from day 6 to day 16. Carbofuran residue was undetected on day 23 of the experiment. From Table 3, it was found that the rate of degradation of carbofuran in sea water, in the dark, was uniformly slow and this was not similar to the rate of degradation of carbofuran in the other water samples (river water in different conditions and sea water exposed to sunlight). The rate of degradation of carbofuran in sea

Table 2: Residue of carbofuran in filtered and non filtered river water exposed to sunlight and filtered river water in the dark (\pm SD)

Time (day)	Filtered river water in the dark		Filtered river water exposed to sunlight		River water exposed to sunlight	
	Concentration ($\mu\text{g/mL}$)	(\pm SD)	Concentration ($\mu\text{g/mL}$)	(\pm SD)	Concentration ($\mu\text{g/mL}$)	(\pm SD)
0	0.91	0.15	0.91	0.15	0.92	2.06
1	0.90	1.86	0.89	3.02	0.90	1.14
2	0.81	1.33	0.65	4.13	0.80	3.51
4	0.73	7.40	0.56	0.65	0.68	4.31
6	0.62	0.19	0.41	2.62	0.49	7.02
11	0.35	0.38	0.24	0.77	0.33	4.76
18	0.25	2.29	0.15	0.44	0.13	1.20
25	0.11	2.67	0.07	0.62	0.01	3.18

Table 3: Residue of carbofuran in seawater exposed to the sunlight and in the dark (\pm SD)

Time (day)	Seawater exposed to the sunlight		Seawater in the dark	
	Concentration ($\mu\text{g/mL}$)	(\pm SD)	Concentration ($\mu\text{g/mL}$)	(\pm SD)
0	0.92	0.43	0.92	0.43
0.33	0.8	1.89	0.73	0.87
1	0.7	4.17	0.76	0.25
2	0.57	1.24	0.69	0.92
4	0.43	0.29	0.69	0.93
6	0.31	0.52	0.63	1.24
9	0.13	1.45	0.50	2.81
16	0.03	1.61	0.47	1.08
23	ND*	-	0.25	0.05

* Not detected

Table 4: Residue of carbofuran in groundwater in the dark (\pm SD)

Time (day)	Concentration ($\mu\text{g/mL}$)	(\pm SD)
0	0.845	1.67
1	0.809	3.20
2	0.778	4.13
4	0.751	2.43
6	0.761	0.77
9	0.803	1.76
12	0.762	7.10
17	0.875	5.74
27	0.776	10.18
34	0.813	9.86
38	0.739	19.02
52	0.754	12.19
67	0.654	12.58

Table 5: Rate constant of degradation (k) and half-life ($t_{1/2}$) of carbofuran in different types of waters

Water type	Rate constant (day^{-1})	Half-life (day)
River water exposed to sunlight (RWS)	0.1394	5
Filtered River water exposed to sunlight (FRWS)	0.1049	6.6
Filtered River water in dark (FRWD)	0.081	8.6
Seawater exposed to sunlight (SWS)	0.2111	2.86
Seawater in dark (SWD)	0.0546	12.69

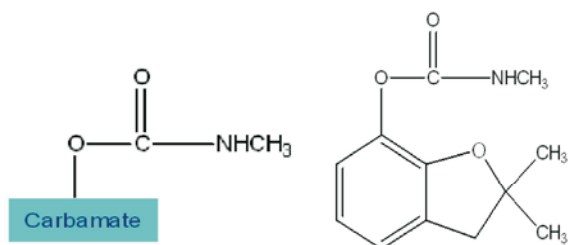


Fig. 1: Molecular structure of carbofuran and carbamate agent group

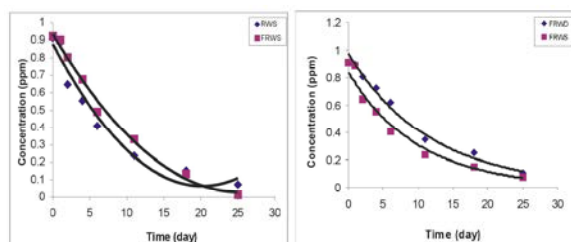


Fig. 2: Comparison the rate of variation of carbofuran residue in RWS with FRWS and in FRWS with FRWD

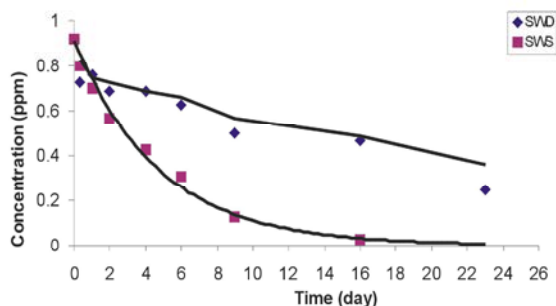


Fig. 3: Rate of variation of carbofuran residue in SWS and SWD

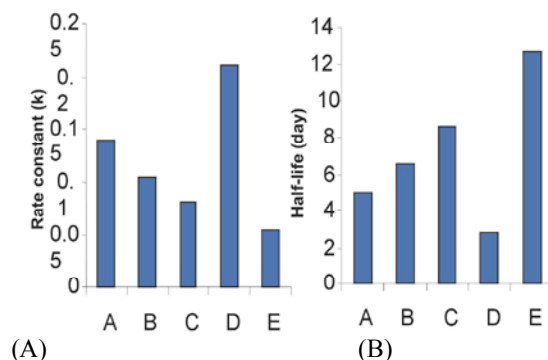


Fig. 4: a. Rate constant of degradation (k) and b. half-life of carbofuran in A. RWS, B. FRWS, C. FRWD, D. SWS, E. SWD

water in the dark was also less than the rates observed in all the other water samples (river water in different conditions and sea water exposed to sunlight) and after 23 days, the residue of carbofuran was 0.25 μg/mL whereas it was not detected in sea water exposed to sunlight for the same time period (Fig. 2).

Due to the absence of sunlight in ground water, experiments were conducted only in the dark to simulate the natural conditions. 50 mL of ground water were spiked at 1 μg/mL of carbofuran and placed outdoors in amber bottles (to stimulate the absence of sunlight). The residue of carbofuran was monitored according to the time schedule for 67 days (Table 4).

Degradation Kinetics: As previously reported [29], chemical degradation can be described using a first-order degradation curve ($C=C_0e^{-kt}$) or ($\ln C=\ln C_0-kt$) where C is the concentration of the compound at the time t, C_0 the concentration of the compound at initial time and k the rate constant. The half-life corresponds to a period of time at which the pesticide concentration is equal to half the initial concentration, so given by $t_{1/2}=\ln 2/k$. By plotting the Ln of recovery versus time, a straight line can be obtained and the rate constant (k) may be derived from it together with the half life ($t_{1/2}$).

The rate constant of reaction (k) for the degradation of carbofuran in filtered river water in the dark, as well as in filtered and non-filtered river water exposed to sunlight were derived from the slope of the curve of $\ln C_0/C_t$ versus time, with values of 0.081, 0.105 and 0.140 and with correlation coefficients (r^2) of 0.9832, 0.9804 and 0.9127 respectively. By using the equation; $t_{1/2}=\ln 2/k$, the half-lives of carbofuran in filtered river water in the dark plus filtered and non-filtered river water exposed to sunlight were calculated as 8.6, 6.6 and 5 days respectively. Consequently the rate of reactions derived for sea water exposed to sunlight and in the dark were 0.211 and 0.055 with correlation coefficients (r^2) of 0.994 and 0.898 respectively. By using the equation; $t_{1/2}=\ln 2/k$, the half-lives were calculated as 3.28 and 12.69 days for sea water exposed to sunlight and in the dark respectively (Table 5 and Fig. 3). This data shows that photochemical degradation and hydrolysis are the main pathways of carbofuran degradation in water. Biological degradation is less significant compared to hydrolysis and photochemical degradation. These results are consistent with other findings [27-28, 30-31].

It is interesting to mention that the rate constant for the degradation of carbofuran in sea water exposed to

sunlight was more than the rate constant of degradation of carbofuran in river water exposed to sunlight. Consequently the half-life of carbofuran in river water exposed to sunlight was longer than the half-life of carbofuran in sea water exposed to sunlight, in line with a similar trend as observed by others. Sonia *et al.* [24] observed that the half-life of carbofuran in sea water exposed to sunlight (7.5 h) was around 6 times faster than the half-life of carbofuran in deionized water exposed to sunlight (41.6 h) with the same pattern of faster degradation in sea water (0.1 h) than in deionized water (3.1 h) under 300 nm light intensity. This difference (6-31 fold) and the differences observed in the present study are most likely due to different water compositions. The presence of ions, organic compounds and chemical sensitizers may enhance the photodegradation of carbofuran [15, 24, 32].

The rate of degradation of carbofuran in sea water in the dark was not faster than that in filtered river water in the dark. Sea water was non filtered so it was likely that because of adsorption carbofuran was less available for degradation and desorption of this chemical caused it to be present in the sea water longer.

For ground water in the dark, the residue of carbofuran was monitored for 67 days. It was observed that the concentration of carbofuran was reduced to 60% of the initial concentration after 67 days (Fig. 4), indicating that the half-life had not been reached. It is obvious that the persistence of carbofuran in ground water is higher than in river and sea water. The longer half-life of carbofuran in ground water is most likely attributed to the low pH (5.70) and absence of light. A similar trend was observed by Seiber *et al.* [27] where they found that the hydrolysis of carbofuran was more than 700 times faster at pH 10 than at pH 7 and this is consistent with the results of the present study.

CONCLUSION

The results of the present study show that carbofuran is more stable in ground water than in other types of water in Malaysia due to the low pH values of the ground water which was obtained from a peat area. The half-life of carbofuran in sea water in the dark was approximately four times longer than that in sea water exposed to sunlight. These results will have an impact on the marine life in the deep ocean because the maximum penetration of sunlight in sea water is to the depth of

100 m only. The stability of carbofuran in river water under different conditions was less than that in other types of water so it is unlikely to be a real concern.

The results also showed that photochemical degradation and hydrolysis are the main pathways for carbofuran degradation in water. Biological degradation in water is not significant and the pH of the water is one of the main factors affecting the degradation of carbofuran in water. Due to the relative stability of carbofuran in ground water of Malaysia, monitoring studies on the residues of carbofuran in ground water are necessary to ensure the safety of well water consumed by the rural population.

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