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Contributed Paper

Carbofuran Persistence in Saline Soil and Saline Water

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Abstract

The persistence of carbofuran in saline soil and saline water was investigated. Soil used in this study was collected from the saline soil paddy field in Ban Phai District, Khon Kaen Province. Saline water was taken from the water trapped above the soil in saline soil paddy field. The salinity was measured using electrical conductivity. There were 4 levels of saline soil samples i.e., no salinity, low salinity, medium salinity and high salinity with the electrical conductivity (EC) of 1, 2.6, 4.6. and 9.0 mmho/cm, respectively. The EC of saline water samples were 1.0, 3.0, 6.0, and 8.0 for none, low, medium and high salinity, respectively. Carbofuran was rapidly degraded in saline soil at all salinity levels. However, salinity did not affect carbofuran degradation in soil. The longer half-life values, 22-33 day, in non-autoclaved soil than in autoclaved soil, 9-18 days, suggesting a non-persistence and biologically degradation of carbofuran in saline soil. Salinity affected the persistence of carbofuran in saline water. As the salinity in water increased the pH of water increased resulting to less persistence of carbofuran. This may due to a chemical hydrolysis since an increased of pH in the saline water resulting to a hydrolysis of carbofuran at high pH. The half-life values in saline water were found to be 17-29 days and 17-33 days in autoclaved and non-autoclaved saline water, respectively, suggesting the degradation of carbofuran in water was not a biologically degradation dependent.

Keywords : carbofuran, saline soil, saline water, persistence, half-life

1. Introduction

Carbofuran is a broad-spectrum insecticide used to control rice water weevil. A primary mechanism of carbofuran degradation in soil and water under neutral to basic conditions is chemical hydrolysis [1, 2] resulting in the metabolite carbofuran phenol. As pH and temperature increased the rate of hydrolysis increased. Dissipation of carbofuran in water also could be influenced by volatilization and photolysis [2, 3]. Sunlight and high temperature increased the rate of carbofuran loss from water [4]. Dissipation of carbofuran in paddy water was rapid with a half-life of carbofuran of 3 days, compared to 10 days in paddy soil. Residues bound to soil particles and less available for microbial degradation and hydrolysis [5]. Depletion of CO_2 by photosyntesis of algae or cyanobacteria increased the pH in paddy water [6] resulting to a hydrolysis of carbofuran at high pH. Degradation of carbofuran in acidic soils is slower than in neutral and alkali soil [2, 4, 7]. Siddaramappa and Seiber [4] reported that carbofuran was biologically degraded in soils under flood condition.

Saline soil means soils that contain salts. A salinity of soil was defined as the salt concentration in the water extracted from a saturated soil. The amount of salt contained in soil or water could be expressed in grams of salt per liter of water or in milligrams per liter. The salinity of water and soil could be measured by an electrical device called electrical conductivity and then expressed in terms of millimhos cm^{-1} or micronhos cm^{-1}. Salts in soil originate from mineral weathering, inorganic fertilizers, soil amendments and irrigation water [8]. Saline soil affect plants in may ways such as water is less easily extracted from soil by plant; nutrient imbalances, reduction of water infiltration and aggravating water stress conditions [8]. Plants affected by salt have dark green leaves, thicker leaves and more succulant than normal [8]. There are about 25 million ha of saline soil areas in the North-east part of Thailand in which 2.1, 5.2, 17.64 and 27.2 million ha of these areas are classified as high salinity area, medium salinity area, low salinity area and more likely to be a saline soil area, respectively. Most of saline soil areas are not being used. However, in some medium salinity area the farmers grow rice. Rice field is known for a heavily use of pesticides due to weed problems and insect problems. Carbofuran is one of the commonly used insecticides in rice field. Salt level might affect the persistence of carbofuran in soil and water.

In previous research carbofuran degradation was studied in a no salinity soil, however, there is no research has been done on carbofuran degradation in saline soil and saline water. Clearly there is a need for further knowledge on fate of carbofuran in these particular soil and water. The objectives of this study were: (i) to determine the relative persistence and fate of carbofuran in saline soil and saline water and (ii) to determine the route of dissipation of carbofuran in saline soil and saline water.

2. MATERIALS AND METHODS

2.1 Saline Soil Samples and Saline Water Samples

Saline soil samples and saline water samples were collected from saline paddy field in Ban Phai District, Khon Kaen Province. The salinity levels in samples were tested by the electrical conductivity.

Soil samples were collected using soil probes with a diameter of 3-cm to depth of 0-15-cm. They were passed through a 2-mm sieve and kept at 4°C until used. Soil textures were analyzed by Hydrometer method.

Water samples were taken from the water trapped above the soil in saline soil paddy field. A high salinity water sample, 20 mmho/cm, was diluted by a fresh water to low salinity, medium salinity and high salinity water which the EC of 3, 6 and 8 mmho/cm, respectively. The samples were kept at 4°C until used.

2.2 Persistence of Carbofuran in Saline Soil Study

Persistence of carbofuran in saline soil was determined by mixing 50 g dry weight of non autoclaved and autoclaved soil with carbofuran solution to provide a concentration of 1-mg kg^{-1} soil in closed 0.5-L jars. Autoclaved soil samples were prepared by autoclaving the soil three times at 121 °C for 1-h at 1-day interval. Then samples were incubated at 30°C. Triplicate samples were taken at 0, 10, 20, 30 and 40 days. Fifty grams of soil samples were extracted with 50 mL of methanol. During the extraction, the mixture was shaken for 30 min on a reciprocating shaker and then filtered through a filter paper. Filtrates were analyzed for carbofuran concentration by C-18 reversed HPLC, Schimadzu Model C-R7A, using 1:1 acetonitrile:deionized water at 1mL min^{-1} as carrier solvent and UV detection at 220 nm. Under these conditions carbofuran had retention time of 4.6 min. Carbofuran concentration was quantified by measurement of peak height and comparison with external standards. The carbofuran concentrations were fitted to a modified first-order kinetic model;

$C = Coe^{-kt}$ where C was the mean concentration of carbofuran as a function of time in days (ug kg^{-1}), Co was the initial carbofuran concentration (ug kg^{-1}), k was the rate constant (day^{-1}) and t was time (days).

2.3 Persistence of Carbofuran in Saline Water Study

A high salinity water sample, 20 mmho/cm, was diluted by a fresh water to low salinity, medium salinity and high salinity water which the EC of 3, 6 and 8 mmho/cm, respectively. Autoclaved water samples were prepared by autoclaving the samples at 121°C for 15 min. Then 100 mL of water samples were added with carbofuran solution to provide a concentration of 1mg L^{-1}. Samples were incubated at 30°C. Triplicate samples were taken at 0, 10, 20, 30 and 40 days. Carbofuran in water was extracted by solid phase extraction using Sep-pack C18 cartridge (Cat.no. 8B-S001-EAK, Phenomenex). The cartridge was conditioned with 1 mL of methanol. The sample was passed onto the cartridge at the rate of 3mL/min. Carbofuran was eluted with 15 mL of methenol and then carbofuran concentration was analyzed by HPLC as the method mentioned above. The carbofuran concentrations were also fitted to a modified first order kinetic model and then the half-life values of carbofuran in saline water were calculated.

3. Results and Discussion

Properties of soils were shown in Table 1. Non-saline soil and low salinity soil had a similar soil texture i.e., sandy loam. The loam texture was very similar in medium salinity and high salinity soils. EC of saline soil ranged from 1.06 to 9.9 mmho cm^{-1}. Soil pH ranged from 7.8 to 9.3 with the lowest pH in high salinity soil and the highest pH in low salinity soil.

Properties of saline water were shown in Table 2. EC ranged from 1 to 8 mmho cm^{-1}. Water pH ranged from 6.4 to 7.3 with the increased in pH as the salinity level increased.

3.1 Persistence of Carbofuran in Saline Soil

Degradation of carbofuran in non-autoclaved saline soil (Figure 1) and autoclaved saline soil (Figure 2) were described by a modified first-order kinetic model. The coefficients of determination, r^2, ranged between 0.91 to 0.98 and indicated good fit of the data to the first-order kinetic model (Table 3). The half-life values were calculated for non-autoclaved and autoclaved soil (Table 3). The half-lives of autoclaved soil and non-

Table 1. Selected physicochemical properties of saline soil.

Salinity level	EC (mmho cm^{-1})	pH	moisture (%)	sand (%)	silt (%)	clay (%)
No salinity	1.06	8.1	8.2	55	40	5
Low salinity	2.60	9.3	9.1	60	30	10
Medium salinity	4.60	8.0	10.0	50	35	15
High salinity	9.00	7.8	9.5	53	35	12.5

Table 2. Selected physicochemical properties of saline water.

Salinity level	EC (mmho cm^{-1})	pH
No salinity	1.0	6.4
Low salinity	3.0	6.7
Medium salinity	6.0	6.9
High salinity	8.0	7.3

autoclaved soil were significantly different (p-value<0.05) suggesting a biologically degradation dependent. Other researchers [4, 7, 9-12] found evidence of the involvement of microorganisms in the degradation of carbofuran in soils. The half-life values of carbofuran, in autoclaved and non-autolcaved soils, at each saline level were not significantly different (p-value>0.05) suggesting salinity did not affect carbofuran degradation in soil.

3.2 Persistence of Carbofuran in Saline Water

Carbofuran degradation in saline water was not a biologically degradation dependent. The half-lives of non-autoclaved water and autoclaved water were not significantly different (p-value>0.05) (Table 4). The sentence is a modified first-order kinetic was used to discribe degradation of carbofuran in non-autoclaved saline water and autoclaved saline water as shown in Figures 3 and 4, respectively. Our finding was supported by Siddaramappa and Seiber [4] who found that degradation of carbofuran in water was mainly by non-biologically process suggesting a chemical breakdown.

Getzin [1] and Seiber *et al.* [2] stated that a primary mechanism of carbofuran in soil and water under neutral to basic conditions was chemical hydrolysis resulting in the metabolite carbofuran phenol. The other influences of carbofuran dissipation in water included volatilization and photolysis [2, 3]. Sunlight and high temperature increased the rate of carbofuran loss from water [4]. Depletion of CO_2 by photosyntesis of algae or cyanobacteria increased the pH in paddy water [6] resulting to a hydrolysis of carbofuran at high pH.

Salinity affected carbofuran degradation in saline water i.e., carbofuran was less persistence at higher salinity level (Table 4). This may due to the fact that as the salinity level in water increased the pH increased resulting to an increase of the rate of hydrolysis.

We noticed that the half-life values of saline soil (Table 3) were much lower than the half-life values of saline water (Table 4). A more basic condition in saline soil (Table 1) may be responsible to this trend.

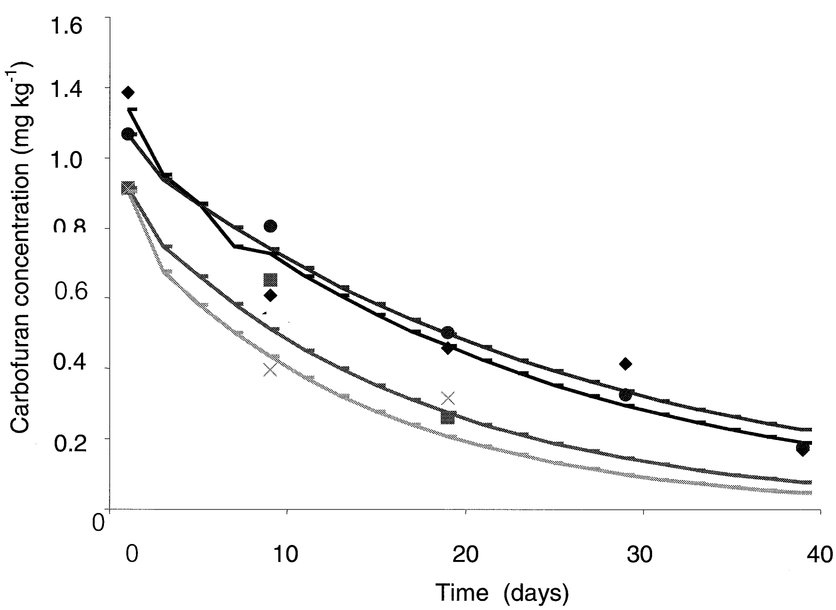

Figure 1. Disssipation of carbofuran in non-autoclaved saline soil, (■ = no salinity; ✖ = low salinity; ● = medium salinity; ◆ = high salinity; solid lines = carbofuran concentrations).

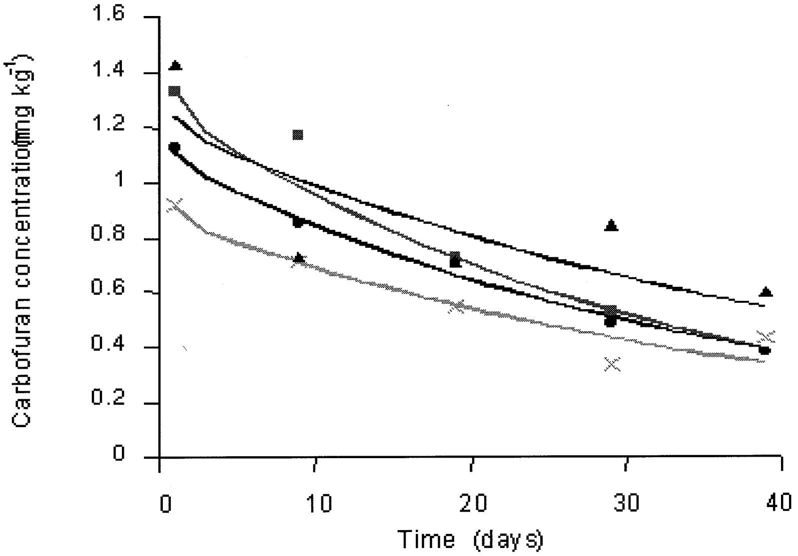

Figure 2. Disssipation of carbofuran in autoclaved saline soil, (■ = no salinity; ✖ = low salinity; ● = medium salinity; ▲ = high salinity; solid lines = carbofuran concentrations in autoclaved saline soil fitted to the first order kinetic model).

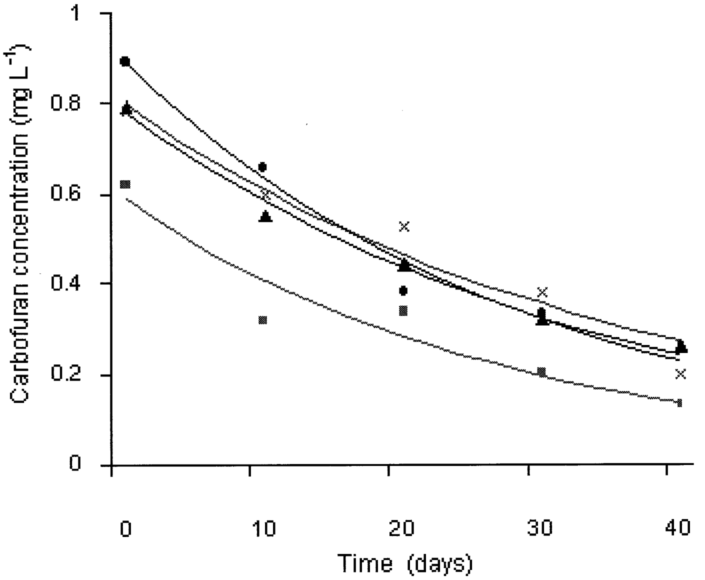

Figure 3. Disssipation of carbofuran in non-autoclaved saline water, (■ = no salinity; ✖ = low salinity; ● = medium salinity; ▲ = high salinity; solid lines = carbofuran concentrations in autoclaved saline water fitted to the first order kinetic model).

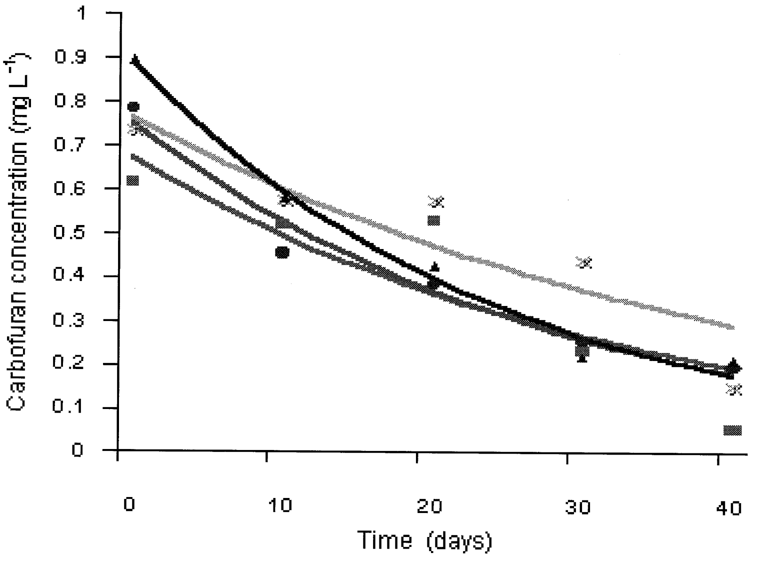

Figure 4. Disssipation of carbofuran in autoclaved saline water, (■ = no salinity; ✖ = low salinity; ● = medium salinity; ▲ = high salinity; solid lines = carbofuran concentrations in autoclaved saline water fitted to the first order kinetic model).

Table 3. Degradation rate constant (k) and half-lives ($t_{1/2}$) of carbofuran from non-autoclaved and autoclaved saline soils.

Salinity level	Non-autoclaved soil			Autoclaved soil		
	k1 (day^{-1})	$t_{1/2}$ (days)	r^2 ✝	k1 (day^{-1})	$t_{1/2}$ (days)	r^2 ✝
No salinity	0.06	11	0.91	0.04	22	0.90
Low salinity	0.07	9	0.95	0.03	28	0.95
Medium salinity	0.04	18	0.98	0.04	26	0.98
High salinity	0.05	15	0.95	0.03	33	0.99

✝ Coefficients of determination for non-linear regressions.

Table 4. Degradation rate constant (k) and half-lives ($t_{1/2}$) of carbofuran from non-autoclaved and autoclaved saline water.

Salinity level	Non-autoclaved water			Autoclaved water		
	k1 (day^{-1})	$t_{1/2}$ (days)	r^2 ✝	k1 (day^{-1})	$t_{1/2}$ (days)	r^2 ✝
No salinity	0.03	23	0.76	0.02	33	0.90
Low salinity	0.02	29	0.81	0.03	26	0.95
Medium salinity	0.04	19	0.96	0.04	20	0.98
High salinity	0.04	17	0.99	0.04	17	0.99

✝ Coefficients of determination for non-linear regressions.

4. Conclusions

In this study we found:

4.1 Biological process was a major route of carbofuran degradation in saline soil.

4.2 Salinity level did not affect carbofuran degradation in soil.

4.3 Chemical hydrolysis was a major dissipa-tion route of carbofuran in saline water and that biological process was of less significance.

4.4 Carbofuran was less persistence in saline soil than in saline water which may due to a more basic condition of saline soil.

4.5 Our data suggested that carbofuran used in saline paddy field were not persistent due to its rapid dissipation in water and soil. Neutral to basic condition of saline water and saline soil favored a rapid dissipation of carbofuran.

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