EnvironmentAsia
The international journal published by the Thai Society of Higher Education Institutes on Environment

Available online at www.tshe.org/EA
EnvironmentAsia 3(2) (2010) 20-28

Adsorption Kinetics of Carbamate Pesticide in Rice Field Soil

Soontree Khuntong [a], Sanya Sirivithayapakorn [b], Pannee Pakkong [c] and Cheema Soralump [b]

[a] *Faculty of Resources and Environment, Kasetsart University, Si Racha Campus*
199 Sukhumvit Rd. Si Racha Chonburi 20230, Thailand
[b] *Environmental Engineering Department, Faculty of Engineering, Kasetsart University, Bangkok, Thailand*
[c] *Applied Radiation and Isotopes, Faculty of Sciences, Kasetsart University, Bangkok, Thailand*

Abstract

Ultrasonic extraction (75.55%) with petroleum ether:acetone (1:1, v/v) was employed for extraction of carbofuran in rice field soil. The amounts of carbofuran were determined by reverse phase HPLC. The analytical method provided high precision and accuracy with the relative error of 0.47%. The percentage of recoveries varied from 84% to 77% in the concentration ranges of 10–40 mg/L of spiked soil samples. The carbofuran residues in the rice field soil significantly decreased year by year because of pesticide properties, soil properties and degradation conditions. A high amount of residues was found in the plots that contained high organic contents. The adsorption of carbofuran in soil reached equilibrium within 23 h. The percentage of adsorption varied from almost 30% to 80% depending on concentrations of carbofuran. The adsorption of carbofuran agreed with Freundlich isotherms; $q = 7.07 \times 10^{-5} C_f^{2.5092}$; with the correlation coefficient of 0.9281. Organic carbon coefficient, K_{oc}, was 1.91×10^{-3} mg/L calculated from K_d, and half-life (8.9 d) of adsorbed carbofuran. The GUS index (6.37) calculated from K_{oc} presented a high lixiviation potential. The positive ΔG indicated the non-spontaneous reaction. Carbofuran rapidly desorbed from soil at the desorption rate of 0.0228 mg/kg soil d. Kinetic studies provided the first order reaction with the reaction rate of 0.0779 mg/d and half-life of 8.9 days.

Keywords: carbofuran; rice field; solvent extraction; soil contamination; pesticide adsorption; adsorption kinetics; desorption

1. Introduction

Rice is the main source of carbohydrate for a large part of the world. In tropical areas, rice is normally grown once or twice a year. During cultivation, water is usually used to flood the growing area to eliminate weeds and plant pests and for a short period of time between the growing seasons, when old rice stems are removed and soil is plowed to prepare for the next season. From these rice growing practices, together with extensive uses of biocides over the past decades, accumulation of biocides are expected in soil even though many biocides have been banned from use for several years. One of biocides popularly used biocide in rice fields is carbofuran.

Carbofuran, 2,3-dihydro-2,2-dimethylbenzofuranyl-methylcarbamate was marketed since 1965 under the trade name of Furadan. It is an odorless, white crystalline solid and available as granules or water emulsifiable liquid (Pinakini and Kumar, 2006). It was one of the most widely used insecticides, nematicides and acaracides applied to control insects of rice fields, sugarcane, tobacco and so on (Yen *et al*., 1997). It was known as a more persistent insecticide than other carbamate or organophosphorus insecticides. The residues of carbofuran were found in tissues and eggs of hens (0.33-0.15 mg/kg) as well as in milk (FAO, 1997)

Many metabolic pathways including photolysis could degrade carbofuran in which hydroxylation and oxidation at the C-3 position yielding 3-hydroxy carbofuran and 3-ketocarbofuran were the major pathways. Photolysis and hydrolysis were two main degradation processes in soil. The natural attenuation at the site occurred in 4-year interval (Campbell *et al*., 2004). Microbial degradation and moisture content of soil affect the persistence of carbofuran in soil (Katsumata *et al*., 2005). Since carbofuran is mostly applied in rice fields, it can react with water generating C-N bonds and breaking C-X bonds (X stands for –OH) (Seiber *et al*., 1978). Factors enhancing the hydrolysis of carbofuran include high pH of water, microbial communities and light intensities (Siddaramappa *et al*., 1978). The calculated half-life was 320 days under acid and 150 days under alkaline conditions (Pinakini and Kumar, 2006). Unlike the FAO, Chaudhry and Ali (1998) found that the half-life of carbofuran ranged from 3 to10 weeks with degradation rate of 7 to 10 times faster in alkaline soil (pH 7.9) than in acid to neutral soils (pH 4.3-6.8).

The accumulation of carbofuran in soil can be found in surface and groundwater. The methods of remediation of carbofuran in soil include oxidation with ozone, photodegradation, combined ozone and UV irradiation, Fenton degradation, biological degradation, coagulation and adsorption are available for remediation of carbofuran in soil (Burrow *et al*., 2002; Wang and Lemley, 2003; Benitez *et al*., 2002; Bano and Musarrat, 2004; Gupta *et al*., 1994).

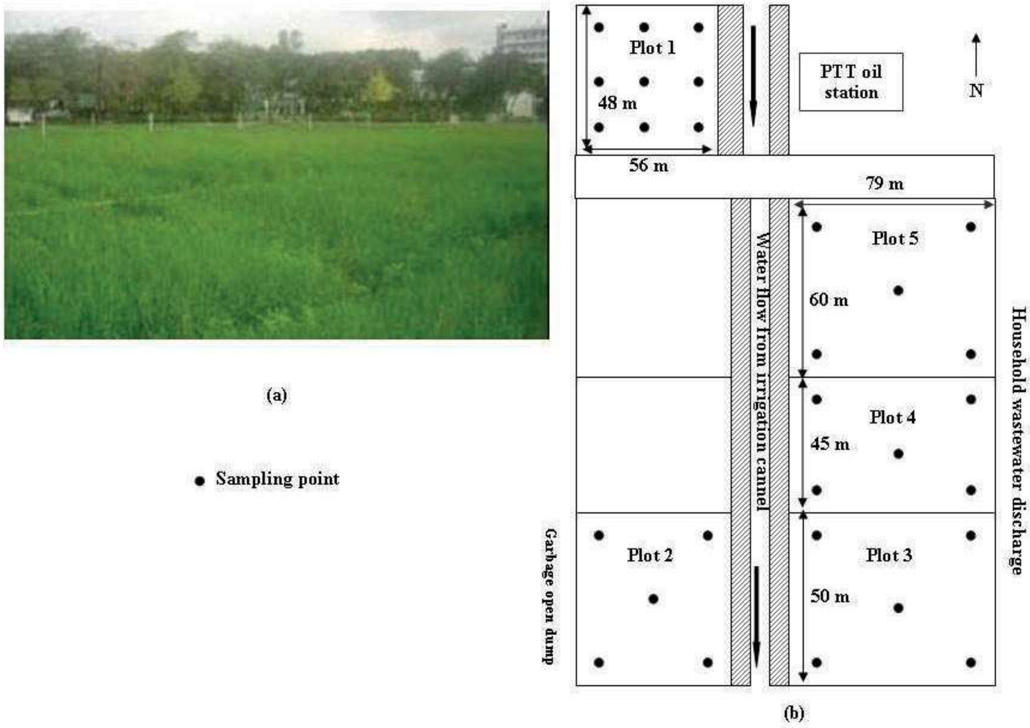
Adsorption of carbofuran resulted from the accumulation of carbofuran in soil and the adsorption isotherms mostly corresponded with Freundlich isotherms (Singh *et al*., 1994; Hsieh and Kao, 1998) and also agreed with the monolayer Langmuir equilibrium model (Gupta *et al*., 2006). Adsorption in soil may be enhanced by increasing soil pH, organic matter and clay contents. For adsorption equilibrium kinetics, Gupta reported that adsorption of carbofuran on carbon slurry at 25, 35 and 45^{o}C fitted with a pseudo-second order kinetic model. The rate constants, K of carbofuran at 15 and 25^{o}C were 7.769×10^{-9} and 7.367×10^{-8}, respectively, and the negative sign ΔG of 40.697 and 44.715 kJ/mol indicated that adsorption of carbofuran in sandy clay loam were spontaneous with ΔH^{o} of 160.6 kJ/mol (endothermic reaction) and ΔS^{o} of 402 kJ/mol (Mear *et al*., 1996).

In this study, carbofuran concentrations were determined from rice field soils after banning of biocide, and adsorption mechanisms were investigated to characterize the adsorption isotherms as well as free energy (ΔG) of the adsorption of carbofuran in the rice field.

2. Materials and Methods

2.1. Site selection for soil sampling and preparation of soil samples.

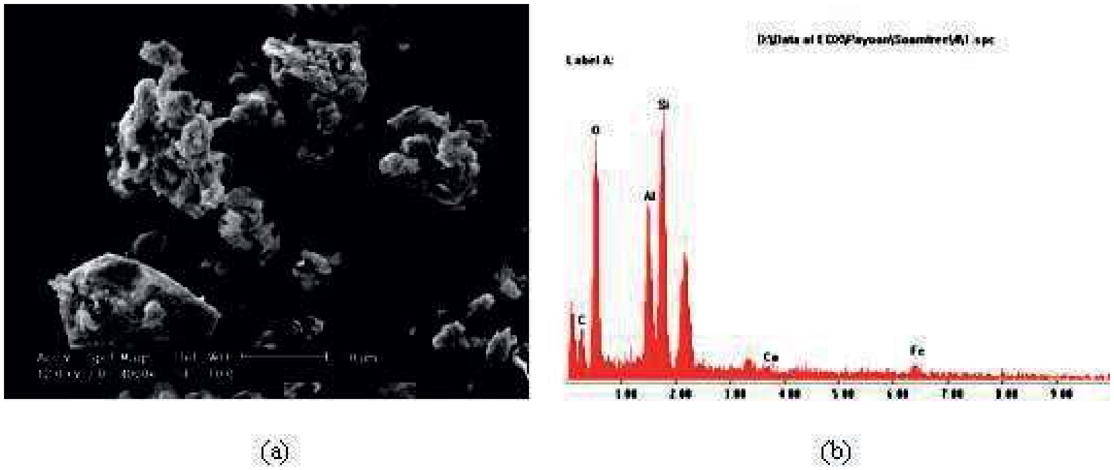
The rice field soils were sampled from the demonstration field at the Bureau of Rice Research and Development, Department of Rice, Ministry of Agriculture and Cooperative located in Kasetsart University, Bangkok. This field is a good representation of rice growing practice in Thailand and her neighboring countries. It was the only rice grown in the field and grown twice a year during the growing season. The soil was inundated with water for about one month between the growing seasons. Water was drained from the field and the soil was plowed and exposed to sunlight. The soil was also considered homogenous since it was repeatedly plowed for years. During growing season, Furadan was repeatedly applied as nematicide in granule formulation. Soil samples were collected at the beginning of the first and second growing season before cropping. Nine sample points in the first field and five sample points in each second to fifth field (Fig. 1) were collected for rice field soil at a depth of around 0-20 cm in October, 2006, May and November, 2007. The first field was used as a



(a)

(b)

Figure 1. (a) The demonstration rice fields (b) Five sampling sites for soil collection.



(a) (b)

Figure 2. (a) Scanning electron micrograph of soil colloid and (b) X-Ray spectrum of soil colloid.

reference field for determination of adsorption and desorption of carbofuran from soil because, comparatively, it was isolated from any contamination. The second field was located close to an open garbage dump to the west. The third, forth and fifth fields were located close to household wastewater discharge to the east.

After soil sampling, the soils were air-dried, ground and sieved through a 250 µm screen and kept in darkness. Composite soil samples were employed for soil characteristics (soil pH, soil classification, organic matter content, Cation Exchange Capacity, CEC) at the Department of Soil Sciences, Faculty of Agriculture, Kasetsart University. Table 1 shows physical properties of soil. The microscopic structure of soil colloid was examined by a Scanning Electron Microscope equipped with an Energy Dispersive Spectrometer, EDS ((Phillips: XL30 & EDAX)) at Department of Material Engineering, Faculty of Engineering, Kasetsart University. Ground soil samples were placed on Pirani 501 device (0.5 x 0.5 cm2) for SEM and EDS analysis. An image of soil colloid from the Scanning Electron Microscope is provided in Fig. 2(a). The semi-quantitative analysis of soil compositions are given in Fig. 2(b).

2.2. Chemicals and equipments.

Carbofuran (99%) was purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Analytical grade organic solvents: petroleum ether (Lab Scan), hexane (Unilab) and acetonitrile (analytical grade) and acetonitrile (HPLC grade) purchased from Lab Scan. Water used for HPLC was prepared in house from preparation Millipore Simplicity 185. Alumina (extra pure) was purchased from Riedel-de Haën.

The instruments used were a High Performance Liquid Chromatograph (HPLC) assisted by a UV detector (Shimadzu LC-10AT VP), Ultrasonic bath (Bandelin Sonorex Super AK 514 BH), Soxhlet Extractor (Gerhardt 16), Rotary Evaporator (Büchi Rotavapor R-114), Mechanical Shaker (Scrinker II, Panapolytech) and Centrifuge (Hettich EBA 20 Zentrifugen).

The spiked samples from each site of any field were prepared by homogenization. Ultrasonic extraction of carbofuran coupled with HPLC methods was used to determine the amount of carbofuran from the rice field soils. The method of soil sample spiking was modified from Tor *et al*. (2006). Thus, spiked soil samples were prepared by adding a fixed amount of standard solution of pesticide to 10 grams of soil. Ten milliliters of acetone was added to the spiked soil sample and the suspension was mixed for 30 min with a mechanical shaker. After evaporation of the solvent at room temperature, the sample was kept in a stopper conical flask and stored in darkness at 4^{o}C for three days. To determine the amounts of pesticides in soil, ultrasonic extraction with 75.55% recovery was used. The recoveries of ultrasonic extraction from four concentration ranges (10 - 40 mg/L) of carbofuran varied from 77 - 84%. Detailed procedures of this extraction method were described in Khuntong *et al*., 2008.

Five concentration ranges of pesticide: 5, 10, 15 20 and 25 mg/L were prepared by diluting 100 mg/L of stock solution of carbofuran. The normalization provided by Skoog *et al*., 1996 was used to obtain the calibration graph and the limit of detection for HPLC. The amount of extracted pesticides was analyzed and the efficiencies of extraction were also determined. Carbofuran residues in rice field soils in the three collection periods; October 2006, May 2007 and November 2007 were determined.

2.3. Adsorption/desorption of carbofuran in soil.

Adsorption equilibrium was initially determined for the appropriate adsorption time. Adsorption isotherms were obtained using the batch equilibrium methods. Each one gram of soil sample was weighed into a 125-ml polyethylene bottle which was filled with ten-ml aqueous solution of carbofuran at the initial concentrations (C_i) ranging from 20 to 300 mg/L. The suspensions were mechanically shaken at 1,500 rpm at room temperature for 24, 48 and 72 h. After shaking, the suspensions were centrifuged at 3,000 rpm for 15 min. The supernatants were filtered through 0.22 micron filter and the concentration was determined by HPLC. The adsorbed amounts of carbofuran in soil (C_f) were calculated from the difference between C_i and concentrations of the supernatants. The adsorption data were calculated using the logarithmic model from Freundlich isotherm (Fig. 4).

For desorption, the fixed amounts of carbofuran solutions were added into each ten gram of ground soil and mixed well. Each suspension was mechanically shaken at 1,500 rpm for 10 h. After shaking, all of the suspensions were centrifuged at about 3,000 rpm for 15 min. The supernatants were filtered through 0.22 micron filter and the concentrations of supernatant liquids were determined by HPLC. The initial concentrations of adsorbed carbofuran on soil were calculated from the difference between the initial concentration of aqueous carbofuran solution and the concentration of carbofuran in the supernatant liquids. Each soil residue was then filled with ten milliliters of deionized water and shaking continued at 1,500 rpm for 2, 4, 6,…, 24 h. Every two h, samples were removed and centrifuged at 3000 rpm and the supernatant was analyzed for the amount of carbofuran desorbed from the soil. The desorption rate was determined by the graph between desorption times (x) and logarithmic amounts of desorbed carbofuran (y) in Fig. 7. Finally, adsorption kinetics was also calculated.

3. Results and Discussion

Physical properties of rice field soil are provided in Table 1. The soil could be classified as clay by textural triangle (Brady and Weil, 2004). The microscopic structure and composition of soil colloid are presented in Fig. 2 and it showed the soil in flake-like structure. The spot of x-ray spectrum showed the major components of silicate soil contained silicon, oxygen and aluminum.

Table 1. Properties of soil colloid.

Properties	Values
pH	5.5
Organic matter (% by weight)	3.74
Sand (% by weight)	9.6
Silt (% by weight)	33
Clay (% by weight)	57.4
Cation Exchange capacity (cmol/kg)	23.0

The chromatogram of carbofuran indicated the single peak at 6.4 min. The detection limit of measuring method was 282.83 µg/L. The concentrations of five replication measurements were 15.12, 15.23, 14.99, 15.01 and 15.00 mg/L with the average value of 15.07 ± 0.09 mg/L. The relative error was calculated from [(15.07–15.00)/15.00] x 100 = 0.47%. The calculated relative error lies within ±5%, indicating a high accuracy, while the small values of standard deviation indicated a high precision.

3.1. Carbofuran residues in the rice field soil.

Fig. 3 shows carbofuran residues in a rice field during three consecutive growing seasons; October, 2006, May, 2007 and November, 2008. Also, although carbofuran was prohibited more than 5 years before, residual carbofuran still remained. There are many reasons for this: first, since soil pH was 5.5 and carbofuran is stable in acidic condition (Siddaramappa and Seiber, 1979); second, the persistence of carbofuran in rice field soil could be caused by the low air-water partition coefficient, K_{aw} of 1.23×10^{-7} (de Melo Plese *et al*., 2005) which indicates that carbofuran preferably dissolves in aqueous phase ($K_{aw} < 4.0 \times 10^{-6}$) and was not volatile under atmospheric temperature (Trapp and Matthies, 1998); third, persistence of carbofuran generated from physical attraction of carbofuran into the interlayer of silicate clay and chemical bonding of carbamate with the ionic sites of silicate clay (Mear *et al*., 1996); fourth, photochemical reactions significantly occur only on soil surface (Scheunert *et al*., 1993); fifth, when the soil is directly exposed to sunlight, in temperatures, which exceed 35°C, may increase the accumulation of the pesticides at the soil surface by convection movement of evaporating water (Bowmer, 1991) and sixth, the lack of oxygen presented in anaerobic conditions caused relatively low biodegradation by aerobic microorganisms (Redondo *et al*., 1994). When comparing these carbofuran concentrations in the rice field soil, carbofuran accumulated higher in stems, and in leaves of rice (54.4 µg/kg) dry weight than in rice grain (Teerakun and Reungsang, 2005).

The accumulation of carbofuran was lowest in the first plot since it was comparatively isolated from other contaminations while the second plot was near an open garbage dump with leachate discharged into the plot, and the plots number three, four and five might have

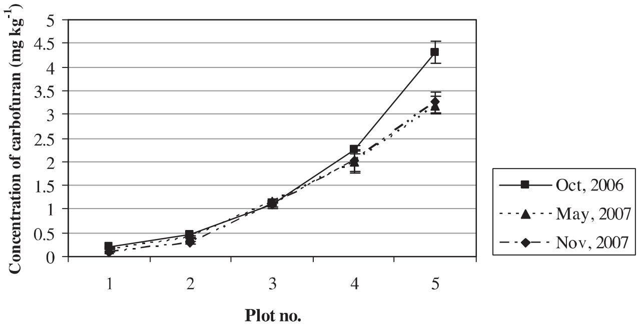


Figure 3. Carbofuran residues in rice field (*means±SD, n=3*)

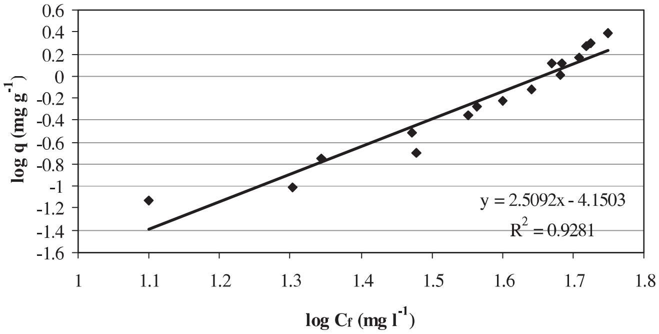


Figure 4. Adsorption isotherm of carbofuran on soil for 24 h of adsorption.

been affected by household wastewater discharged nearby. Also the higher clay and organic matter contents may enhance the accumulation of carbofuran in soil as reported by Hsieh and Kao (1998). After twice plowing per year, the soil was directly exposed to sunlight for not more than two months. Since the main degradation pathways are hydrolysis and photolysis (Campbell *et al*., 2004; Soler *et al*., 2006), carbofuran could be broken down with less exposure of sunlight in rice field. From Fig. 3, the carbofuran residue decreased from the first to the third growing season (October 2006 to November 2007), possibly because of soil tillage and drainage of water. Soil tillage might increase exposure of soil to sunlight enhancing photodegradation of carbofuran.

3.2. Adsorption of carbofuran on rice field soil.

The rapid adsorption occurred at the beginning since there was only physical affinity between the soil and carbofuran, and there was a difference in concentration gradient between bulk solution and surface of soil. Carbofuran was continuously adsorbed to soil and reached equilibrium at nearly 23 h (data not shown). The adsorption time beyond 23 h was applied to determine adsorption isotherms and desorption kinetics.

Table 2. Amounts of carbofuran (*mg; means ± SD, n=3*) and percentages of carbofuran adsorbed in soil.

Initial amount (mg)	**Adsorbed amount (mg)**	**Percentage of adsorption**
0.2	0.0541 ± 0.045	27.04
0.3	0.0992 ± 0.000	33.07
0.4	0.1517 ± 0.037	37.92
0.5	0.2006 ± 0.002	40.11
0.6	0.2826 ± 0.020	47.11
0.8	0.4449 ± 0.008	55.61
0.9	0.5306 ± 0.011	58.95
1	0.6101 ± 0.011	61.01
1.2	0.7788 ± 0.018	64.90
1.5	1.0317 ± 0.029	68.78
1.6	1.1416 ± 0.022	71.35
1.8	1.2948 ± 0.020	71.93
2	1.4939 ± 0.021	74.70
2.4	1.8526 ± 0.026	77.19
2.5	1.9683 ± 0.025	78.73
3	2.4235 ± 0.025	80.78

Adsorption of carbofuran on rice field soil was performed by variation of concentration ranges from 20 to 300 mg/L and adsorption times during 1 to 3 days. Amounts of carbofuran adsorbed on silicate clay are given in Table 2. The percentage of adsorption depended on concentrations of carbofuran. The concentrations of carbofuran from 20 up to 50 mg/L corresponded to adsorption of Malaysian clay soil (Farahani *et al*., 2007). From the previous study, a high amount of organic matter played an important role in the high adsorption of carbofuran in clay soil (Heieh and Kao, 1998).

The Freundlich isotherms (Fig. 4) were obtained from the slope and intercept of linear regression line between log C_f (mg/L) and log q (mg/kg). The equation was presented by $q = KC_f^{1/n}$. The high correlation coefficient of the line was 0.9281. The Freundlich adsorption exponent (1/n, 2.5092) was obtained from slope of this line and the extent of adsorption K_d from the intercept of the line. The 1/n values which were greater than unity (>1.0) indicating a relative increase due to the increasing of initial concentrations. The isotherm is then represented as $q = 7.07 \times 10^{-5} C_f^{2.5092}$.

The adsorption coefficient equaled the concentration of solute in stationary phase divided by concentration of solute in the mobile phase, which was quite similar to the equilibrium constant of adsorption. The adsorption coefficients were almost 10^4 times higher than the previous values reported by Mear *et al*. (7.367×10^{-8} and 7.769×10^{-9} at 25 and 15°C, respectively) (Mear *et al*., 1996), the lower Kd showed higher adsorption of carbofuran. The calculated value of Koc was 1.91 x 10-3 mg/L which indicated a low affinity with soil particles and a very high mobility to soil solution. The low affinity in soil particles might be due to low content of soil organic matter. The values of *K* could be applied for determination of Gibb's free energy, ΔG by

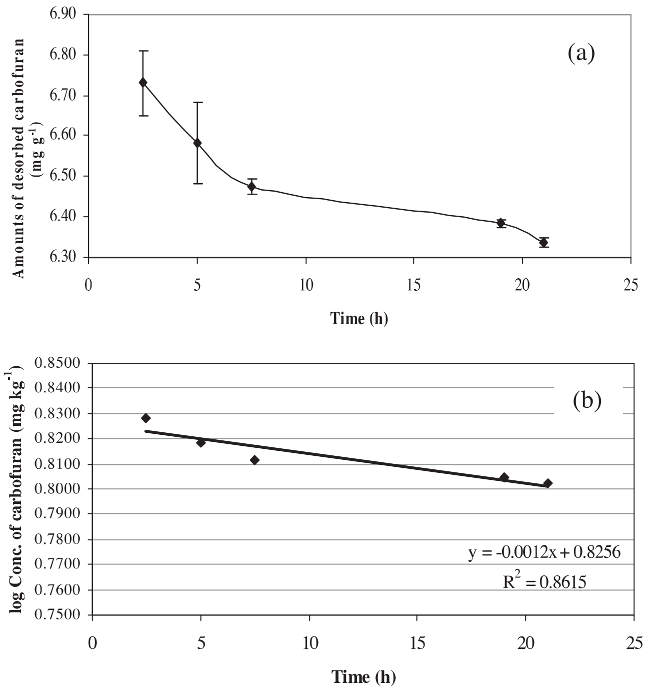


Figure 5. (a) Desorption of carbofuran from rice field soil (*means* ± *SD; n=3*). (b) Logarithmic plot between means of concentrations of carbofuran (mg/kg) and time (h).

the equation: $\Delta G^o = -RT \ln K_{eq}$ where R was the universal gas constant (8.314 J/mol/K), T was 303 Kelvin, and the equilibrium constant, K_{eq}. The positive ΔG (24.079 kJ/mol) indicated that the adsorption of carbofuran in soil was nonspontaneous. It did not agree with Singh *et al*. (1994).

3.3. Desorption of carbofuran from rice field soil.

The characteristics of adsorption [Fig. 5(a)], indicate that carbofuran rapidly desorbed from soil at the beginning because of the large difference in concentration gradient between soil and water. When the concentration of carbofuran in soil and water approached equilibrium, carbofuran still continuously desorbed albeit at a slower rate than at the initial condition. At the final state, decrease of carbofuran may be caused by degradation from hydrolysis and photolysis pathways.

The desorption rate can be obtained from the slope of the linear logarithmic plot between desorbed amounts (mg/kg) and time [Fig. 5(b)]. The desorption rate was 0.0288 mg/kg soil/d.

3.4. Adsorption kinetics.

The adsorption kinetics was expressed from concentration of carbofuran in each concentration range plotted against adsorption time as shown in Fig. 6. The decrease of concentration over time, dC/dt at average

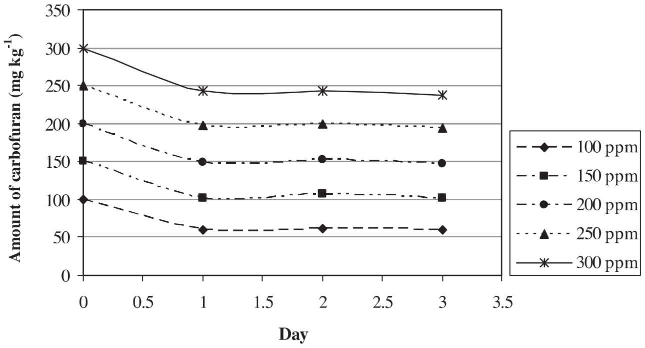


Figure 6. Adsorption kinetics of carbofuran at 303 Kelvin.

C of each line at initial state was used to construct the graph for determination of the reaction rate constant, *k* (Fig. 6). The concentration was utilized at the initial state because adsorption was only one mechanism at the initial state indicated by the straight line at the beginning. Later, the concentration is relatively constant.

The reaction rate constant was calculated from the slope of the linear regression line in Fig. 7 in which that the adsorption of carbofuran was the first order kinetics. The reaction rate constant was 0.0779 mg/day corresponding to the slope of the regression line.

Following the first order reaction, the half life of adsorption could be determined from: $C/C_o = e^{-kt}$ where C_o and C were the initial concentration and concentration of carbofuran at time t and *k* was the reaction rate constant. The half life of carbofuran in rice field soil calculated from the slope was 8.9 days, which was quite different from Lysan sand; 112 days and Ottawa sands: 91 days (Campbell, 2004). The half-life which was detected at a depth of 2–20 cm after 7 and 14 days was similar to that in a field study by Johnson and Lavy in 1994. Our half-life value in rice field also agreed with Mabury *et al*. (1996) which ranged from 2 to 26 days. The first order kinetics agreed with Campbell in both Lysan sand [$X_i = X_o$ exp (-0.0182t+0.0504) and Ottawa sand [$X_i = X_o$ exp (-0.0151t–0.0938), where X_i was the concentration at day 1, X_o the initial concentration, and t was the time (Campbell, 2004). For very long term and continuous application of carbofuran in this field,

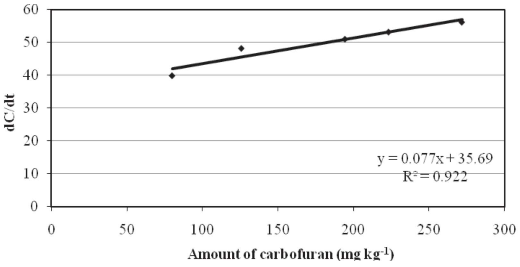


Figure 7. The reaction rate constant constructed from average concentration of carbofuran and dC/dt at 303 Kelvin.

the residues still accumulated and persisted even though application was stopped for more than five years. Adsorption was one of many mechanisms for reduction of carbofuran it this field. Carbofuran was not adsorbed into the soil in large amounts, but it could be strongly adsorbed on the surface of clay particles. The natural attenuation of carbofuran was very slow as residues were still detected. The degradation of carbofuran in this field should be studied.

The carbon organic partition coefficient, K_{oc} was used to determine the lipophilicity in the assessment of both the uptake and physiological distribution of carbofuran and prediction of their environmental fate (IUPAC Glossary of Terms Used in Toxicology, n.d.). The calculated value of K_{oc} was 1.91 x 10^{-3} mg/L, which indicated a low affinity with soil particles and a very high mobility to soil solution. The low affinity in soil particle might be due to low content of soil organic matter. Since water supplied to the field was almost standing water; carbofuran may be re-adsorbed to soil colloids (de Melo Plese *et al.*, 2005). The Groundwater Ubiquity Score, GUS index, was based on graphical examination of a plot formed by two widely available pesticide properties: the half-life ($t_{1/2}$) in soil and the K_{oc} (Gustafson, 1989). The GUS index could be determined by de Melo Plese *et al.*, by GUS = [4-log(K_{oc})] x log $t_{1/2}$.

The calculated GUS index was 6.37 which presented a high lixiviation potential (GUS > 2.8). Most herbicides are relatively persistent and weakly adsorbing, with GUS mostly exceeding 2.8; then the potential to contaminate groundwater can be influenced by other factors, including soil conditions, application methods, and irrigation practices (Gan, 2002). The values were different from de Melo Plese *et al.*, (2005), but agreed with those reported by Bosch and Truman (2002) and Cogger *et al*. (1998) who detected high amounts of carbofuran residues in soils from Plains, Georgia and Washington, USA, respectively.

4. Conclusion

Ultrasonic extraction with a mixture of petroleum ether and acetone was available for extraction of carbofuran from clay with 75% recovery, and the extraction efficiencies were significantly different from Soxhlet extraction. Rice field soil was sampled for three consecutive growing seasons; October 2006, May and November, 2007. The residue of carbofuran was higher in the 3rd field (261 ± 0.38), 4th (2.309 ± 0.49) and 5th (2.426 ± 0.4) than the 1st 1(0.178 ± 0.01) and 2nd (0.191 ± 0.05) mg/kg, due to the high contents of organic matter from wastewater discharge.

Adsorption of carbofuran reached equilibrium at 23 h. The percentage of adsorption varied from almost 30% to 80% depending on the initial concentrations of carbofuran. The Freundlich isotherms were: $q = KC_f^{1/n}$; with the correlation coefficients of 0.9281. The distribution coefficient, K_d was 7.07 x 10^{-5} mg/kg. The Freundlich adsorption exponent (1/n) value which was greater than unity (2.5092) indicated the relative increase from the increasing of initial concentrations. The positive Gibb's free energy (ΔG) of adsorption (24.078 kJ/mol) indicated nonspontaneous adsorption processes of carbofuran in rice field soil. Carbofuran rapidly desorbed from soil at the beginning because of the difference in concentration gradient between soil and solution. After equilibrium, carbofuran still continuously desorbed albeit at a slower rate than at the initial condition. At the final state, decrease of carbofuran might be due to the degradation from hydrolysis and photolysis. The desorption rate was 0.0228 mg/kg soil/d. The percentage of desorption was approximately 55% from the beginning to 21 h.

Our kinetic study indicates a first order reaction with the reaction rate of 0.0779 mg/d and half-life of 8.9 days. The K_{oc} (1.91 x 10^{-3} mg/L) indicates a low affinity with soil particles and a very high mobility to soil solution. It also suggests a high lixiviation potential to groundwater.

Finally, the residues of any pesticides that are adsorbed in rice field soil can be reduced by practical cropping to enhance natural attenuation without chemicals required. Continuous tillage of soil allows soil for direct exposure to sunlight and brings about aerobic conditions for increasing chemical and biological degradation.

Acknowledgement

We would like to show appreciation and sincere thanks to Faculty of Resources and Environment for financial support and providing all equipment. We also thank our colleges and students in the Department of Environmental Science, Faculty of Resources and Environment, Kasetsart University, Si Racha Campus.

References

Bano N, Musarrat J. Characterization of a novel carbofuran degrading *Pseudomonas* sp. with collateral biocontrol and plant growth promoting potential. FEMS Microbiology Letters 2004; 231: 13-17.

Benitez FJ, Acero JL, Real FJ. Degradation of carbofuran by using ozone, UV radiation and advanced oxidation processes. Journal of Hazardous Materials 2002; B89: 51-65.

Bosch DD, Truman CC. Agrochemical transport to groundwater through coastal plain soils. Transactions of the ASAE 2002; 45: 1385-96.

Bowmer KH. Atrazine persistence and toxicity in two irrigated soils of Australia. Australian Journal of Soil Research 1991; 29: 339-50.

Brady NC, Weil RR. The Nature and Properties of soils. 13th edition. Prentice Hall, New Jersey. 2002; 316-41.

Burrow HD, Canle LM, Santaballa JA, Steenken S. Reaction pathways and mechanisms of photodegration of pesticides. Journal of Photochemistry and Photobiology B: Biology 2002; 67: 71-108.

Campbell S, David MD, Woodward L, Li XQ. Persistence of carbofuran in marine sand and water. Chemosphere 2004; 54: 1155-61.

Chaudhry GR, Ali AN. Bacterial metabolism of carbofuran. Applied and Environment Microbiology 1988; 54: 1414-19.

Cogger CG, Stark JD, Bristow PR, Getzin LW, Montgomery M. Transport and persistence of pesticides in alluvial soils; II, Carbofuran. Journal of Environmental Quality 1998; 27: 551-56.

De Melo Plese LP, Paraiba LC, Foloni LL, Trevizan LRP. Kinetics of carbosulfan hydrolysis to carbofuran and the subsequent degradation of this last compound in irrigated rice fields. Chemosphere 2005; 60: 149-56.

Farahani GHN, Zakaria Z, Kuntom DA, Dzolkifli D, Ismail BS. Adsorption and desorption of carbofuran in Malaysian soils. 2007. Advances in Environmental Biology 2007; 1(1): 20-26.

Gan, J. Pesticide and Groundwater Quality. Pesticide Wise A Quarterly Publication of the Department of Environmental Sciences 2002. http://www.pw.ucr.edu/textfiles/PesticideWiseWinter2002.htm Mar, 2008. Gustafson DI. Groundwater Ubiquity Score: A simple method for assessing pesticide leachability. Environmental Toxicology and Chemistry 1989; 8(4): 339-57.

Gupta VK, Ali I, Saini VK. Adsorption of 2,4-D and carbofuran pesticides using fertilizer and steel industry wastes. Journal of Colloid and Interface Science 2006; 299: 556-63.

Hsieh T, Kao MM. Adsorption of carbofuran on lateritic soils. Journal of Hazardous materials 1998 5B; 58: 275-284.

Johnson W G, Lavy TL. In-situ dissipation of benomyl, carbofuran, thiobencarb and triclopyl at three soil depths. Journal of Environmental Quality 1994; 23(3): 556-62.

Katsumata H Matsuba K, Kaneco S, Suzuki T, Ohta K, Yobiko Y. Degradation of carbofuran in aqueous solution by Fe(III) aqua-complexes as effective photocatalysts. Photochemistry and Photobiology A 2005; 170: 239-45.

Khuntong S, Chomsurin C, Sirivithayapakorn S, Pakkong P. Investigation of carbofuran residues in rice field soil, adsorption in soil. The International Symposium on Lowland Technology, ISLT 2008. 24-26 September 2008. Busan, Korea, 2008. 601-07.

Hsieh TL, Kao MM. Adsorption of carbofuran on lateritic soils. Journal of Hazardous Materials 1998; 58: 275-84.

Mabury SA, Cox JS, Crosby DG. Environmental fate of rice pesticides in California. Reviews of Environment Contamination and Toxicology 1996; 1996; 147: 71-117.

Mear AM, Saint JL, Privat M. Adsorption mechanisms of carbofuran on silica: structure, kinetics, and solubility influence. Ecotoxicology and Environment Safety 1996; 35: 163-73.

Pinakini KS, Kumar TSM. Serial chlorinesterase estimation in carbamate poisoning. Journal of Forensic Medicine and Toxicology 2006; 13: 274-76.

Redondo MJ, M. Ruiz J, Boluda R, Font G. Persistence of pesticide residues in orchard soil. Science of the Total Environment 1994; 156: 199-205.

Scheunert I, Mansour M, Dörfler U, Schroll R. Fate of pendimethalin, carbofuran and diazinon under abiotic and biotic conditions. Science of the Total Environment 1993; 132: 361-69.

Seiber JN, Catahan MP, Barril CR. Loss of carbofuran from rice paddy water: chemical and physical factors. Journal of Environmental Health 1978; 13B: 131-48.

Siddaramappa R, Tirol AC, Seiber JN, Heinrichs EA, Watanabe I. The degradation of carbofuran in paddy water and flooded soil of untreated and treated rice fields. Journal of Environmental Health 1978; 13B: 369-80.

Siddaramappa R, Seiber JN. Persistence of carbofuran in flooded rice soils and water. Prog Water Technol II 1979; 11: 103-41.

Singh RP, Kumari K, Dhirendra D. Influence of different factors on the adsorption of carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl–*N*-methyl carbamate) on soils. Ecotoxicology and Environment Safety 1994; 29: 70-79.

Skoog DA, West DM, Holler FJ. Fundamental of Analytical Chemistry. 7th ed. Saunders Collage Publishing. Fort Worth, USA. 1996; 60-63.

Soler C, Manes J, Picó Y. Determination of carbosulfan and its metabolites in oranges by liquid chromatography ion-trap triple-stage mass spectrometry. Journal of Chromatography A 2006; 1109: 228-41.

Teerakun M, Reungsang A. Determination of plant species for the phytoremediation of carbofuran residue in rice field soils. The Songklanakarin Journal of Science and Technology 2005; 27(5): 967 -73.

Tor A, Aydin ME, Özcan S. Ultrasonic solvent extraction of organochlorine pesticides from soil. Analytica Chimica Acta 2006; 559(2): 173-80.

Trapp S, Matthies M, Chemodynamics and Environmental Modeling. Springer, Heidelberg. 1998. Wang Q, Lemley A. Oxidative degradation and detoxification of aqueous carbofuran by membrane anodic Fenton treatment. Journal of Hazardous Materials B 2003; 98: 241-55.

Yen JH, Hsiao FL, Wang YS. Assessment of the insecticide carbofuran's potential to contaminate groundwater through soils in the subtropics. . Ecotoxicology Environment Safety 1997; 38: 260-65.

FAO Corporate Document Repository. Pesticide residues in food-1997. http://www.fao.org/docrep/W8141E/w814e0i.htm Feb, 2008. United States National Library of Medicine, National Institute of Health. IUPAC Glossary of Terms Used in Toxicology. http://sis.nlm.nih.gov/enviro/iupacglossary/glossaryo.html. Feb, 2008.

Received 9 January 2010
Accepted 15 February 2010

Correspondence to
Dr. Soontree Khuntong
Faculty of Resources and Environment,
Kasetsart University, Si Racha Campus
199 Sukhumvit Rd.
Si Racha Chonburi 20230,
Thailand
e-mail: srcstk@ku.ac.th