

## Simulation of the fate of the insecticide carbofuran in a rice field using a level IV fugacity model

L. C. Paraíba<sup>1\*</sup>, L. P. de M. Plese<sup>2</sup>, L. L. Foloni<sup>2</sup> and J. M. Carrasco<sup>3</sup>

<sup>1</sup> EMBRAPA Meio Ambiente, Rodovia Campinas Mogi-Mirim, SP 340 km 127.5.  
CxP: 69. CEP 13820-000. Jaguariúna (São Paulo). Brazil

<sup>2</sup> Departamento de Água e Solo, Faculdade de Engenharia Agrícola, Universidade Estadual de Campinas.  
CxP: 6011. CEP 13081-970. Campinas (São Paulo). Brazil

<sup>3</sup> Departamento de Biotecnología, Escuela Técnica Superior de Ingenieros Agrónomos.  
Universidad Politécnica de Valencia. Camino de Vera, s/n. 46022 Valencia. Spain

### Abstract

The object of this work was to verify the utility of a level IV fugacity model to simulate the environmental fate of the insecticide carbofuran when employed in the cultivation of irrigated rice. The model simulated the dynamic distribution of carbofuran in a system comprising of air, water, rice plants and the soil. The results indicated preferential compartments quality, and provided further knowledge of the fate of carbofuran in rice cultivation. Field experiments on rice were carried out to test the correspondence between simulated and measured carbofuran concentration in water and soil. Simulated concentrations had higher values in the compartments water > soil > rice plants > air. The model can be a useful tool for simulating the environmental fate of this insecticide and can be coupled with sensitivity and uncertainty analyses to test the influence of all input parameters on the outputs.

**Additional key words:** carbamate, carbosulfan, *Oryza sativa*, *Oryzophagus oryzae*, pesticide, weevil.

### Resumen

#### Simulación del comportamiento ambiental del insecticida carbofurano en campos de arroz por el modelo de fugacidad nivel IV

El objetivo de este trabajo fue comprobar la utilidad del modelo de fugacidad nivel IV para simular el comportamiento ambiental del insecticida carbofurano empleado en cultivos de arroz. Con este modelo se simuló la distribución dinámica del carbofurano en un sistema constituido por aire, agua, plantas de arroz y suelo. Los resultados indican los compartimentos preferenciales y permiten predecir el comportamiento ambiental del carbofurano. Para validar el modelo, se realizaron experimentos en campos de arroz verificando la correspondencia entre las concentraciones simuladas y las concentraciones del carbofurano en agua y suelo. Los valores de las concentraciones simuladas en los compartimientos fueron agua > suelo > plantas de arroz > aire. Este modelo puede ser útil para simular el comportamiento ambiental de este insecticida y se puede aplicar el análisis de sensibilidad y de incertidumbre para determinar la influencia de los parámetros de entrada en las salidas del modelo.

**Palabras clave adicionales:** carbamato, carbosulfano, gorgojo, *Oryza sativa*, *Oryzophagus oryzae*, plaguicida.

### Introduction

*Oryzophagus oryzae* (Coleoptera: Curculionidae), commonly known as the rice-infesting weevil, is a major pest of irrigated rice (*Oryza sativa*) crops. Its larvae cause severe damage to rice roots after flooding and consequently drastically reduce plant nutrient

uptake (Carbonari, 2000). When this pest is not controlled grain yield losses may reach 40%. One control procedure is insecticide application, which in recent years has been common in Brazil. Carbofuran has been the most widely used insecticide and the control procedure is the direct application of carbofuran into irrigation water when weevil larvae are detected.

Effectiveness is shown by taking some plants and shaking them into the water, the larvae are visible on the surface of the water (Prando, 2002). Although

\* Corresponding author: [lourival@cnpma.embrapa.br](mailto:lourival@cnpma.embrapa.br)  
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carbofuran has good agronomic efficiency, this insecticide has environmental restrictions due to the risk of contamination. A problem frequently associated with carbofuran is the death of forest animals as observed in Virginia by Stinson *et al.* (1994). Dietrich *et al.* (1995) reported similar problems for carbofuran granules applied to field crops in Switzerland. Crepeau and Kuivila (2000) suggested the continuous presence of carbofuran in water channels and rivers might cause severe, sub-lethal or chronic damage to aquatic organisms. Gupta (1994) observed carbofuran was toxic to micro crustaceans and vertebrates in the same food chain, and Norberg-King *et al.* (1991) affirmed that carbofuran was toxic to aquatic wildlife. In 1985, the United States Environmental Protection Agency (EPA) announced a special review of all registered uses of granular carbofuran in the United States because of concerns about its negative impact on birds (James, 1995). Although carbofuran is quickly degraded in the environment, Wayland and Boag (1990, 1995) and Wayland (1991) applied it to prairie wetlands and reported declines in populations of *Gammarus lacustris*, *Chironomus tentans* and *Hyalella azteca*; nymphs of *Enallagma* genus showed reduced survival. Carbofuran persistence in paddy water and in the soil solution has been studied in tablelands and channels, because carbofuran is mainly degraded by hydrolysis (Seiber *et al.*, 1978; Siddaramappa and Seiber, 1979; Tejada and Magallona, 1985; Jinhe *et al.*, 1989; Mora *et al.*, 1996; Trevizan *et al.*, 2002). However, Chiron *et al.* (1995) demonstrated that carbamate insecticide concentrations exceeding  $0.5 \mu\text{g L}^{-1}$ , the limit established by the European Community are rarely found in the environment.

Hydrolysis of carbofuran (2,3-dihydro-2,2-dimethyl-benzofuran-7-yl methylcarbamate) in pH range 7-10 is consistent with simple hydrolysis mediated by hydroxyl ions (Seiber *et al.*, 1978). Other factors that might accelerate hydrolysis are high pH (Siddaramappa *et al.*, 1978; Siddaramappa and Seiber, 1979; Chapam and Cole, 1982; Ramanand *et al.*, 1991), the microbial community (Siddaramappa and Seiber, 1979) and light intensity (Seiber *et al.*, 1978; Siddaramappa *et al.*, 1978). Volatilization, photolysis and oxidation are important in carbofuran dissipation (Seiber *et al.*, 1978; Deuel *et al.*, 1979; Mabury and Crosby, 1996). Tejada and Magallona (1985) and Rouchaud *et al.* (1990) observed that the main carbofuran metabolites are the 3-ketocarbofuran (2,3-dihydro-2,2-dimethyl-3-oxo-benzofuran-7-yl methylcarbamate), carbofuran-phenol (2,3-dihydro-2,2-dimethyl-benzofuran-7-ol) and

3-ketocarbofuran-phenol (7-hydroxy-2,2-dimethyl-benzofuran-3(2H)-one).

The objective of this work was to verify the utility of a level IV fugacity model to simulate the environmental fate of the insecticide carbofuran in irrigated rice. This fugacity model is a linear system of ordinary differential equations used to estimate fugacities and, hence, the carbofuran concentration in different environmental compartments (i.e. air, water, rice plants and soil). The classification of fugacity models in levels I, II, III and IV is a consequence of the complexity of the calculations and the hypotheses involved in formulation of each level (Mackay, 2001; Paraíba *et al.*, 2002).

## Material and Methods

### Model development

The relationship between fugacity and concentration is given by:

$$C = Zf \quad [1]$$

where  $C$  ( $\text{mol m}^{-3}$ ) is the pesticide concentration,  $f$  (Pa) is the pesticide fugacity and  $Z$  ( $\text{mol m}^{-3} \text{ Pa}^{-1}$ ) is the fugacity capacity. The fugacity capacity depends on the compartment and on the pesticide physical-chemical properties. Thus, due to the proportionality between  $C$  and  $Z$ , compartments with high fugacity capacities for a pesticide will also have high pesticide concentrations. The compartments of the rice cultivation system modelled in this work are air ( $i = a$ ), water ( $i = w$ ), rice plants ( $i = r$ ) and soil ( $i = s$ ),  $i \in I = \{a, w, r, s\}$ .

The pesticide partition coefficient,  $k_{ij}$ , between the compartments  $i$  and  $j$  is defined as:

$$k_{ij} = \frac{C_i}{C_j} \quad [2]$$

where  $C_i$  and  $C_j$  are the pesticide concentrations of compartments  $i$  and  $j$  in identical volumetric units such as  $\text{mol m}^{-3}$ , respectively. When  $f_i = f_j$  the partition coefficient  $k_{ij}$  is determined by:

$$k_{ij} = \frac{Z_i}{Z_j} \quad [3]$$

where  $Z_i$  and  $Z_j$  are the fugacity capacities of compartments  $i$  and  $j$ , respectively.

The fugacity capacity of air ( $Z_a$ ) is defined by:

$$Z_a = \frac{1}{RT} \quad [4]$$

where  $T$  (K) is the air temperature and  $R$  ( $8.314 \text{ m}^3 \text{ Pa mol}^{-1} \text{ T}^{-1}$ ) is the gas constant. The fugacity capacity of water ( $Z_w$ ) is defined by:

$$Z_w = \frac{1}{H} + \frac{oc_w \rho_w k_{oc}}{H} \quad [5]$$

where  $H$  ( $\text{m}^3 \text{ Pa mol}^{-1}$ ) is Henry's constant of the pesticide,  $oc_w$  ( $\text{m}^3 \text{ m}^{-3}$ ) is the organic carbon volumetric fraction of the water,  $\rho_w$  ( $\text{kg m}^{-3}$ ) is the water density ( $999.5 \text{ kg m}^{-3}$ ) and  $k_{oc}$  ( $\text{m}^3 \text{ kg}^{-1}$ ) is the organic carbon partition coefficient of the pesticide. Henry's constant was estimated by:

$$H = \frac{p_m p_v}{w_s} \quad [6]$$

where  $p_m$  ( $\text{g mol}^{-1}$ ) is the pesticide molar mass,  $p_v$  (Pa) is the pesticide vapor pressure and  $w_s$  ( $\text{g m}^{-3}$ ) is the pesticide aqueous solubility. The fugacity capacity of the rice plants ( $Z_r$ ) was estimated by:

$$Z_r = (x_w Z_w + x_l k_{ow} Z_w) \rho_r / \rho_w \quad [7]$$

where  $\rho_r$  ( $\text{kg m}^{-3}$ ) is the rice plant density,  $k_{ow}$  ( $\text{m}^3 \text{ m}^{-3}$ ) is the pesticide octanol-water partition coefficient,  $x_w$  ( $\text{m}^3 \text{ m}^{-3}$ ) is the water volumetric fraction of the rice plant and  $x_l$  ( $\text{m}^3 \text{ m}^{-3}$ ) is the volumetric fraction of lipids of the rice plant (Trapp and McFarlane, 1995; Cousins and Mackay, 2001). The fugacity capacity of the soil ( $Z_s$ ) was estimated by:

$$Z_s = \frac{\theta}{H} + \frac{oc_s \rho_s k_{oc}}{H} \quad [8]$$

where  $\theta$  ( $\text{m}^3 \text{ m}^{-3}$ ) is the water volumetric fraction of the soil,  $\rho_s$  ( $\text{kg m}^{-3}$ ) is the density of soil,  $oc_s$  ( $\text{m}^3 \text{ m}^{-3}$ ) is the organic carbon volumetric fraction of the soil, and  $k_{oc}$  ( $\text{m}^3 \text{ kg}^{-1}$ ) is the organic carbon partition coefficient of the pesticide (Mackay *et al.*, 1996).

Pesticide mass flow resulting from diffusion between two contiguous compartments  $i$  and  $j$ ,  $N_{ij}$  ( $\text{mol h}^{-1}$ ), can be calculated by:

$$N_{ij} = d_{ij} (f_i - f_j) \quad [9]$$

where  $d_{ij}$  ( $\text{mol Pa}^{-1} \text{ h}^{-1}$ ) is the transfer coefficient. According to Fick's first law, these transfer coefficients are given by:

$$d_{ij} = \frac{A_{ij} D_{pi} D_{pj} Z_i Z_j}{\delta_{ij} (D_{pi} Z_i + D_{pj} Z_j)} \quad [10]$$

where  $A_{ij}$  ( $\text{m}^2$ ) is the contact area between compartments  $i$  and  $j$ ,  $D_{pi}$  ( $\text{m}^2 \text{ h}^{-1}$ ) is the pesticide diffusivity in compartment  $i$ ,  $D_{pj}$  ( $\text{m}^2 \text{ h}^{-1}$ ) is the pesticide diffusivity in compartment  $j$ ,  $\delta_{ij}$  (m) is the thickness of the diffusion layer between compartments  $i$  and  $j$  (Zitko and McLeese, 1980).

The water and soil contact areas between the 0.0-0.2 m depth was calculated by the expression:

$$A_{ws} = \rho_s S_s V_s \quad [11]$$

where  $S_s$  ( $\text{m}^2 \text{ kg}^{-1}$ ) is the soil specific surface area. The value of  $S_s$  was estimated by the relationship:

$$S_s = 10^3 (1313.78 oc_s + 117.00 cl_s + 116.90 st_s + 5.15 sd_s) \quad [12]$$

where  $cl_s$  ( $\text{m}^3 \text{ m}^{-3}$ ) is the clay volumetric fraction of the soil,  $st_s$  ( $\text{m}^3 \text{ m}^{-3}$ ) is the silt volumetric fraction of the silt and  $sd_s$  ( $\text{m}^3 \text{ m}^{-3}$ ) is the sand volumetric fraction of the soil (Paraiba *et al.*, 2004).

Pesticide diffusivity in air  $D_{pa}$  ( $\text{m}^2 \text{ h}^{-1}$ ) was estimated by:

$$D_{pa} = \frac{3.6 \times 10^{-4} T^{1.75} \sqrt{M_{pa}}}{(\sqrt[3]{v_p} + \sqrt[3]{v_a})^2} \quad [13]$$

where  $v_p$  ( $\text{cm}^3 \text{ mol}^{-1}$ ) is the molar volume of the pesticide,  $v_a$  ( $\text{cm}^3 \text{ mol}^{-1}$ ) is the molar volume of the air ( $20.0 \text{ cm}^3 \text{ mol}^{-1}$ ) and  $M_{pa}$  is given by:

$$M_{pa} = \frac{p_m + a_m}{p_m p_a} \quad [14]$$

where  $a_m$  ( $\text{g mol}^{-1}$ ) is the molar mass of air ( $28.9 \text{ g mol}^{-1}$ ) (Lyman *et al.*, 1990). Pesticide diffusivity in water,  $D_{pw}$  ( $\text{m}^2 \text{ h}^{-1}$ ), was estimated by:

$$D_{pw} = \frac{2.056 \times 10^{-7} T \sqrt{\phi_w w_m}}{\mu_w (v_p)^{0.6}} \quad [15]$$

where  $\phi_w$  (2.6) is an association term for the water,  $w_m$  ( $18 \text{ g mol}^{-1}$ ) is the molar mass of water and  $\mu_w$  ( $8.9 \times 10^{-1}$  centipoises) is the water viscosity (Weber and DiGiano, 1996). Considering that rice plants have a high water volumetric fraction ( $> 0.8 \text{ m}^3 \text{ m}^{-3}$ ), the model supposes that the diffusivity of the pesticide in rice plants is equal

to the diffusivity of the pesticide in water ( $D_{pw} = D_{pw}$ ). Pesticide diffusivity in soil  $D_{ps}$  ( $\text{m}^2 \text{h}^{-1}$ ) can be estimated by:

$$D_{ps} = \frac{D_{pw} \phi_s^2}{(1 - \phi_s) \rho_s \phi_s k_{oc} + \phi_s} \quad [16]$$

where  $\phi_s$  ( $\text{m}^3 \text{m}^{-3}$ ) is the soil porosity (Wu and Gschwend, 1986).

Pesticide disappearance or transformation in air, water, rice plants and the soil can occur by physical and chemical process, by biological degradations, by dilution during rice growth or by water volume variation in rice fields. These pesticide processes are assumed to be first-order and are described by:

$$\frac{dC_i}{dt} = -\lambda_i C_i \quad [17]$$

where  $\lambda_i$  ( $\text{h}^{-1}$ ) is the transformation rate which was estimated by:

$$\lambda_i = \frac{\ln 2}{t_{1/2}^i} \quad [18]$$

where  $t_{1/2}^i$  ( $h$ ) is the pesticide half-life in compartment  $i \in I = \{a, w, r, s\}$ . Thus, in a level IV fugacity model the term that describes pesticide transformation or disappearance in a compartment  $i$  is given by:

$$V_i Z_i \frac{df_i}{dt} = -\lambda_i f_i V_i Z_i \quad [19]$$

where  $V_i$  ( $\text{m}^3$ ) is the volume of compartment  $i$ .

Pesticide advection in compartment  $i$  can be introduced into the model as a first-order process. In fact, advection can be regarded as a constant speed, defined as the algebraic sum between the entry flow  $G_i C_{Bi}$  and the exit flow  $G_i C_i = G_i Z_i f_i$ , where  $G_i$  ( $\text{m}^3 \text{h}^{-1}$ ) is the matter flow  $i$  entering compartment  $j$  with concentration  $C_{Bi}$  and leaving this compartment with concentration  $C_i$  (Mackay, 2001).

It is assumed that direct transfer of pesticide mass occurs from the air to water and rice plants, from water to air, soil and rice plants, from rice plants to air and water and from soil to water. Thus, the mass distribution of the pesticide is given by a system of ordinary differential equations:

$$\frac{df_a}{dt} = \frac{N_{wa}}{V_a Z_a} + \frac{N_{ra}}{V_a Z_a} + \frac{G_a C_{Ba}}{V_a Z_a} - \frac{G_a f_a}{V_a} - \lambda_a f_a \quad [20]$$

$$\frac{df_w}{dt} = \frac{N_{aw}}{V_w Z_w} + \frac{N_{rw}}{V_w Z_w} + \frac{N_{sw}}{V_w Z_w} + \frac{G_w C_{Bw}}{V_w Z_w} - \frac{G_w f_w}{V_w} - \lambda_w f_w \quad [21]$$

$$\frac{df_r}{dt} = \frac{N_{wr}}{V_r Z_r} + \frac{N_{ar}}{V_r Z_r} - \lambda_r f_r \quad [22]$$

$$\frac{df_s}{dt} = \frac{N_{ws}}{V_s Z_s} + \frac{G_s C_{Bs}}{V_s Z_s} - \frac{G_s f_s}{V_s} - \lambda_s f_s \quad [23]$$

with initial condition given by  $f_a(0) = f_s(0) = f_r(0) = 0$  and  $f_w(0) = (A_r P_d)/(V_w Z_w)$ , where  $A_r$  ( $\text{m}^2$ ) is the total area of rice field and  $P_d$  ( $\text{mol m}^{-2}$ ) is the pesticide dose. For  $i \in I = \{a, w, r, s\}$  and  $t \geq 0$ , the simulated concentrations  $C_i = C_i(t)$  are obtained by:

$$C_i = Z_i f_i(t) \quad [24]$$

The observed soil concentration was estimated from the observed soil solution concentration using the equation given by:

$$C_s = \frac{\phi_s \rho_s k_{oc}}{P_m} C_{ss} \quad [25]$$

where  $C_{ss}$  ( $\text{mg L}^{-1}$ ) is the observed soil solution concentration of carbofuran.

## Field experiment and input dates

A field experiment was carried out on 200 ha of irrigated rice crop located in Bariri municipality, State of São Paulo, Brazil ( $22^\circ 02' 45''$  S and  $48^\circ 43' 46''$  W altitude 450 m). The area was subdivided in 1.5 and 2.5 ha rice fields that were separated by irrigation and drainage channels. The experimental unit was 2 ha and was located at the first water entry to avoid contamination. Soil is classified as a *Gleissolos* (Oliveira *et al.*, 1999). Soil samples, collected before the start of the experiment, did not contain carbofuran. The area was managed according to the usual procedures for an irrigated rice crop. There was a pre-sowing irrigation to induce germination of red rice and other weeds. The area was flooded and drained. After weed emergence the following herbicides were applied: glyphosate at  $3.3 \text{ L ha}^{-1}$  and 2,4-D at  $0.75 \text{ L ha}^{-1}$  (Foloni, 1999). Twenty-two days after post-emergence weed control (22 November 2002), rice cv IRG 420 was seeded with a NPK fertilizer of 05-25-25 at  $250 \text{ kg ha}^{-1}$ . One day after sowing clomazone was applied at  $0.66 \text{ L ha}^{-1}$ . Following that the field was irrigated by fast flooding and drained to inducing seed germination. Fifteen days after seedling emergence,

the area was flooded again and this water was maintained in the field until the day before harvest. A dressing of nitrogen was applied as urea at 27 and 45 d after sowing at 50 and 80 kg ha<sup>-1</sup>, respectively. Before application of the carbofuran the water layer was maintained on the field for 48 h. The crop was harvested 105 days after sowing.

### Soil solution and water sampling

The soil solution sampler was a porous capsule attached to a PVC tube (1.27 cm inner diameter and 30 cm long), two silicone corks (one in a plastic bottle and the other in the PVC tube) and a hose. The soil solution was pumped through the hose to the bottle with a manual pump. When the soil was dry, 8 samplers were randomly installed in the experimental area at 20 cm depth, 9 days before rice sowing. Laminar water flow was also collected using plastic bottles. Samples were obtained by fast bottle immersion at 8 randomly selected places in the plot. Temperature and pH were determined for all laminar water and soil solution samples using a portable pH-meter (PG1400, GENAKA). Samples were immediately placed in an icebox for transportation and were stored at -18°C. Laminar water and soil solution were sampled at 24, 48, 96, 192, 384 and 768 hours after carbofuran application.

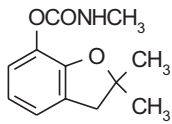
### Analytical procedure

All samples were stored at -18°C for five months prior to laboratory analysis. Carbofuran extraction from water consisted of a 100 ml sample extraction of dichloromethane (Leppert *et al.*, 1983). Carbofuran was measured using a gas chromatography system HP-5MS capilar column (length - 30 m, diameter - 0.25 mm); (film thickness - 0.25 µm), with the oven temperature programmed as follows: initial = 100°C, for 1 min; slope: 25°C up to 280°C, kept for 2.5 min. A mass selective detector (MSD) was coupled to the chromatograph, which was operated in the ion monitoring system (SIM), analysing a single fragment (fragment 160) for carbofuran measurements.

### Carbofuran physicochemical properties and input dates

The carbofuran physicochemical characteristics required for the study and the simulation of insecticides behaviour and environmental fate by a level IV fugacity model are presented in Table 1. Carbofuran was applied at  $1.05 \times 10^{-4}$  mol m<sup>-2</sup> (0.23 kg ha<sup>-1</sup>) that gave a concentration of  $1.04 \times 10^{-3}$  mol m<sup>-3</sup> (0.2301 mg L<sup>-1</sup>) in the water at 24 h after application. This fell to  $3.67 \times 10^{-6}$  mol m<sup>-3</sup> ( $8.1 \times 10^{-4}$  mg L<sup>-1</sup>) at 768 h after application.

**Table 1.** Carbofuran physicochemical characteristics

Characteristics	Values
Common name <sup>1</sup>	Carbofuran
CAS <sup>1</sup>	1563-66-2
Class <sup>1</sup>	Carbamate
Agronomic function <sup>1</sup>	Insecticide and nematicide
Chemical abstract name <sup>1</sup>	2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate
IUPAC name <sup>1</sup>	2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate
Chemical structure <sup>1</sup>	
Formulae molecular <sup>1</sup>	C <sub>12</sub> H <sub>15</sub> NO <sub>3</sub>
Molar mass <sup>1</sup>	221.3 g mol <sup>-1</sup>
Molar volume <sup>2</sup>	194.4 cm <sup>3</sup> mol <sup>-1</sup>
Vapor pressure <sup>1</sup>	$3.1 \times 10^{-5}$ Pa (20°C)
Water solubility <sup>1</sup>	351 mg L <sup>-1</sup> (20°C)
log k <sub>ow</sub> <sup>1</sup>	1.52 (20°C)
k <sub>oc</sub> <sup>3</sup>	0.022 m <sup>3</sup> kg <sup>-1</sup>

<sup>1</sup> Tomlin (2000). <sup>2</sup> Estimated by Weber and DiGiano (1996). <sup>3</sup> Hornsby *et al.* (1995).

## Numerical simulation and input dates

Carbofuran half-lives in water and in soil solution were estimated as 78 and 241 h, respectively (Plese *et al.*, 2005). Carbofuran half-life in air and rice plants was determined as 12 h and 36 h, respectively (Tejada and Magallona, 1985). These measured carbofuran half-life values for soil, water, air and rice plants were used as the input values for the numerical simulations.

The thickness of the diffusion layer between contiguous compartments was selected as  $1.0 \times 10^{-4}$  m (Zitko and Mc Leese, 1980). Soil density, porosity, and organic carbon, clay, silt and sand volumetric fraction were measured using site-specific soil samples and had values of  $1.54 \times 10^3$  kg m<sup>-3</sup>, 0.42, 0.017, 0.25, 0.09 and  $0.64$  m<sup>3</sup> m<sup>-3</sup>, respectively. The organic carbon volumetric fraction of the water was  $1.2 \times 10^{-3}$  m<sup>3</sup> m<sup>-3</sup>. The average volumetric fraction of water in soil was  $0.48$  m<sup>3</sup> m<sup>-3</sup> at 0-0.2 m depth. The specific surface area of the soil was estimated as  $6.94 \times 10^4$  m<sup>2</sup> kg<sup>-1</sup> [Eq. 12]. The contact areas between the compartments air and water, water and soil, air and rice plants, and water and rice plants were estimated as  $2.0 \times 10^4$ ,  $4.03 \times 10^{11}$  [Eq. 11],  $1.5 \times 10^4$ , and  $3.0 \times 10^3$  m<sup>2</sup>, respectively.

The density of the rice plants, volumetric fraction of water and lipids in rice plants were  $1.03 \times 10^3$  kg m<sup>-3</sup>, 0.80 and 0.02, respectively. The average air temperature was 298°K. For  $i, j \in I$  the model supposes that  $d_{ij} = d_{ji}$  and  $d_{sr} = d_{rs}$ . Volumes of air, water, rice plants and soil were  $8.0 \times 10^4$ ,  $2.0 \times 10^3$ ,  $1.2 \times 10^3$ , and  $5.0 \times 10^3$  m<sup>3</sup> respectively.

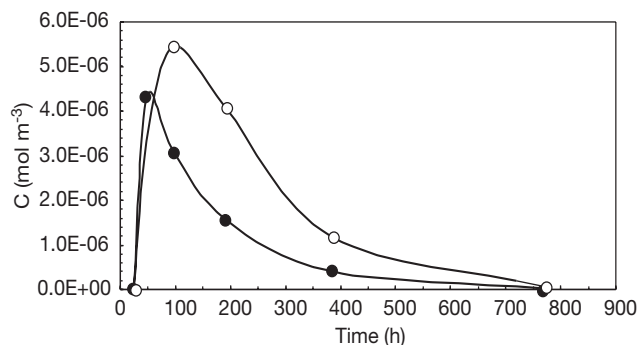
The transfer coefficients between air and water, water and soil, water and rice plants, and air and rice plants was estimated at 350.16,  $2.7 \times 10^{12}$ ,  $1.03 \times 10^5$ , 262.65 mol Pa<sup>-1</sup> h<sup>-1</sup> [Eq. 6] (Zitko and Mc Leese, 1980). For all  $i \in I$ ,  $G_i = 0$  and  $G_w = 1.89 \times 10^{-5}$  m<sup>3</sup> h<sup>-1</sup>.  $G_w$  was estimated according to Voltolini *et al.* (2002), considering daily rainfall, water evaporation, rice evapotranspiration and water recharge of the rice field. The time range for the numerical simulations was 1000 h. The algorithm proposed by Paraíba *et al.* (1999) was used to numerically simulate fugacity and concentration using the Matlab code (Matlab, 1992).

## Results and Discussion

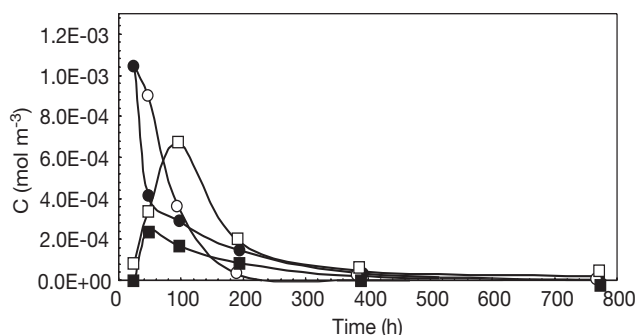
The simulations showed that the time required for the fugacity values to stay within a range of a final equilibrium value is over 1,000 h. It is after this time

has elapsed that there should be an analysis of the distribution of carbofuran in air, water, rice plants and soil using a steady state fugacity model type (level I, II or III fugacity model). Fugacity decreases uniformly in all compartments until it reaches equilibrium with fugacity values around  $10^{-12}$  Pa [Eqs. 20-23]. Carbofuran concentration decreases in water while it increases in air, rice plants and soil up to a maximum and then decreases (Figs. 1-2). The main reasons for carbofuran behaviour in these environmental compartments can be explained by its properties such as high water solubility, low vapour pressure, low soil-water partition coefficient and a low octanol-water partition coefficient that lead to high affinity to water (simulated and measured) and rice plants (simulated). Carbofuran concentration showed higher values in the following compartments: water > soil > rice plants > air. In general, carbofuran is only applied to water and it is then transferred to rice plants and soil.

The calculated fugacity capacities of the air, water, rice plants and soil were  $4.04 \times 10^{-4}$ ,  $2.2 \times 10^4$ ,  $3.3 \times 10^4$  and  $3.8 \times 10^4$  mol m<sup>-3</sup> Pa<sup>-1</sup>, respectively. The calculated carbofuran air-water partition coefficient was  $1.83 \times 10^{-8}$  [Eq. 3]. Pesticides with  $k_{aw} \leq 4.0 \times 10^{-6}$  are not volatile under atmospheric temperatures (Trapp and Harland, 1995). As a result carbofuran does not volatilize under normal atmospheric temperatures. The calculated carbofuran rice-water partition coefficients was 1.52 [Eq. 3]. These partition coefficients partially explain the simulated concentration levels in the rice plants. Soil sorption and soil-water partition coefficient of carbofuran,  $k_{oc} = 0.022$  m<sup>3</sup> kg<sup>-1</sup> and  $k_{sw} = 1.75$  [Eq. 3], respectively, indicate a low affinity with soil solid particles and a high affinity with both laminar water and the soil solution.



**Figure 1.** Carbofuran concentrations in air (●  $1.0E+6 \times C_a$ ) and in rice plants (○  $C_r$ ) as simulated by a level IV fugacity model.



**Figure 2.** Simulated and measured carbofuran concentration in soil (●  $C_s$  - simulated, ○  $C_s$  - measured), and in water (■  $C_w$  - simulated, □  $C_w$  - measured).

The level IV fugacity models used here underestimated the water carbofuran concentrations and partially underestimated the soil carbofuran concentrations ( $t < 120$  h) (Fig. 2). This can be associated with the definition assumed of the fugacity capacity of the water and soil, and the carbofuran half-life in water and soil used in this work. A level IV fugacity model can reasonably predict carbofuran concentration in the rice growing environment. As the carbofuran concentrations was not measured in air and rice plants no conclusions were drawn concerning predictions of carbofuran concentration in these two compartments. Generally, the level IV fugacity model used in this study have shown a good possibility for use as a tool to predict the fate of organic chemicals in different environmental compartments. The results suggest that the model could be used to determine which environmental compartment was more vulnerable to carbofuran. Generally the results suggest that the model is appropriate and can be used to estimate carbofuran fate and exposure in an environmental compartments system for screening for risk analysis. The level IV fugacity model can be considered a useful tool for simulating the environmental fate of this insecticide and could be coupled with sensitivity and uncertainty analyses to test the influence of all input parameters and make assumptions on the outputs.

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