Fugacity concept use for prediction of carbofuran environmental behaviour in irrigated rice crops

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ABSTRACT

The objectives of this work were to use the level IV fugacity model to simulate the environmental fate of carbofuran as employed in rice cultivation. The fugacity model was used to simulate the dynamic distribution of the carbofuran in a system comprising air, water, rice plants and soil. Results indicate the preferential compartments of the pesticide, facilitating the strategies for monitoring environmental quality, and providing further knowledge of the environmental fate of carbofuran. Experiments under field conditions were carried out to verify the correspondence between simulated and measured values of carbofuran concentration in water and soil.

INTRODUCTION

Carbofuran is a systemic carbamate insecticide and a cholinesterase inhibitor that has been used in rice cultivation. It is highly toxic to vertebrates and is used to control insects in a wide variety of agricultural crops including coffee, corn, sugar cane and rice (Tomlin, 2000). In Brazil, it is usually applied directly to the soil in granular form 15 to 30 days after rice germination in order to control rice beetle larvae (*Oryzophagus oryzae*). Plese *et al.* (2005) modelled the kinetics of carbofuran hydrolysis and the subsequent degradation in an irrigated rice fields of Brazil. This study had the aim of employing a level IV fugacity model to simulate the distribution of carbofuran insecticide in different compartments of a rice field. The level IV fugacity model is presented as a system of ordinary differential equations within a fugacity framework that estimates carbofuran concentrations in different environmental compartments (Mackay, 2001).

MATERIALS AND METHODS

The relationship between fugacity and concentration is given as follows:

$$C = Zf$$

Where C is the pesticide concentration (mol/m^3), f is the pesticide fugacity (Pa) and Z is the fugacity capacity (mol/m^3 Pa^1). The compartments of the rice cultivation system modeled in this work are air (i = a), water (i = w), rice plants (i = r) and soil (i = s), i.e., $i \in I = \{a, w, r, s\}$.

The fugacity capacity of air is defined as:

$$Z_a = \frac{1}{RT}$$

Where Z_a is the fugacity capacity of air, T is the air temperature (K) and R is the gas constant (i.e. 8.314 m^3 Pa/mol T). The fugacity capacity of water is defined as:

$$Z_w = \frac{1}{H} + \frac{OC_w \rho_w k_{oc}}{H}$$

Where Z_w is the fugacity capacity of water and H is Henry's constant of the pesticide (m^3 Pa/mol), OC_w is the organic carbon volumetric fraction of the water (m^3/m^3), ρ_w is the water density (kg/m^3), and k_{oc} is the organic carbon partition coefficient of the pesticide (m^3/kg). The fugacity capacity of the rice plants was estimated as:

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

Where Z_r is the fugacity capacity of the rice plants, ρ_r is the rice plant density (kg/m^3), k_{ow} is the pesticide octanol-water partition coefficient (m^3/m^3), x_w is the water volumetric fraction of the rice plant (m^3/m^3) and x_l is the lipids volumetric fraction of the rice plant (m^3/m^3) (Trapp & Farlane, 1995). The fugacity capacity of the soil was estimated as:

$$Z_s = \frac{\theta}{H} + \frac{OC\rho_s k_{oc}}{H}$$

Where Z_s is the fugacity capacity of the soil, θ is the water volumetric fraction of the soil (m^3/m^3), ρ_s is the density of soil (kg/m^3), OC is the organic carbon volumetric fraction of the soil (m^3/m^3), and k_{oc} is the organic carbon partition coefficient of the pesticide (m^3/kg^1). Pesticide mass flow resulting from diffusion between two contiguous compartments i and j can be calculated as:

$$N_{ij} = d_{ij}(f_i - f_j)$$

Where N_{ij} is the pesticide mass flow between compartments i and j (mol/h), and d_{ij} is the transfer coefficient (mol/Pa h). According Fick's first law, these transfer coefficients is given as:

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

Where A_{ij} is the contact area between compartments i and j (m^2), D_{ij} is the pesticide diffusivity in compartment i (m^2/h), D_{pj} is the pesticide diffusivity in compartment j (m^2/h), δ_{ij} is the thickness of the diffusion layer between compartments i and j (m). The water and soil contact areas between the 0.0-0.2 m depth was calculated by the following expression:

$$A_{ws} = \rho_s S_s V_s$$

Where S_s is the soil specific surface area (m^2/kg). The pesticide diffusivity in air was estimated as:

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

Where D_{pa} is the pesticide diffusivity in air (m^2/h), v_p is the molar volume of the pesticide (cm^3/mol) and v_a is the molar volume of the air (i.e. 20.0 cm^3/mol). M_{pa} is given by:

$$M_{pa} = \frac{p_m + a_m}{p_m p_a}$$

Where a_m is the molar mass of air (i.e. 28.9 g/mol). Considering that rice plants have high water volumetric fraction (>0.8 m/m), the model supposes that the diffusivity of the pesticide in rice plants is equal to the diffusivity of the pesticide in water, i.e., $D_{pr} = D_{pw}$. Pesticide disappearance or transformations in air, water, rice plants and soil can occur by physical and chemical process or biological degradations, by dilution during rice growth or by water volume variation in rice fields. These pesticide process was assumed as first-order processes and are described by:

$$\frac{dC_i}{dt} = -\lambda_i C_i$$

Where λ_i is the transformation rate (h) which were estimated by:

$$\lambda_i = \frac{\ln 2}{t^i_{1/2}}$$

Where $t^i_{1/2}$ is the pesticide half-life in compartment i (h). Thus, in the level IV fugacity model the term that describes the pesticide transformation or disappearance in a compartment i is given by:

$$V_i Z_i \frac{df_i}{dt} = -\lambda_i f_i V_i Z_i$$

Where V_i is the volume of compartment i (m^3). Pesticide advection in compartment i can be introduced in 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 $G_i C_i$, or in terms of fugacity as $G_i Z_i f_i$, where G_i is the matter flow i entering compartment i (m^3/h) with concentration C_{Bi} and leaving this compartment with concentration C_i (Mackay, 2001). The mass distribution of the pesticide is given by system of ordinary differential equations:

$$\frac{df_a}{dt}=\frac{N_{wa}(f_w-f_a)}{V_aZ_a}+\frac{N_{ra}(f_r-f_a)}{V_aZ_a}+\frac{G_aC_{Ba}}{V_aZ_a}-\frac{G_af_a}{V_a}-\lambda_af_a$$

$$\frac{df_w}{dt}=\frac{N_{aw}(f_a-f_w)}{V_wZ_w}+\frac{N_{sw}(f_s-f_w)}{V_wZ_w}+\frac{N_{rw}(f_r-f_w)}{V_wZ_w}+\frac{G_wC_{Bw}}{V_wZ_w}-\frac{G_wf_w}{V_w}-\lambda_wf_w$$

$$\frac{df_r}{dt}=\frac{N_{ar}(f_a-f_r)}{V_rZ_r}+\frac{N_{wr}(f_w-f_r)}{V_rZ_r}-\lambda_rf_r \text{ and } \frac{df_s}{dt}=\frac{N_{ws}(f_w-f_s)}{V_sZ_s}+\frac{G_sC_{Bs}}{V_sZ_s}-\frac{G_sf_s}{V_s}-\lambda_sf_s$$

The initial condition is defined as:

$$f_a(0)=f_s(0)=0 \text{ and } f_w(0)=(A_rP_d)/(V_wZ_w)$$

A_r is the total area of rice field (m^2) and P_d is the pesticide dose (mol m^{-2}). For $i \in I$ and $t \geq 0$, the concentrations $C_i = C_i(t)$ are obtained by $C_i = Z_i f_i(t)$.

The field experiment was carried out in a 200 ha area of irrigated rice crop located in the municipality of Bariri, State of São Paulo, Brazil (22°02'45" S and 48°43'46" W). The area was subdivided in 1.5 and 2.5 ha rice fields that were separated by irrigation and drainage channels. The entire area is managed according to usual procedures for irrigated rice crop. A soil solution sampler consisted of a porous capsule attached to a PVC tube (1.27 cm inner diameter and 30 cm length), two silicone corks (one in a plastic bottle and another in the PVC tube) and a hose. The soil solution was pumped through the hose up to the bottle using a manual pump. When the soil was dry, eight samplers were randomly installed in the experimental area at 20 cm depth, nine days before rice sowing. The paddy water, or laminar water was also collected using plastic bottles and samples were obtained by fast bottle immersion in eight randomly places in the plot. Temperature and pH were determined in all laminar water and soil solution samples using a portable pH-meter (PG1400, GENAKA). Samples were immediately placed in icebox for transportation and stored at -18°C. Laminar water and soil solution were sampled at 24, 48, 96, 192, 384 and 768 hours after carbofuran application. Carbofuran extraction from water consisted of 100 ml sample extraction of dichloromethane. Carbofuran was measured using a gas chromatography system HP-5MS capillar column (length - 30 m, diameter - 0.25 mm); (film thickness - 0.25 µm), with oven temperature programmed as follows: initial = 100°C, for 1 min; slope: 25°C up to 280°C, kept for 2 min and 30 s. Carbofuran physicochemical characteristics provided as input parameters were molar mass, molar volume, vapor pressure, aqueous solubility, octanol-water partition coefficient, and organic carbon partition coefficient in soil (Tomlin, 2000). Carbofuran was applied at rate 1.05×10^{-4} mol/m^2 (i.e. 0.23 kg/ha) that resulted in a concentration of 1.04×10^{-3} mol/m^3 in the water 24 h after application, 768 h after application the concentration had declined to 3.67×10^{-6} mol/m^3.

DISCUSSION

The carbofuran half-life in water at 29°C and pH 6.6 and soil solution in irrigated rice field capacity was estimated as 78 and 241 h, respectively (Plese *et al.*, 2005). The carbofuran half-life in air and rice plants was determined as 12 h and 36 h, respectively (Tejada & Magallona, 1985). These measured carbofuran half-life in soil, water, air and rice plants were used as

silt and sand volumetric fraction were measured using site-specific soil sample and had values of 1.54×10^3 kg/m^3, 0.42, 0.017, 0.25, 0.09 and 0.64 m^3/m^3, respectively. The water density and organic carbon volumetric fraction of the water was 1.01×10^3 kg/m^3 and 1.2×10^{-3} m^3/m^3, respectively. The average volumetric fraction of water in soil was 0.48 m^3/m^3 at 0-0.2 m depth. The specific surface area of the soil was estimated as 6.94×10^4 m^2/kg. The contact areas between the compartments air and water, water and soil, air and rice plants, and water and rice plants were estimated as 2.0×10^4, 4.03×10^{11}, 1.5×10^4, and 3.0×10^3 m^2, respectively. The density of rice plants, volumetric fraction of water and lipids in rice plants were 1.03×10^3 kg/m^3, 0.80 and 0.02, respectively. Water density and air temperature were 1.0×10^3 kg/m^3 and 298 K, respectively. 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 8.0×10^4, 2.0×10^3, 1.2×10^3, and 5.0×10^3 m^3, respectively. The transfer coefficients between air and water, water and soil, water and rice plants, and air and rice plants was estimated as 350.16, 2.7×10^{12}, 1.03×10^5, 262.65 mol/Pa h. For all $i \in I$, $G_i = 0$ and $G_w = 1.89\times10^{-5}$ m^3/h. G_w was estimated considering daily precipitation, water evaporation, rice evapotranspiration and water recharge area of the rice field. The time range for numerical simulations was 1000 h. We used the algorithm proposed by Paraíba *et al.* (1999) to numerically simulate fugacity and concentration using the Matlab code. Simulations have shown that the time required for the fugacity values to stay within a range of a final equilibrium value is over 1000 hours. Fugacity decreases in a uniform way in all compartments until it reaches the equilibrium level with fugacity values around 10^{-12} Pa.

We observed that carbofuran concentrations in water decreases while it increases in air, rice plants and soil until maximas are reached (Figures 1,2). Carbofuran concentrations were highest in the following compartments: water > soil > rice plants > air. In general, carbofuran is applied only to water and then is transferred to rice plants and soil. The estimated fugacity capacities in the air, water, rice plants and soil were 4.04×10^{-4}, 2.2×10^4, 3.3×10^4 and 3.8×10^4 mol/m^3 Pa^1, respectively. The estimated carbofuran rice-water partition coefficient was 1.52 (unitless). This partition coefficient partially explains the simulated concentration levels in rice plants. Soil sorption and soil-water partition coefficient of carbofuran (k_{oc} = 0.022 m^3/kg and k_{sw} = 1.75, respectively) indicate low affinity with soil solid particles and high affinity with both laminar water and soil solution. The level IV fugacity model used in this work underestimated the water and soil solution carbofuran concentrations (Figure 2). We believe that level IV fugacity model can reasonably predict carbofuran concentration in the rice environment. As the concentrations in air and rice plants were not measured, we cannot draw conclusions concerning predictions of carbofuran concentrations in these compartments. Results suggest that the model can be used to determine which environmental compartment is more vulnerable to carbofuran.

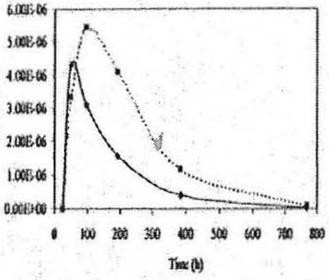

Figure 1. Carbofuran concentrations in air (◆ 1.0E+6×C_a) and rice plants (■ C_r) as simulated by level IV fugacity model.

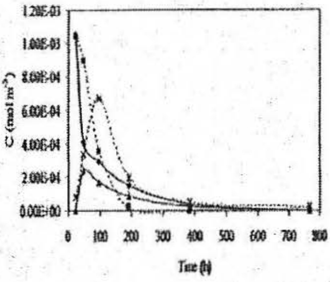

Figure 2. Measured and simulated carbofuran concentration in soil (◆ C_s - simulated) and (■ C_s - measured), and water (▲ C_w - simulated) and (× C_w - measured).

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