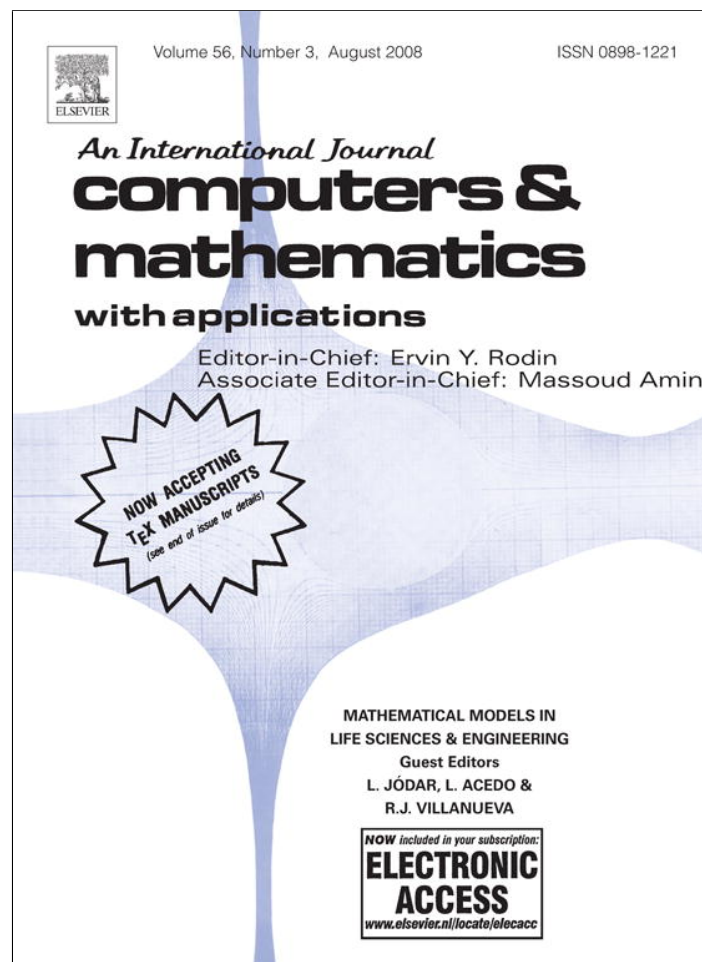


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# Modelling the pesticide concentration in a rice field by a level IV fugacity model coupled with a dispersion-advection equation

Wilson A. Contreras<sup>a,b,\*</sup>, Damián Ginestar<sup>b</sup>, Lourival C. Paraíba<sup>c</sup>, Rafael Bru<sup>b</sup>

<sup>a</sup> *Mathematics Department, Faculty of Basic Sciences, University of Pamplona, Km 1 way Bucaramanga, Colombia*

<sup>b</sup> *Instituto de Matemática Multidisciplinar, Universidad Politécnica de Valencia, 46022, Valencia, Spain*

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

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## Abstract

The numerical simulation of a level IV fugacity model coupled to a dispersion-advection equation to simulate the environmental concentration of a pesticide in rice fields is presented. The model simulates the dynamic distribution of the pesticide in a compartmental system constituted by air, water, rice plants and bottom sediment together with saturated soil layers. The level IV fugacity model is given by a linear system of ordinary differential equations that considers the fugacities and, consequently, the concentrations of the pesticide in air, water, rice plants and bottom sediment. The dispersion-advection equation simulates the pesticide leaching in the saturated layers of the soil, considering the hydrodynamic dispersion, the pesticide degradation rate and the soil pesticide absorption in the saturated soil layer.

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*Keywords:* Carbofuran pesticide; Level IV fugacity model; Dispersion-advection equation; Leaching

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## 1. Introduction

The aim of this work is to study the models used to simulate the environmental concentration of pesticides, such as a level IV fugacity model represented by a system of ordinary differential equations, which is illustrated in depth in modelling the elusiveness by means of dynamic systems [1], and the model applied to transportation of pesticides in a soil column. This model contains a dispersion-advection equation with initial and contour conditions. With this model we simulate the concentration of a pesticide in a compartmental system composed by air, water, rice field, sediment and a soil column.

The level IV fugacity model (FUGIV) will be represented by a lineal system of ordinary differential equations which estimates the fugacities and, consequently, the concentrations of the pesticide in air, water, plants rice and sediment. The equation of the dispersion-advection (EDA) will be represented by a one-dimensional partial differential equation, which simulates the pesticide leaching in the water-saturated soil profile; the water-saturated soil profile. The

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\* Corresponding author at: Mathematics Department, Faculty of Basic Sciences, University of Pamplona, Km 1 way Bucaramanga, Colombia.

*E-mail addresses:* [wilcones@doctor.upv.es](mailto:wilcones@doctor.upv.es) (W.A. Contreras), [dginestar@mat.upv.es](mailto:dginestar@mat.upv.es) (D. Ginestar), [lourival@cnpma.embrapa.br](mailto:lourival@cnpma.embrapa.br) (L.C. Paraíba), [rbru@mat.upv.es](mailto:rbru@mat.upv.es) (R. Bru).

EDA model considers the hydrodynamics dispersion, the rate degradation of the pesticide in floor of the aquifer, and the coefficient of absorption of the pesticide.

The modelling for fugacity allows the calculation of the total distribution of the mass of a pesticide among compartments and it facilitates the estimation of the concentration of the pesticide in each compartment. Mathematical models based on the thermodynamic theory of fugacity are frequently outlined by a system of linear differential equations describing the total mass balance of a chemical substance in an environment composed of homogeneous and well-mixed compartments, media or phases. The classification of the models of fugacity in the levels I, II, III and IV is a consequence of the complexity of the calculations and of the hypotheses involved in the formulation of each level. When all the fugacities are equal and constant in all compartments, the percentile distribution of the mass is calculated directly; this case corresponds to the well-known level I fugacity model. Level II fugacity model considers that there are degradations and advections [2], [3]. Level III fugacity model supposes that the fugacities are not in equilibrium and each fugacity can have different values, which are determined by a system of linear algebraic equations when there is degradation, advection, emission and transfer of the substance from one compartment to another in stationary state or steady state conditions [4–6]. In addition, there is another model describing the unsteady state behaviour of a substance in the environment, which permits the observation of substances whose emission and fugacity vary with time, and to determine the time in which the system reaches the steady state condition. This last model type, known as level IV fugacity model, usually is described by a system of differential equations [2] or by a dynamic control system [7,1]. Different fugacity models analysing changes in concentration in time can be found in [8–14]. Some fugacity models account for temporal and spatial differences in temperature by defining seasonally fluctuating temperatures in the model compartments and deriving temperature-dependent partitioning, transference and degradation parameters [15,16].

The dispersion-advection equation that will be used in the coupled model is based on the model presented by Jury et al. [17]. This model is a mathematical description of the fate of a single application of the unsaturated zone soil. The model includes processes of evaporation to a chemical free atmosphere, leaching via percolating water, diffusion, absorption and reaction. The equations describe the movement of the chemical as a linear functions of concentration, the isotherm absorption is also linear and all reactions are assumed to follow first-order kinetics. Local equilibrium between soil–solid, soil–water and soil–air is assumed.

The rest of the paper is structured as follows: in Section 2 the level IV fugacity model for the compartments air, water, plants and sediment is reviewed. In the Section 3 the coupled model to take into account the soil column is described. Section 4 is devoted to present the numerical discretization used for the model. In Section 5 some numerical results for the simulation of the concentration of the Carbofuran insecticide are presented. Finally, the main conclusions of the paper are summarized in Section 6.

## 2. Level IV fugacity model

The distribution of a small quantity of a chemical substance between two compartments denoted by the indices  $i$  and  $j$ , under equilibrium fugacity, constant temperature and pressure yields constant ratios between these two concentrations. The partition coefficient controlling the distribution of a substance between these two compartments is numerically defined as  $k_{ij} = C_i/C_j$ , where  $C_i$  and  $C_j$  are the concentrations of the substance in each one of the compartments. The relationship between fugacity and concentration is given by  $C_i = Z_i f_i$ , where  $C_i$  ( $\text{mol m}^{-3}$ ) is the concentration,  $f_i$  (Pa) is the fugacity and the proportionality constant  $Z_i$  ( $\text{mol m}^{-3} \text{Pa}^{-1}$ ) is the capacity of fugacity. The estimate of the capacity of fugacity,  $Z_i$ , of a substance in a compartment  $i$  depends on the nature of the compartment and on the partition coefficient of the substance in this compartment. The partition coefficient  $k_{ij}$ , under equilibrium fugacity ( $f_i = f_j$ ), is determined by the quotient between  $Z_i$  and  $Z_j$ , i.e.,  $k_{ij} = Z_i/Z_j$ , consequently,  $Z_i = k_{ij} Z_j$ .

Pesticides tend to accumulate in compartments in which the capacity of fugacity is relatively high. Lipophilic pesticides present high concentrations in compartments rich in lipids, because in these compartments the capacity of fugacity for this pesticide is relatively higher than in other compartments. Thus, we can suppose that the capacity of fugacity of a compartment for a pesticide expresses the solubility of the pesticide in this compartment [2]. Since the capacity of fugacity of a compartment describes the affinity of a pesticide for the compartment and it is a property of the compartment, it is necessary to define the capacity of fugacity of each one of the compartments, considering the physicochemical characteristics of the pesticide and of the compartment [2]. As the compartments of the rice

cultivation system modelled in this work are air ( $i = a$ ), water ( $i = w$ ), rice plants ( $i = r$ ) and sediment ( $i = s$ ) it is necessary to define the capacity of fugacity for each one of these compartments.

The capacity of fugacity of the air is defined by

$$Z_a = \frac{1}{RT} \quad (1)$$

where  $Z_a$  ( $\text{mol m}^{-3} \text{ Pa}^{-1}$ ) is the capacity of fugacity of the air,  $T$  (K) is the air temperature and  $R = 8.314 \text{ m}^3 \text{ Pa mol}^{-1} \text{ T}^{-1}$  is the gas constant [2].

The capacity of fugacity of the water,  $Z_w$  ( $\text{mol m}^{-3} \text{ Pa}^{-1}$ ), is defined by

$$Z_w = \frac{1}{H} \quad (2)$$

where  $H$  ( $\text{m}^3 \text{ Pa mol}^{-1}$ ) is the Henry's constant for the pesticide [2]. Henry's constant can be estimated by

$$H = \frac{p_m p_v}{s_w} \quad (3)$$

where  $p_m$  ( $\text{g mol}^{-1}$ ) is the molar mass of the pesticide,  $p_v$  (Pa) is the vapour pressure of the pesticide and  $s_w$  ( $\text{g m}^{-3}$ ) is the aqueous solubility of the pesticide [2].

The capacity of fugacity of the rice plants can be defined by

$$Z_r = (x_w Z_w + x_l k_{ow} Z_w)(\rho_r / \rho_w) \quad (4)$$

where  $Z_r$  ( $\text{mol m}^{-3} \text{ Pa}^{-1}$ ) is the capacity of fugacity of the rice plants,  $\rho_w$  ( $\text{kg m}^{-3}$ ) is the water density,  $k_{ow}$  is the octanol–water pesticide partition coefficient,  $\rho_r$  ( $\text{kg m}^{-3}$ ) is the rice plants' density,  $x_w$  is the rice plants' water volumetric fraction and  $x_l$  is the rice plants' lipids volumetric fraction [18,19].

The capacity of the sediment is defined by

$$Z_s = \frac{\rho_s o c_s k_{oc}}{H} \quad (5)$$

where  $Z_s$  ( $\text{mol m}^{-3} \text{ Pa}^{-1}$ ) is the capacity of fugacity of the sediment,  $\rho_s$  ( $\text{kg m}^{-3}$ ) is the density of sediment,  $o c_s$  is the sediment's organic carbon volumetric fraction and  $k_{oc}$  ( $\text{m}^3 \text{ kg}^{-1}$ ) is the soil organic carbon partition coefficient of the pesticide [20].

The mass flow of the pesticide resulting from diffusion between two contiguous compartments  $i$  and  $j$  can be calculated by the product of the difference ( $f_i - f_j$ ) times the transfer coefficient  $d_{ij}$  ( $\text{mol h}^{-1} \text{ Pa}^{-1}$ ). This coefficient is estimated by the following expression:

$$d_{ij} = \frac{A_{ij} D_{pi} D_{pj} Z_i Z_j}{\delta_{ij} (D_{pi} Z_i + D_{pj} Z_j)} \quad (6)$$

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 diffusivity of pesticide in compartment  $i$ ,  $D_{pj}$  ( $\text{m}^2 \text{ h}^{-1}$ ) is the diffusivity of pesticide in compartment  $j$ ,  $\delta_{ij}$  (m) is the thickness of the diffusion layer between compartments  $i$  and  $j$ ,  $Z_i$  ( $\text{mol m}^{-3} \text{ Pa}^{-1}$ ) is the capacity of fugacity of the compartment  $i$  and  $Z_j$  ( $\text{mol m}^{-3} \text{ Pa}^{-1}$ ) is the capacity of fugacity of the compartment  $j$  [8].

The diffusivity of a pesticide in air,  $D_{pa}$  ( $\text{m}^2 \text{ h}^{-1}$ ), can be empirically estimated by the following equation:

$$D_{pa} = \frac{3.6 \times 10^{-4} T^{1.75} \sqrt{M_{pa}}}{\left(\sqrt[3]{v_p} + \sqrt[3]{v_a}\right)^2} \quad (7)$$

where  $v_p$  ( $\text{cm}^3 \text{ mol}^{-1}$ ) is the molar volume of the pesticide and  $v_a = 20.1 \text{ cm}^3 \text{ mol}^{-1}$  is the molar volume of the air.  $M_{pa}$  is defined by

$$M_{pa} = \frac{p_m + a_m}{p_m p_a} \tag{8}$$

where  $a_m = 28.9 \text{ g mol}^{-1}$  is the molar mass molar of air, and  $p_m$  is the molar mass of the pesticide [21].

The diffusivity of the pesticide in the water,  $D_{pw}(\text{m}^2 \text{ h}^{-1})$ , can be empirically estimated by

$$D_{pw} = \frac{2.664 \times 10^{-8} T \sqrt{\phi_w w_m}}{\mu_w (v_p)^{0.6}} \tag{9}$$

where  $\phi_w = 2.6$  is an association term for the solvent (water),  $w_m = 18 \text{ g mol}^{-1}$  is the molar mass of the water and  $\mu_w = 8.9 \times 10^{-1} \text{ cP}$  is the water viscosity [22]. Considering that rice plants have high water volumetric fraction ( $\geq 0.8$ ), the model supposes that the diffusivity of the pesticide in rice plants is equal to the diffusivity of the pesticide in the water, i.e.  $D_{pr} = D_{pw}$ .

The diffusivity of the pesticide in sediment,  $D_{ps}(\text{m}^2 \text{ h}^{-1})$ , can be estimated empirically by equation

$$D_{ps} = \frac{D_{pw}(\phi_s)^2}{(1 - \phi_s)\rho_s oc_s k_{oc} + \phi_s} \tag{10}$$

where  $\phi_s$  is the sediment porosity [23]. The contact area between water and sediment can be empirically estimated by equation

$$A_{ws} = \rho_s S_{sa} V_s \tag{11}$$

where  $\rho_s (\text{kg m}^{-3})$  is the sediment density,  $A_{ws} (\text{m}^2)$  is the area of contact between water and sediment,  $S_{sa} (\text{m}^2 \text{ kg}^{-1})$  is the specific superficial area of the sediment and  $V_s (\text{m}^3)$  is the volume of the sediment. The  $S_{sa}$  value can be estimated by relationship

$$S_{sa} = 10^3(1313.78 oc_s + 117.00 cl_s + 116.90 st_s + 5.15 sd_s) \tag{12}$$

where  $oc_s$  is the volumetric fraction of organic carbon in sediment,  $cl_s$  is the volumetric fraction of clay in sediment,  $st_s$  is the volumetric fraction of the silt in sediment and  $sd_s$  is the volumetric fraction of the sand in sediment [24].

Pesticide transformations in air, water, rice plants and sediment can occur by dissipation, by chemical or biological degradation or by dilution of the growth of the rice plants or by water variation volume in rice fields [2]. These transformations are assumed as first-order processes and are described by

$$\frac{df_i}{dt} = -\lambda_i f_i \tag{13}$$

where  $i \in I = \{a, w, r, .s\}$ . The value  $\lambda_i > 0 (\text{h}^{-1})$  is the transformation rate coefficient or the apparent degradation rate. These coefficients were estimated by the relationship

$$\lambda_i = \frac{\ln(2.0)}{t_{1/2}^i} \tag{14}$$

where  $t_{1/2}^i (h)$  is the half-life of the pesticide in compartment  $i$ .

Mass 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 of the entry flow,  $G_i C_i$ , or in terms of fugacity as  $G_i Z_i f_i$ , where  $G_i (\text{m}^3 \text{ h}^{-1})$  is the matter flow entering compartment  $i$  with concentration  $C_{Bi}$  and leaving this compartment with concentration  $C_i$ .

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 the following system of ordinary differential equations:

$$\begin{aligned} \frac{df_a}{dt} &= \frac{d_{wa} f_w}{V_a Z_a} + \frac{d_{ra} f_r}{V_a Z_a} + \frac{G_a C_{Ba}}{V_a Z_a} - \frac{d_{aw} f_a}{V_a Z_a} - \frac{d_{ar} f_a}{V_a Z_a} - \frac{G_a f_a}{V_a} - \lambda_a f_a \\ \frac{df_w}{dt} &= \frac{d_{aw} f_a}{V_w Z_w} + \frac{d_{rw} f_r}{V_w Z_w} + \frac{d_{sw} f_s}{V_w Z_w} + \frac{G_w C_{Bw}}{V_w Z_w} - \frac{G_w f_w}{V_w} - \frac{d_{wa} f_w}{V_w Z_w} - \frac{d_{ws} f_w}{V_w Z_w} - \frac{d_{wr} f_w}{V_w Z_w} - \lambda_w f_w \end{aligned}$$

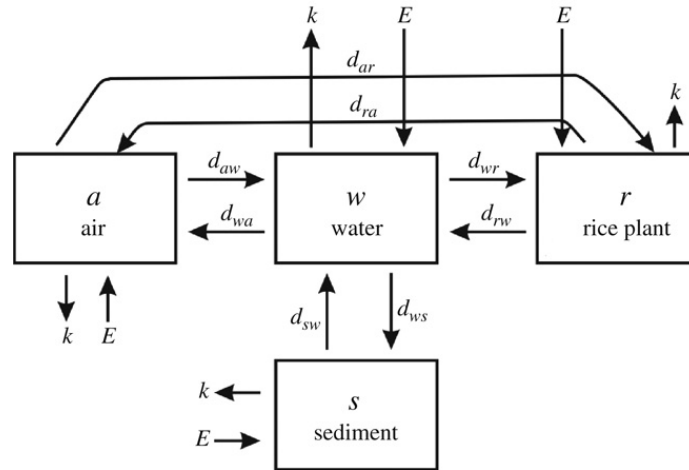


Fig. 1. Graphical representation of the compartments that take part in the level IV fugacity model.

$$\begin{aligned} \frac{df_r}{dt} &= \frac{d_{wr} f_w}{V_r Z_r} + \frac{d_{ar} f_a}{V_r Z_r} - \frac{d_{rw} f_r}{V_r Z_r} - \frac{d_{ra} f_r}{V_r Z_r} - \lambda_r f_r \\ \frac{df_s}{dt} &= \frac{d_{ws} f_w}{V_s Z_s} + \frac{G_s C_{Bs}}{V_s Z_s} - \frac{G_s f_s}{V_s} - \frac{d_{sw} f_s}{V_s Z_s} - \lambda_s f_s \end{aligned} \quad (15)$$

with initial conditions given by  $f_a(0) = f_r(0) = f_s(0) = 0$  and  $f_w(0) = (A_r P_d)/(V_w Z_w)$ , where  $A_r$  ( $m^2$ ) is the area of the rice field,  $P_d$  ( $mol\ m^{-2}$ ) the applied dose of the pesticide,  $V_a$  ( $m^3$ ) is the air volume,  $V_w$  ( $m^3$ ) is the total water volume,  $V_r$  ( $m^3$ ) is the total volume of the rice plants and  $V_s$  ( $m^3$ ) is the total volume of the sediment. For  $i \in \{a, w, r, s\}$  and  $t \geq 0$ , the concentration  $C_i = C_i(t)$  are determined by  $C_i(t) = Z_i f_i$ , when the solutions of the system of differential equations,  $f_i = f_i(t)$ , are known.

The diagram shown in Fig. 1 is a scheme of the interrelation between the processes of the emission, transference, degradation and the advection of a substance in, and between, the compartments air, water, rice plant and sediment.

### 3. Coupled model with the convection-advection equation

When a column of soil is taken into account, new terms have to be added to the model (15). The variation of the fugacity in the water is modified by a term of the form

$$\frac{vC(0, t)}{\delta_w Z_w}$$

where  $v$  ( $m\ h^{-1}$ ) is the speed of the water in pores,  $\delta_w$  ( $m$ ) is the height of the water layer and  $C(0, t)$  ( $mol\ m^{-3}$ ) is the pesticide concentration in the superficial soil solution. This term gives an account of the pesticide concentration that escapes from the water compartment forward from the sediment compartment and from the sediment to the top of the soil column.

Moreover, it must be considered that the pesticide concentration which the rice plant removes by the roots, that is, the average of the pesticide concentration the plant absorbs. This contribution is represented by the integral

$$\bar{C}(t) = \frac{1}{\delta_r} \int_0^{\delta_r} C(z, t) dz$$

where  $C(z, t)$  ( $mol\ m^{-3}$ ) is the pesticide concentration in the column of soil, in the depth  $z$  and time  $t$  and  $\delta_r$  ( $m$ ) is the average length of the rice plants' roots. The whole process is represented in Fig. 2.

To set the total mass balance equations of the pesticide, we recall that for two neighbouring compartments  $i$  and  $j$  there will be a positive gradient for fugacities until the equilibrium of fugacities is reached ( $f_i = f_j$ ). In addition, we suppose that direct transfer of the mass of the pesticide occurs between air and water, water and sediment, air and rice plants and water and rice plants. Thus, the total mass balance equations described by a level IV fugacity model



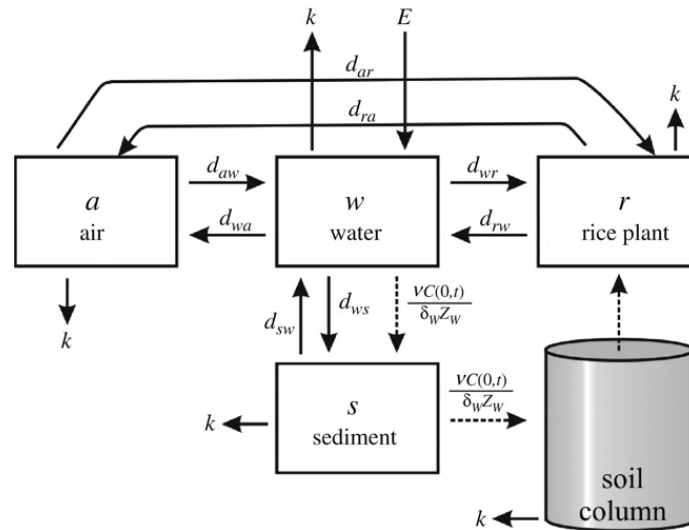


Fig. 2. Graphical representation of the compartments that take part in the level IV fugacity model coupled with a dispersion-advection equation.

coupled by a dispersion-advection equation is given by the following system of the differential equations:

$$\begin{aligned}
 \frac{df_a}{dt} &= \frac{d_{wa}f_w}{V_a Z_a} + \frac{d_{ra}f_r}{V_a Z_a} + \frac{G_a C_{Ba}}{V_a Z_a} - \frac{d_{aw}f_a}{V_a Z_a} - \frac{d_{ar}f_a}{V_a Z_a} - \frac{G_a f_a}{V_a} - \lambda_a f_a \\
 \frac{df_w}{dt} &= \frac{d_{aw}f_a}{V_w Z_w} + \frac{d_{rw}f_r}{V_w Z_w} + \frac{d_{sw}f_s}{V_w Z_w} + \frac{G_w C_{Bw}}{V_w Z_w} - \frac{vC(0,t)}{\delta_w Z_w} \\
 &\quad - \frac{G_w f_w}{V_w} - \frac{d_{wa}f_w}{V_w Z_w} - \frac{d_{ws}f_w}{V_w Z_w} - \frac{d_{wr}f_w}{V_w Z_w} - \lambda_w f_w \\
 \frac{df_r}{dt} &= \frac{d_{wr}f_w}{V_r Z_r} + \frac{d_{ar}f_a}{V_r Z_r} + \frac{Q_w T_{scf}}{\delta_r V_r Z_r} \int_0^{\delta_r} C(z,t) dz - \frac{d_{rw}f_r}{V_r Z_r} - \frac{d_{ra}f_r}{V_r Z_r} - \lambda_r f_r \\
 \frac{df_s}{dt} &= \frac{d_{ws}f_w}{V_s Z_s} + \frac{G_s C_{Bs}}{V_s Z_s} - \frac{G_s f_s}{V_s} - \frac{d_{sw}f_s}{V_s Z_s} - \lambda_s f_s.
 \end{aligned} \tag{16}$$

For  $i, j \in \{a, w, r, s\}$  the model assumes that  $d_{ij} = d_{ji}$ ,  $d_{as} = d_{rs} = 0$  and  $C_{Bi} = 0$ .  $Q_w$  ( $\text{m}^3 \text{h}^{-1}$ ) is the water flow rate transpired by rice plants and  $T_{scf}$  is the pesticide transpiration stream coefficient factor.

The  $T_{scf}$  value is typically estimated by the relationship [25]

$$T_{scf}[\text{Briggs}] = 0.784 \exp\left(-\frac{(\log_{10}(k_{ow}) - 1.78)^2}{2.44}\right) \tag{17}$$

or by the relationship proposed in [26], given by

$$T_{scf}[\text{Hsu}] = 0.7 \exp\left(-\frac{(\log_{10}(k_{ow}) - 3.07)^2}{2.78}\right). \tag{18}$$

In the proposed model the  $T_{scf}$  value has been calculated as the average

$$T_{scf} = \frac{T_{scf}[\text{Briggs}] + T_{scf}[\text{Hsu}]}{2}. \tag{19}$$

Concentrations of the pesticide in the column of soil, immediately below of the sediment layer are estimated by a one-dimensional dispersion-advection equation

$$D \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} - R \left( \frac{\partial C}{\partial t} - C \left( \mu - \frac{Q_w T_{scf}}{V_r} \right) \right) = 0. \tag{20}$$

The coefficient of effective dispersion includes the molecular diffusion of the pesticide in soil solution and the hydrodynamic dispersion and is estimated by the relationship

$$D = \frac{\sqrt[3]{\theta^{10}}}{\phi^2} D_{pw} + \alpha v \tag{21}$$

where  $\theta$  is the soil water volumetric fraction,  $\phi$  is the porosity of the soil profile,  $\alpha(m)$  is a factor that expresses the water dispersion in the soil matrix and  $v$  ( $m\ h^{-1}$ ) is the pore water velocity in the soil matrix. The term  $\alpha v$  ( $m^2\ h^{-1}$ ) represents the hydrodynamic dispersion [27].  $z_\infty$  represents a virtual point limit of the limitless soil depth, that is, the soil depth.

The retardation factor of the pesticide is calculated by the expression

$$R = 1 + \frac{\rho v_{oc} k_{oc}}{\theta} \tag{22}$$

where  $\rho$  ( $kg\ m^{-3}$ ) is the soil bulk density,  $v_{oc}$  is the soil carbon organic volumetric fraction,  $\theta$  is the soil water volumetric fraction and  $k_{oc}$  ( $m^3\ kg^{-1}$ ) is the soil organic carbon partition coefficient of the pesticide [27].

The contour conditions for the model are given by [28]

$$vC(0, t) - D \frac{\partial C(0, t)}{\partial z} = vZ_w f_w(t) \quad t \geq 0 \tag{23}$$

and

$$\frac{\partial C(z_\infty, t)}{\partial z} = 0 \quad t \geq 0 \tag{24}$$

where  $C = C(z, t)$  ( $mol\ m^{-3}$ ),  $D$  ( $m^2\ h^{-1}$ ),  $v$  ( $m\ h^{-1}$ ),  $R$  and  $\mu$  ( $h^{-1}$ ) are the concentration of the pesticide in the soil solution, the coefficient of effective dispersion, the pore water velocity, the pesticide retardation factor, and the pesticide half-life in the soil profile, respectively.

For the coupled model we assume the initial condition

$$C(z, 0) = 0 \quad 0 < z < z_\infty. \tag{25}$$

#### 4. Numerical solutions

First we present the discretization of the system of ordinary differential equations of the model of fugacity of level IV (15) to find the numerical solution of the concentration in the compartments of air, water, sediment and plant of rice. Since the typical time scales for the different compartments are of different orders of magnitude an implicit method is used to avoid stability problems. Particularly, first-order Euler implicit method is used [29]. In this way, for Eq. (15) we should solve, for each time step of length  $\Delta t$ , the following system of linear equations:

$$[\mathbf{M}_1] [f^{n+1}] = [f^n] + [\mathbf{B}]$$

with

$$\mathbf{M}_1 = \begin{bmatrix} (1 - \Delta t A_1) & -\Delta t A_2 & -\Delta t A_3 & 0 \\ -\Delta t B_1 & (1 - \Delta t B_2) & -\Delta t B_3 & -\Delta t B_4 \\ -\Delta t H_1 & -\Delta t H_2 & (1 - \Delta t H_3) & 0 \\ 0 & -\Delta t F_1 & 0 & (1 - \Delta t F_2) \end{bmatrix}$$

and

$$f^{n+1} = \begin{bmatrix} f_a^{n+1} \\ f_w^{n+1} \\ f_r^{n+1} \\ f_s^{n+1} \end{bmatrix}; \quad f^n = \begin{bmatrix} f_a^n \\ f_w^n \\ f_r^n \\ f_s^n \end{bmatrix}; \quad \mathbf{B} = \begin{bmatrix} \Delta t A_4 \\ \Delta t B_5 \\ H_4 \Delta t \Delta z \sum_{i=0}^{nr-1} C_i^n \\ \Delta t F_3 \end{bmatrix}$$



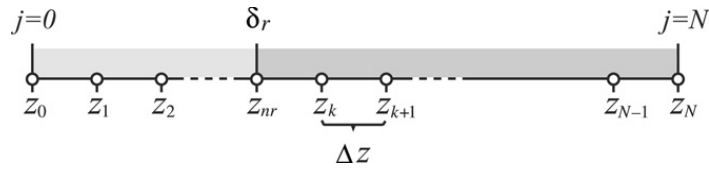


Fig. 3. Graphical representation of the mesh used for the discretization of the advection-dispersion equation.

where,

$$\begin{aligned}
 A_1 &= \left( -\frac{d_{aw}}{V_a Z_a} - \frac{d_{ra}}{V_a Z_a} - \frac{G_a}{V_a} - \lambda_a \right), & A_2 &= \frac{d_{wa}}{V_a Z_a}, & A_3 &= \frac{d_{ra}}{V_a Z_a}, & A_4 &= \frac{G_a C_{Ba}}{V_a Z_a} \\
 B_1 &= \frac{d_{aw}}{V_w Z_w}, & B_2 &= \left( -\frac{d_{wa}}{V_w Z_w} - \frac{d_{wr}}{V_w Z_w} - \frac{d_{ws}}{V_w Z_w} - \frac{G_w}{V_w} - \lambda_w \right), \\
 B_3 &= \frac{d_{rw}}{V_w Z_w}, & B_4 &= \frac{d_{sw}}{V_w Z_w}, & B_5 &= \frac{G_w C_{Bw}}{V_w Z_w} \\
 H_1 &= \frac{d_{ar}}{V_r Z_r}, & H_2 &= \frac{d_{wr}}{V_r Z_r}, & H_3 &= \left( -\frac{d_{ra}}{V_r Z_r} - \frac{d_{rw}}{V_r Z_r} - \lambda_r \right), & H_4 &= \frac{Q_w T_{scf}}{\delta_r V_r Z_r} \\
 F_1 &= \frac{d_{ws}}{V_s Z_s}, & F_2 &= \left( -\frac{d_{sw}}{V_s Z_s} - \frac{G_s}{V_s} - \lambda_s \right), & F_3 &= \frac{G_s C_{Bs}}{V_s Z_s}.
 \end{aligned}$$

When we consider the coupled model with the column of soil we have to discretize the spatial part of the dispersion-advection equation assuming a finite length for the column of soil,  $L$ . This discretization is based on the mesh shown in Fig. 3 and the central finite differences approximations [30]

$$\left. \frac{\partial C(t, z)}{\partial z} \right|_{z_j} \approx \frac{C(t, (j+1)\Delta z) - C(t, (j-1)\Delta z)}{2\Delta z} \tag{26}$$

and

$$\left. \frac{\partial^2 C(t, z)}{\partial z^2} \right|_{z_j} \approx \frac{C(t, (j+1)\Delta z) - 2C(t, j\Delta z) + C(t, (j-1)\Delta z)}{(\Delta z)^2}. \tag{27}$$

For the time discretization we also use the implicit Euler method, obtaining the following system of equations:

$$\begin{aligned}
 \xi C_0^{n+1} - (2\Delta t\alpha)C_1^{n+1} - \delta f_w^{n+1} &= C_0^n \\
 -\Delta t(\alpha + \beta)C_{j-1}^{n+1} - (1 + \Delta t(2\alpha - k))C_j^{n+1} - \Delta t(\alpha - \beta)C_{j+1}^{n+1} &= C_j^n, \quad j = 1, \dots, N-1 \\
 -2\Delta t\alpha C_{N-1}^{n+1} + (1 + \Delta t(2\alpha - k))C_N^{n+1} &= C_N^n
 \end{aligned} \tag{28}$$

where,

$$\xi = \left( \left( \frac{2\Delta z\Delta t v}{D} \right) (\alpha + \beta) + (1 + \Delta t(2\alpha - k)) \right), \quad \delta = \left( \left( \frac{2\Delta z\Delta t v Z_w}{D} \right) (\alpha + \beta) \right)$$

and

$$\alpha = \frac{D}{R\Delta z^2}, \quad \beta = \frac{v}{2R\Delta z}, \quad k = \mu - \frac{Q_w T_{scf}}{V_r}.$$

For each time step, a system of linear equations has to be solved. This system for the whole coupled model has the following block structure:

$$\begin{bmatrix} \mathbf{M}_1 & \begin{matrix} 0 \\ \frac{\Delta t v}{\delta_w Z w} \\ 0 \\ 0 \end{matrix} & 0 \\ \hline 0 & -\delta & 0 & 0 & \begin{matrix} \xi \\ -2\Delta t \alpha & 0 & \dots \end{matrix} \\ \hline 0 & \begin{matrix} -\Delta t(\alpha + \beta) \\ 0 \\ \vdots \\ 0 \end{matrix} & \mathbf{M}_2 \end{bmatrix} \begin{bmatrix} \mathbf{f}^{n+1} \\ C_0^{n+1} \\ \vdots \\ C^{n+1} \end{bmatrix} = \begin{bmatrix} \mathbf{f}^n \\ C_0^n \\ \vdots \\ C^n \end{bmatrix} + \begin{bmatrix} \mathbf{Bn} \\ 0 \\ \vdots \\ 0 \end{bmatrix}$$

with,

$$\mathbf{M}_2 = \begin{bmatrix} (1 + \Delta t(2\alpha - k)) & -\Delta t(\alpha - \beta) & & & \\ -\Delta t(\alpha + \beta) & (1 + \Delta t(2\alpha - k)) & -\Delta t(\alpha - \beta) & & \\ & \ddots & \ddots & \ddots & \\ & & & \ddots & \\ & & & & -\Delta t(\alpha + \beta) & (1 + \Delta t(2\alpha - k)) & -\Delta t(\alpha - \beta) \\ & & & & & -2\Delta t \alpha & (1 + \Delta t(2\alpha - k)) \end{bmatrix}$$

and

$$\mathbf{C}^{n+1} = \begin{bmatrix} C_1^{n+1} \\ C_2^{n+1} \\ \vdots \\ \vdots \\ C_N^{n+1} \end{bmatrix}; \quad \mathbf{C}^n = \begin{bmatrix} C_1^n \\ C_2^n \\ \vdots \\ \vdots \\ C_N^n \end{bmatrix}; \quad \mathbf{Bn} = \begin{bmatrix} \Delta t A_4 \\ \Delta t B_5 \\ H_4 \Delta t \Delta z \sum_{i=0}^{nr-1} C_i^n \\ \Delta t F_3 \\ 0 \\ \vdots \\ 0 \end{bmatrix}.$$

We have to remark that the term  $H_4 \Delta t \Delta z \sum_{i=0}^{nr-1} C_i^n$  is evaluated at time  $t_n$ , to simplify the scheme.

### 5. Simulation results

The pesticide used for the modelización of this work is the Carbofuran, (2,3-dihydro-2,2-dimethyl-7-benzofuranol methylcarbamate), which is an insecticide of the carbamates class, a cholinesterase inhibitor and is commonly used in rice culture [31]; its characteristics required for the study using a level IV fugacity model are presented in Table 1.

In Table 2, the values of the general parameters of geometry, pesticide dose and transfer coefficients used for the simulations are presented [34,8].

Carbofuran half-lives in water and in soil solution were estimated as 78 h and 241 h, respectively [31]. Carbofuran half-life in air and rice plants was determined as 12 h and 36 h, respectively [35]. The temperature of the experiment is considered to be of 298 K (25 °C).

Table 1  
Carbofuran physicochemical characteristics (taken from references [22,32,33])

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

Table 2  
Values of general parameters

Parameter	Notation	Value	Units
Area plantation	Ar	100 × 100	m <sup>2</sup>
Dose pesticide	Pd	1.05 × 10 <sup>4</sup>	mol m <sup>-2</sup>
Volume water	Vw	2.0 × 10 <sup>3</sup>	m <sup>3</sup>
Volume air	Va	8.0 × 10 <sup>4</sup>	m <sup>3</sup>
Volume rice	Vr	1.2 × 10 <sup>3</sup>	m <sup>3</sup>
Volume soil	Vs	5.0 × 10 <sup>3</sup>	m <sup>3</sup>
Transfer coefficient	<i>d<sub>aw</sub></i>	350.16	mol Pa <sup>-1</sup> h <sup>-1</sup>
Transfer coefficient	<i>d<sub>ar</sub></i>	262.65	mol Pa <sup>-1</sup> h <sup>-1</sup>
Transfer coefficient	<i>d<sub>wr</sub></i>	1.03 × 10 <sup>5</sup>	mol Pa <sup>-1</sup> h <sup>-1</sup>
Transfer coefficient	<i>d<sub>ws</sub></i>	2.7 × 10 <sup>12</sup>	mol Pa <sup>-1</sup> h <sup>-1</sup>

For the soil we have considered the following parameters: soil density  $1.54 \times 10^3 \text{ kg m}^{-3}$ , the porosity of the soil profile 0.17, the soil water volumetric fraction 0.48, the soil organic carbon volumetric fraction 0.17, the factor for water dispersion in the soil matrix 0.12, the pore water velocity in the soil matrix  $0.0024 \text{ m h}^{-1}$  and the soil bulk density  $1580 \text{ kg m}^{-3}$ . For the water: The organic carbon volumetric fraction of the water  $1.2 \times 10^{-3}$ , water density  $999.5 \text{ kg m}^{-3}$ . For the rice plants: The total water flow rate transpired by rice plants is estimated in  $8.7 \times 10^{-5} \text{ m}^3 \text{ h}^{-1}$ , the average root length of the rice plants 0.03 m, The density of the rice plants  $1.03 \times 10^3 \text{ kg m}^{-3}$ , volumetric fraction of water and lipids in rice plants were 0.80 and 0.02 respectively and water layer height 0.3 m.

For all  $i \in \{a, w, r, s\}$ ,  $G_i = 0$  and  $G_w = 1.89 \times 10^{-5} \text{ m}^{-3} \text{ h}^{-1}$ ,  $G_w$  was estimated according to [36].

The calculated capacity of fugacity of the air is  $Z_a = 4.0362 \times 10^{-4}$ , water  $Z_w = 3.6176 \times 10^3$ , rice plants  $Z_r = 5.4513 \times 10^3$  and sediment  $Z_s = 5.4513 \times 10^3$  Resulting the partition coefficients  $k_{aw} = 1.1157 \times 10^{-7}$ ,  $k_{rw} = 1.5069$  and  $k_{sw} = 1.0288$ .

We have considered a finite column of soil of length  $L = 1 \text{ m}$ . The time range for numerical simulations was 400 h, with  $\Delta t = 0.003 \text{ h}$  and  $\Delta z = 0.02 \text{ m}$

In Fig. 4 we show the evolution of the pesticide concentration in the air compartment. It reaches its maximum value about  $t = 0.3 \text{ h}$  and then it decreases. At  $t = 400 \text{ h}$  the concentrations is practically negligible.

The curves for the concentration of the pesticide in the compartments water and sediment are very similar as can be seen in the Fig. 5. The behaviour is similar in both compartments because of the high value of the coefficient of transference between these two compartments  $d_{ws} = 2.7 \times 10^{12} \text{ mol Pa}^{-1} \text{ h}^{-1}$ .

The evolution of the pesticide concentration in the plant is shown in Fig. 6. It can be observed that the maximum concentration is reached at approximately 51 h and it practically has disappeared 400 h after the product has been applied.

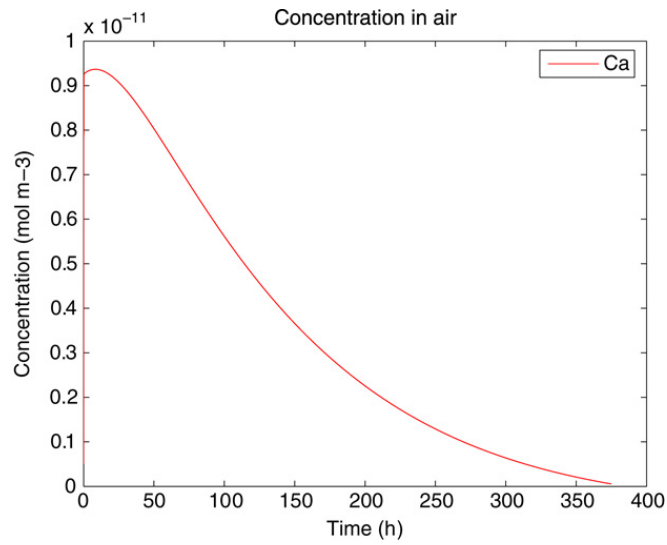


Fig. 4. Graphical representation of the concentration in the air compartment.

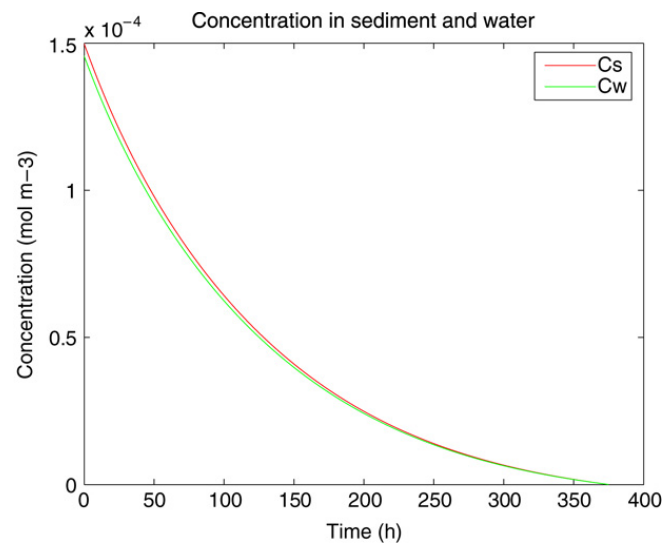


Fig. 5. Graphical representation of the concentration in the sediment and water compartments.

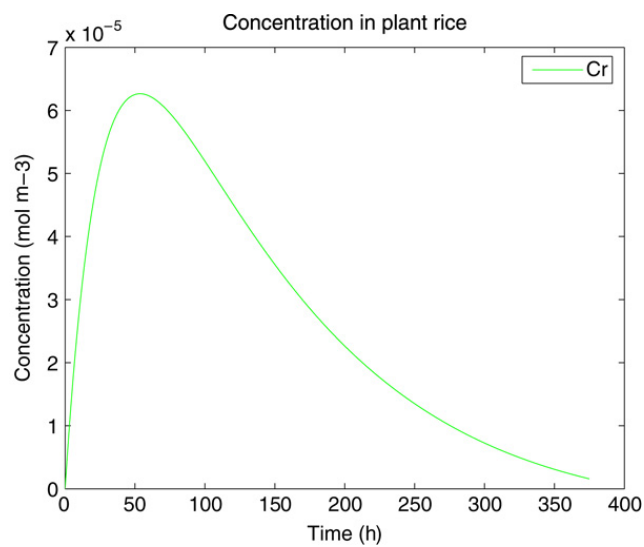


Fig. 6. Graphical representation of the concentration in the rice compartment.

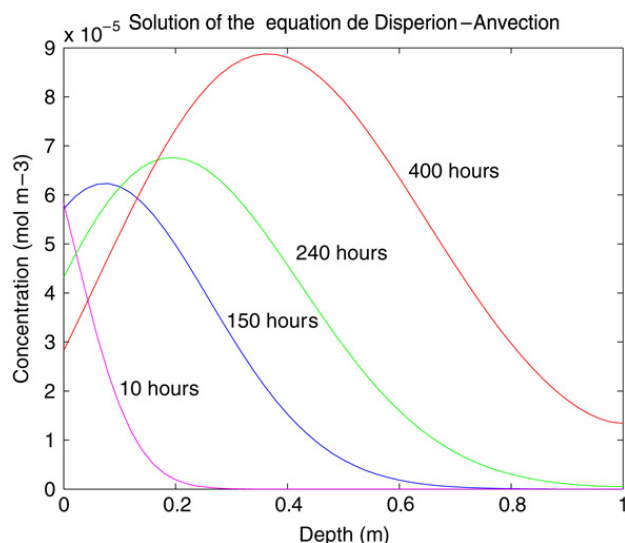


Fig. 7. Graphical representation of the concentration in the soil column compartment for different times.

The profiles of pesticide concentrations along the soil column at  $t = 10$  h,  $t = 150$  h,  $t = 240$  h and  $t = 400$  h are shown in Fig. 7. It was observed that after 10 hours of having applied the pesticide to the water, the top of the column of soil had a pesticide concentration of about  $5.8 \times 10^{-5} \text{ mol m}^{-3}$  and it propagated until a depth approximated of 0.22 m; 150 h after the application of the pesticide the concentration propagated until a depth of 0.71 m and reached its maximum point to 0.08 m at a rate of  $6.3 \times 10^{-5} \text{ mol m}^{-3}$ ; in 240 h after the application of the pesticide the concentration had propagated to 1 m, reaching its maximum point of concentration 0.22 m with a rate of  $6.85 \times 10^{-5} \text{ mol m}^{-3}$  and finally to 400 h it reached its maximum concentration at 0.38 m with a rate of  $8.9 \times 10^{-5} \text{ mol m}^{-3}$ .

The Carbofuran concentration decreased in water and sediment while it increased in air and rice plants up to a maximum and then decreased. 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 leads to high affinity for water and rice plants [34].

## 6. Conclusions

We have presented an unsteady state level IV fugacity model coupled with a dispersion advection equation to study the fate of insecticide carbofuran. Data and results presented in this work illustrate the use of this coupled model to determine the pesticide fugacities and to compute the pesticide concentrations in air, water, rice plants, sediment and soil solution profile. Results suggest how this model can be used to determine the environmental compartment that is more vulnerable to a chemical compound or the risk of the groundwater contamination by a determined pesticide; more extensively, how to decide among many compounds, which one needs a better environmental analysis. The results suggest that the level IV fugacity model coupled with a dispersion-advection equation is appropriate and permits estimation or anticipation of the pesticide fate and exposure in an environmental compartments system for a screening level risk assessment.

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