LEVEL IV FUGACITY MODEL BY CONTINUOUS TIME CONTROL SYSTEM

L. C. Paraíba[1,3], J. M. Carrasco[2] and R. Bru[3]

[1]*Centro Nacional de Pesquisa de Monitoramento e Avaliação de Impacto Ambiental, CNPMA, EMBRAPA, Jaguariúna, SP, Brazil;* [2]*Departament de Biotecnologia, ETSIA, Universitat Politècnica de València, València, Spain;* [3]*Departament de Matemàtica Aplicada, ETSIA, Universitat Politècnica de València, València, Spain*

ABSTRACT

A continuous time dynamic control system of the 'Level IV Fugacity Model' is presented and applied to selected organic chemicals in evaluative environments system. In order to illustrate the numerical solution by this model a discretization is used to calculate the fugacity, concentration and fugacity settling time for a set of three insecticides applied in a hypothetical three compartmental environmental system. The model employs the fugacity concept and treats three bulk compartments: air, water and bottom sediment. Input to the model consists of a description of the environmental, the physical-chemical and reaction properties of the chemical, and emission rates. Expressions in matrix form are included for emissions, advections, reactions, and inter-phase transference. An algorithm to determine the values of the fugacities, concentrations and fugacity settling time is given.

Keywords: fugacity model, dynamic control system, settling time, compartmental model, insecticide.

INTRODUCTION

The objective of this work is develop a numerical solution from 'Level IV Fugacity Model' [1] by a continuous time dynamic control system and apply this solution in a simulation of three well-known insecticides emitted in a hypothetical three compartmental environmental system. Thereby, is necessary to present a formalism of the 'Level IV Fugacity Model' through a dynamic control system. The 'Level IV Fugacity Model' for an ecosystem constituted by compartments the fugacities change with the time in response to emissions and they are determined by a continuous time dynamic control system describing the total bulk mass balance of the substance.

We will describe as the solution of the 'Level IV' can be outlined as a discrete dynamic control system, obtained to discrete a continuous dynamic system. We will use this model and their solution to simulate the kinetic of the insecticide chlorpyriphos; methyl parathion and trichlorphon in a three bulk compartmental system constitute by air, water and bottom sediment. In this environment, the equations of the mass balance are obtained supposing that the fugacities are not in steady state, that it is known a finite number of emissions and that there are inter-phases transfers, reactions and advections flows of the substances.

The fugacity is a thermodynamic magnitude related to the chemical potential and characterised by the leak trend of a substance in a compartment [2-3]. The fugacity expresses the chemistry activity of a substance and has been applied mainly in thermodynamic problems implicating equilibrium among phases.

Mathematical models based on the thermodynamic theory of the fugacity are outlined frequently by a linear system of equations describing the bulk balance of a chemical substance in an ecosystem constituted by compartments. Thus, when all fugacities are equal and constant in all compartments the concentrations are evaluated directly, this case corresponds to the well-known 'Level I Fugacity Model' or 'Level II Fugacity Model' if in addition there are reactions and advections. 'Level III Fugacity Model' supposes that the distribution of the substance is not in equilibrium and that each fugacity can have different values, which are determined by a linear system of equations when there are reactions, advections, emissions and transfers of the substance among compartments in stationary state [4-5]. In addition, there is another model describing the unsteady state behaviour of a substance in the environment, which permits to observe substances whose emissions vary with the time and to determine the time in which the system reaches the steady state. This last model, known as 'Level IV Fugacity Model', is usually described by a system of differential equations.

The fugacity models and its classification in levels of sophistication are due the work of Mackay [1]. The fugacity nomenclature that we will use in this work is the original papers of Mackay and Paterson [1-2].

Some non-stationary models for the study of the kinetic of a substance in the environment have been proposed for the analysis of the fugacities changing with the time (see [6-8]), but it seems that none of them presents a mathematical formalism through control theory.

NOTATIONS AND DEFINITIONS

The distribution of a small quantity of a chemical substance between two compartments denoted by the indices i and j, respectively, under equilibrium fugacity, constant temperature and pressure, yields constant concentration ratios between these two compartments. The partition coefficient k_{ij} of the substance between two compartments is then defined as the quotient $k_{ij} = C_i / C_j$ of the concentrations of the substance in each one of the compartments.

The relationship between the fugacity and the concentration is given by $C_i = Z_i f_i$, where C_i is the concentration in $mol \cdot m^{-3}$, f_i is the fugacity given in Pascal (Pa) and the constant of proportionality Z_i is the capacity of fugacity in $mol \cdot m^{-3} \cdot Pa^{-1}$. The estimate of the capacity of fugacity Z_i of a substance in a compartment i depends on the nature of the compartment and of the partition coefficient of the substance in this compartment. Furthermore, the partition coefficient k_{ij}, under equilibrium fugacity $(f_i = f_j)$, is determined by the quotient between Z_i and Z_j, that is, $k_{ij} = Z_i / Z_j$, consequently, $Z_i = k_{ij} Z_j$.

In the air, the fugacity of a substance is equal to their partial pressure the one which can be expressed in terms of the concentration in the air C_a and by the equation of the ideal gas given by $f_a = C_a RT°$, where $R = 8.314 Pa \cdot m^3 \cdot mol^{-1}$ is the gas constant and $T°$ is absolute temperature in $°K$. Consequently, the capacity of fugacity of the air is given by $Z_a = 1/RT°$.

The fugacity of a substance dissolved in water is approximated by its partial vapour pressure, the one which is proportional to its concentration in water, that is, $f_w = HC_w$, where C_w is concentration in water in $mol \cdot m^{-3}$ and H is Henry's constant in $Pa \cdot m^3 \cdot mol^{-1}$.

Henry's constant in $Pa \cdot m^3 \cdot mol^{-1}$ can be defined as $H = (Pv \cdot Wm)/Sol$, where Pv is the partial vapour pressure in Pa, Wm is the weigh molecular in $g \cdot mol^{-1}$ and Sol is the aqueous solubility in $g \cdot m^{-3}$. Consequently, the capacity of fugacity of the water is given by $Z_w = 1/H$.

For the bottom sediment, the concentration of a substance C_S can be expressed using the coefficient of adsorption k_d in $m^3 \cdot kg^{-1}$, the concentration of the substance in the water C_w and the density of the bottom sediment ρ_s in $kg \cdot m^{-3}$, such that, $C_s = \rho_s k_d C_w$. In equilibrium, the fugacity of the substance in water f_w is equal to the fugacity of the substance in bottom sediment f_s, that is, $f_s = HC_w$. Therefore, f_s can be written as $f_s = (H/\rho_s k_d)C_s$. Consequently, Z_s values for the bottom sediment is given by $Z_s = (k_d \rho_s)/H$.

The solubility is related empirically with the organic carbon water partition coefficient k_{oc} (see [9]) by the expression

$$\log_{10}(k_{oc}) = 3.64 - 0.55 \log_{10}(Sol) \tag{1}$$

This relation can be used to determine the value of k_d, where $k_d = (oc \cdot k_{oc})/100$ and oc is the content volumetric of organic carbon in the bottom sediment.

The capacity storage of a compartment i is determined by $V_i Z_i$, where V_i and Z_i are, respectively, the volume and the capacity of fugacity of compartment i. In this work, the values of the indices $i = 1, 2$ and 3 represent, respectively, air, water and bottom sediment.

The reaction process is supposed as a first order processes where the reaction constant rate is r_i, in min^{-1}, and the reaction component for each compartment i is $r_i V_i Z_i f_i$.

The advection flow in a compartment i can be introduced in the model as a first order process. In fact, the advection can be considered 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 in $m^3 \cdot min^{-1}$ entering into compartment i with concentration C_{Bi} and leaving this compartment with concentration C_i.

When there is a gradient of fugacity between two compartments i and j results a flow of the substance in the direction of this gradient. The flow of substance is the product of the difference $(f_i - f_j)$ by transfer coefficient d_{ij} between these two compartments. The coefficients of transference d_{ij} and d_{ji} are positive. The differences $(f_i - f_j)$ are positive or negative, depending on the direction on the transfer, determined by the relative values of f_i and f_j. In this work we are suppose that $d_{ij} = d_{ji}$.

The emissions in the compartment i, as function of the time in $mol \cdot min^{-1}$, are denoted by $E_i = E_i(t)$. In this position we are supposing that there is not any effect of dilution, that is, the volume V_i of each one of the compartments is constant.

LEVEL IV FUGACITY MODEL BY A CONTINUOUS CONTROL SYSTEM

For simples hypothetical ecosystem constituted by air $(i = 1)$, water $(i = 2)$ and bottom sediment $(i = 3)$, under unsteady state condition or 'Level IV Fugacity Model', the fugacities are functions of the time and they can be determined by the system of ordinary differential equations. The variation rate of the fugacity in the time, for each one of the compartments, is then calculated using the total bulk mass balance, which is described by the following system of ordinary linear differential equations

$$V_1 Z_1 \frac{df_1}{dt} = E_1 + G_1 C_{B1} + d_{21} f_2 - (G_1 Z_1 + d_{12} + r_1 V_1 Z_1) f_1 \tag{2}$$

$$V_2 Z_2 \frac{df_2}{dt} = E_2 + G_2 C_{B2} + d_{12} f_1 + d_{32} f_3 - (G_2 Z_2 + d_{21} + d_{23} + r_2 V_2 Z_2) f_2 \tag{3}$$

$$V_3 Z_3 \frac{df_3}{dt} = E_3 + G_3 C_{B3} + d_{23} f_2 - (G_3 Z_3 + d_{32} + r_3 V_3 Z_3) f_3 \tag{4}$$

where $f_i = f_i(t)$, and the initial condition $f_i(0) = f_i^0$, for $i = 1, 2, 3$.

The solution of the equation system (2), (3) and (4), for each value of t, the values of the fugacities $f_i = f_i(t)$ are multiplied by the capacity of fugacity Z_i to determine the value of the concentration $C_i = C_i(t)$ of the substance in air, water and bottom sediment.

The system expressed by equation (2), (3) and (4) can be written in matrix form as the following continuous time control system

$$\dot{\mathbf{f}} = \mathbf{A} \cdot \mathbf{f}(t) + \mathbf{I} \cdot \mathbf{u}(t) \tag{5}$$

where the matrix $\mathbf{A}$ and $\mathbf{I}$ are, respectively, given by

$$\mathbf{A} = \begin{bmatrix} \dfrac{-(G_1 Z_1 + d_{12} + r_1 V_1 Z_1)}{V_1 Z_1} & \dfrac{d_{21}}{V_1 Z_1} & 0 \\[2em] \dfrac{d_{12}}{V_2 Z_2} & \dfrac{-(G_2 Z_2 + d_{21} + d_{23} + r_2 V_2 Z_2)}{V_2 Z_2} & \dfrac{d_{32}}{V_2 Z_2} \\[2em] 0 & \dfrac{d_{23}}{V_3 Z_3} & \dfrac{-(G_3 Z_3 + d_{32} + r_3 V_3 Z_3)}{V_3 Z_3} \end{bmatrix}$$

and $\mathbf{I} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$. The vectors $\dot{\mathbf{f}} = \dot{\mathbf{f}}(t)$, $\mathbf{f} = \mathbf{f}(t)$ and $\mathbf{u} = \mathbf{u}(t)$ are, respectively, $\dot{\mathbf{f}} = \begin{bmatrix} \dfrac{df_1}{dt} \\[1.5em] \dfrac{df_2}{dt} \\[1.5em] \dfrac{df_3}{dt} \end{bmatrix}$,

$\mathbf{f}(t) = \begin{bmatrix} f_1(t) \\[1em] f_2(t) \\[1em] f_3(t) \end{bmatrix}$ and $\mathbf{u}(t) = \begin{bmatrix} \dfrac{E_1 + G_1 C_{B1}}{V_1 Z_1} \\[1.5em] \dfrac{E_2 + G_2 C_{B2}}{V_2 Z_2} \\[1.5em] \dfrac{E_3 + G_3 C_{B3}}{V_3 Z_3} \end{bmatrix}$. Where the variable $\mathbf{u}$ is the control vector, $\dot{\mathbf{f}}$ is the

fugacity derivative vector and $\mathbf{f}$ is the state vector of fugacities.

In the control systems theory, the control vector is a variable to be chosen in order to be maintaining the state vector in wished values. In this work, the variables of control are the emissions of the chemical substances.

NUMERICAL SOLUTION

The equation (5) admits the following integral solution in interval $[0, t]$, (see [10] for details),

$$\mathbf{f}(t) = \exp(\mathbf{A}t) \cdot \mathbf{f}(0) + \int_0^t \exp(\mathbf{A} \cdot (t - \tau)) \cdot \mathbf{I} \cdot \mathbf{u}(\tau) d\tau \tag{6}$$

Let m be the number of emissions and let T be the time interval between each emission, without losing of generality we are supposing that the time interval between each emission is the time unity, that is, $T = 1$. Discretizing the equation (6), for each $t = k$, where $k = 0, 1, 2, ..., (m-1)$ we have

$$\mathbf{f}(k+1) = \mathbf{W} \cdot \mathbf{f}(k) + \mathbf{H} \cdot \mathbf{u}(k) \tag{7}$$

where $\mathbf{W} = \exp(\mathbf{A})$, $\mathbf{H} = \int_0^1 \exp(\mathbf{A}\tau) d\tau$ and $\tau = 1 - t$.

We are supposing that the emissions $E_i = E_i(t)$ and consequently the vectors $\mathbf{u} = \mathbf{u}(t)$ are constant in a given interval between any two consecutive instants of emissions, that is, $\mathbf{u}(t) = \mathbf{u}(k)$, for $k \leq t < k+1$.

Thus, if the emissions $E_i(k)$ are known, and consequently the control vectors $\mathbf{u}(k)$, then, it is possible to compute the fugacities and the respective concentrations in these times for each one of the compartments air, water and bottom sediment using the equation (7). Note that $\mathbf{u}(k) = \mathbf{0}$ for all $k \geq m$ and in this case the system (5) is determined by

$$\mathbf{f}(k+1) = \mathbf{W} \cdot \mathbf{f}(k) \tag{8}$$

Algorithm to compute the fugacity, concentration and fugacity settling time

The *fugacity settling time*, is defined, as the time required for the fugacity values stay within a range of the fugacity equilibrium. The fugacity settling time can be conceived as the required time so that the system arrives and stays within a range of the equilibrium point. The following algorithm can compute it.

The computation of the matrices $\mathbf{W}$ and $\mathbf{H}$ when the matrix $\mathbf{A}$ is known can be accomplished by the mathematical scientific package MATLAB [11], which calculates the exponential of a matrix through Padé's approximations with the function *expm* using the command $[\mathbf{W}, \mathbf{H}] = c2d(\mathbf{A}, \mathbf{I}, 1)$.

Algorithm 1 (A pseudo-code algorithm to compute the settling time).

Begin

Compute the matrices $\mathbf{W}$ and $\mathbf{H}$ by $[\mathbf{W}, \mathbf{H}] = c2d(\mathbf{A}, \mathbf{I}, 1)$

For $k = 0$ until $(m-1)$ calculate

Begin

$\mathbf{f}(k+1) = \mathbf{W} \cdot \mathbf{f}(k) + \mathbf{H} \cdot \mathbf{u}(k)$

For $i = 1$ until 3 compute $C_i(k) = Z_i f_i(k)$

Let $tol > 0$ be a tolerance of the origin. For $k > m$ compute

$\mathbf{f}(k+1) = \mathbf{W} \cdot \mathbf{f}(k) + \mathbf{H} \cdot \mathbf{u}(k)$ until $\max\limits_{i,j=1,2,3} \left\{ \left| f_i(k+1) - f_j(k+1) \right| \right\} < tol$

For $i = 1$ until 3 compute $C_i(k) = Z_i f_i(k)$

End;

End.

The first value of $k_s = k$, for which the inequality of *Algorithm 1* is satisfied, determines the fugacity settling time $t_s = k_s$ with the value of tolerance tol. The tolerance value can be established from the limits of chromatography substance detection in the compartments.

NUMERICAL SIMULATIONS

We have selected three well-known insecticides, chlorpyriphos, methyl parathion and trichlorphon to verify our model. We take arbitrarily an environment consisting of air, water and bottom sediment whose dimensions are presented in *Table 1*.

Table 1: Physical characteristic of the system air, water and bottom sediment.

Dimensions	Air	Water	Sediment
Volume (m^3)	10^6	2.0×10^3	10^3
Density $(kg \cdot m^{-3})$	----	----	1.2×10^3
Organic carbon	----	----	3.0%

In this system, we apply independently in the air one mol of chlorpyriphos, methyl parathion and trichlorphon, during sixty minutes, that is, for each insecticide $E_1(k) = (1/60)mol \cdot min^{-1}$ and $E_2(k) = E_3(k) = 0$ with $k = 0, 1, 2, ..., 59$. In all the calculations, the interval of time between each emission is of one minute and $tol = 10^{-8} Pa \cdot min^{-1}$.

The physical and chemical properties of these three insecticides, necessary for the simulation with *Algorithm 1* are presented in *Table 2* and its compilation is had to the work of Yenigün and Shtorink [12].

Table 2: The physical and chemical characteristics of the three simulated insecticides.

Insecticides	Molecular weigh $(g \cdot mol^{-1})$	Solubility $(g \cdot mol^{-1})$	Vapour pressure Pa	k_{oc}
Chlorpyriphos	350.57	2	2.4×10^{-3}	2980
Methyl parathion	263.23	55	1.3×10^{-3}	480
Trichlorphon	257.44	1.54×10^{4}	1.0×10^{-3}	20

For each one of the insecticides of *Table 2*, there is a numerical value to the coefficient of transference of substance between the air and the water and between water and the bottom sediment. These coefficients are presented in *Table 3*, which are the originals work of Zitko and McLeese [13]. The k_{oc} values were estimating by equation (1).

Table 3: Coefficient of transference in $mol \cdot min^{-1} \cdot Pa^{-1}$.

Insecticides	Air $\leftrightarrow$ Water	Water $\leftrightarrow$ Sediment
Chlorpyriphos	1.06	4.16
Methyl parathion	1.25	71.62
Trichlorphon	1.25	1271.45

According to Zitko and McLeese [13], the reaction rate constants in min^{-1} of the three insecticides simulated have its values presented in *Table 4*.

Table 4: The constant reaction rate in the respective compartments (min^{-1}).

Insecticides	Air	Water	Sediment
Chlorpyriphos	4.77×10^{-4}	3.80×10^{-4}	2.85×10^{-5}
Methyl parathion	4.77×10^{-4}	3.80×10^{-4}	2.85×10^{-5}
Trichlorphon	1.90×10^{-4}	1.90×10^{-4}	1.90×10^{-5}

With these dates, with the fugacity model by dynamic control system and the *Algorithm 1*, we can evaluate, during and after finished the emissions, the values of the fugacities and concentrations of three insecticides in the air, water and bottom sediment. Furthermore, they can determine the needed time to stabilise the fugacity, that is, the fugacity settling time. In this example the air is the only one compartment that is receiving emissions. We consider that the advections flows are calculated by expression $G_i = \dfrac{0.693V_i}{r_i}$ and that C_{Bi} are nulls for each one of the insecticides.

Figures 1-6 show, respectively, a typical result of the 'Level IV Fugacity Model' by a dynamic control system, the evolution of the fugacity and the concentration of the chlorpyriphos, methyl parathion and trichlorphon simulated by the *Algorithm 1*.

The fugacity settling time, t_s, determined by *Algorithm 1* for the insecticides chlorpyriphos, methyl parathion and trichlorphon are, respectively, 115,200; 64,800 and 7,200 minutes. With each one of these times we are able to begin the distribution analysis of the insecticides in the compartments air, water and bottom sediment using 'Level I, II or III'.
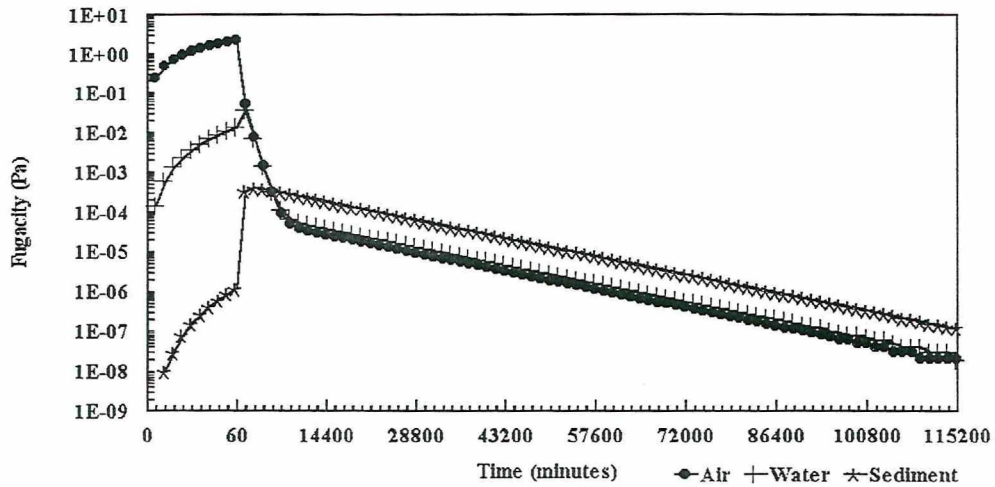
Figure 1. Fugacity of chlorpyriphos in air, water and bottom sediment before and after the emissions, obtained by Algorithm 1.
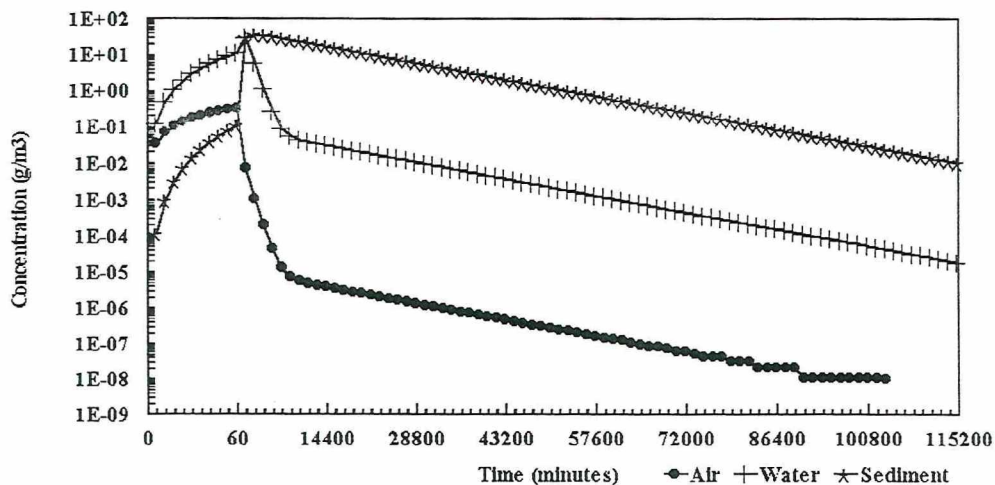
Figure 2. Concentration of chlorpyriphos in air, water and bottom sediment before and after the emissions, obtained by Algorithm 1.

Finished the emissions after 60 initial minutes, we observe from *Figures 1, 3* and *5,* that the fugacities decrease in all compartments until reach levels of equilibrium with fugacities values around $10^{-8} Pa$.
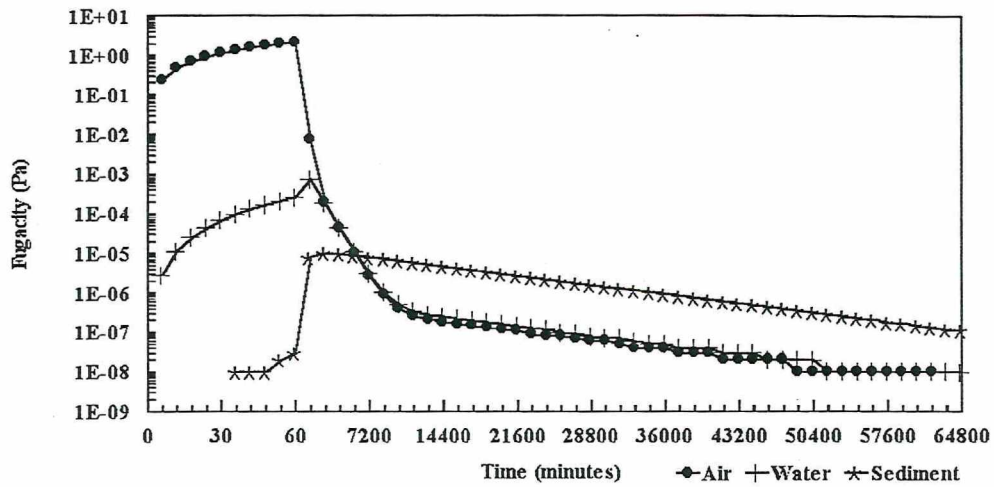

Figure 3. Fugacity of methyl parathion in air, water and bottom sediment before and after the emissions, obtained by Algorithm 1.
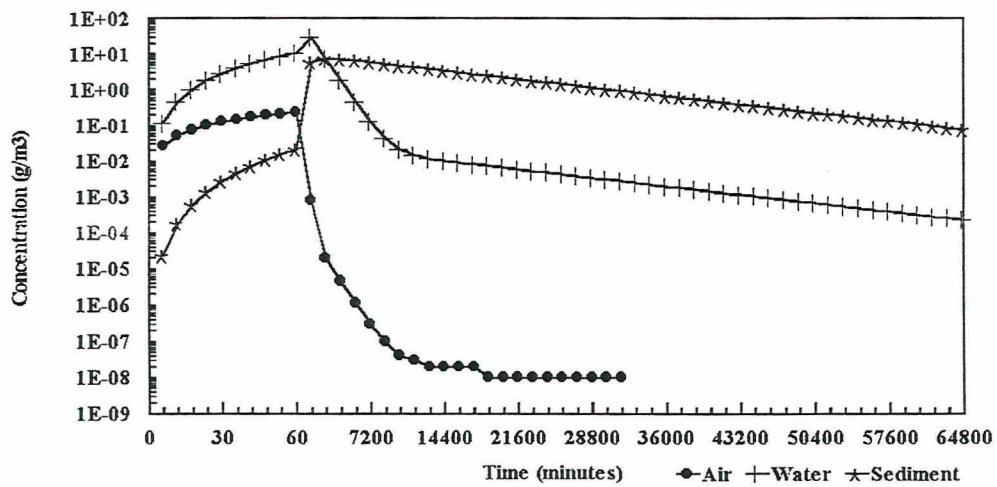

Figure 4. Concentration of methyl parathion in air, water and bottom sediment before and after the emissions, obtained by Algorithm 1.
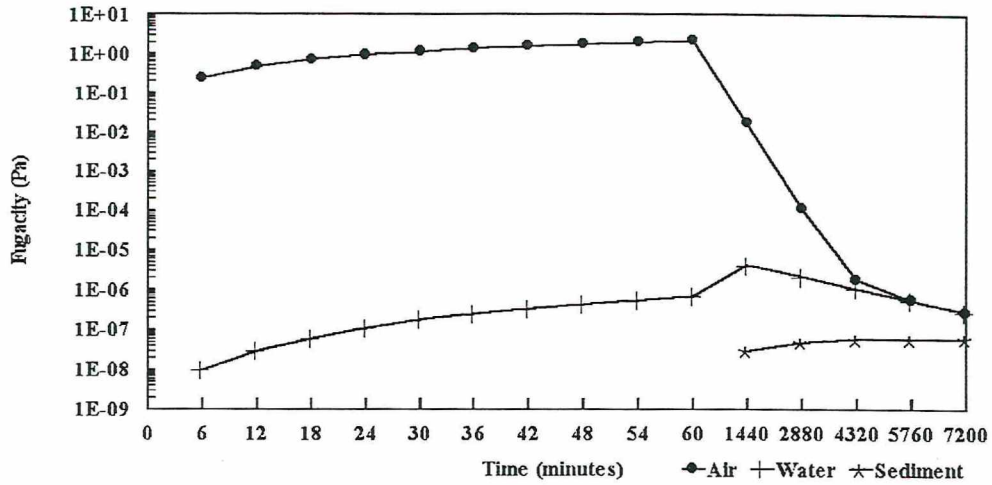
Figure 5. Fugacity of trichlorphon in air, water and bottom sediment before and after the emissions, obtained by Algorithm 1.
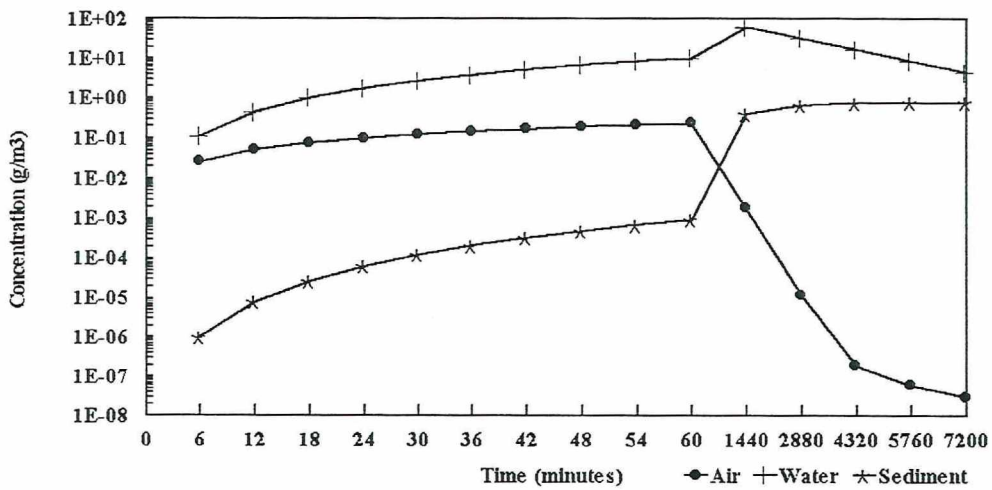

Figure 6. Concentration of trichlorphon in air, water and bottom sediment before and after the emissions, obtained by Algorithm 1.

From *Figure 2* and *Figure 4*, respectively, we can observe that the concentrations of the chlorpyriphos and methyl parathion in air decreases abruptly while increase in bottom sediment. In each figure, simulation conditions and the properties of chlorpyriphos and methyl parathion can explain the slope of the curves. In *Figure 6*, we can observe that the concentration of trichlorphon present maximum values in water. Further, the accumulation of the chlorpyriphos and methyl parathion in the bottom sediment is related to the adsorption properties of these insecticides and the accumulation of trichlorphon in water is related to their solubility in water. The compounds are apply only in the air and then there are transfers from the air to the water and finally to the bottom sediment.

CONCLUSIONS

We have modelled the unsteady state fugacity model by a dynamic control system in continuous time by equation where the state vectors are the fugacities and the control vectors are the emissions. The corresponding discrete time model permits to outline a very simple numerical solution without losing the coherence with the real physical problem. The examples that we present in this work illustrate the utilisation of the 'Level IV Fugacity Model' by a dynamic control system determining the fugacity settling time by *Algorithm 1*. These results suggest how this model can be used in the determination of the more vulnerable environmental compartment to a chemical compound or, more extensively, how to decide among many compounds which one needs a better environmental analysis.

For example, the simulation of the methyl parathion by the model indicates that is more likely to find this substance in the bottom sediment then in the air or water after finished emission. Thereby, we should be accomplished ecotoxicological studies in the organisms of the bottom, while the study of the richlorphon suggests that we are accomplished ecotoxicological analysis in the water.

It is possible to demonstrate that, independently of the number of compartments, the 'Level IV Fugacity Model' modelled by a dynamic control system has the same mathematics properties of the system air, water and bottom sediment simulated in this work.

The 'Level IV Fugacity Model' by a dynamic control system is clearly valid for assessments risk analysis of a substance in the environment, for example, useful to determinate the necessary time so that the system arrives and remains in steady state.

It is possible to demonstrate mathematically that the system of discrete control defined by the par $(\mathbf{W}, \mathbf{H})$ is a nonnegative system, that is, the components of the matrixes $\mathbf{W}$ and $\mathbf{H}$ are not negative. A practical consequence of this result is that we can deduce that if we apply controls not negative and the initial conditions are always not negative we obtained state vectors that in our problem are the fugacities, with not negative values. In future we will study the stability and the properties of nonnegativity of this model.

ACKNOWLEDGEMENT

REFERENCES

1.   D. Mackay, In *Multimedia Environmental Models: The Fugacity Approach*. Lewis Publishers, Ann Arbor, Michigan (1991).

2.   D. Mackay and S. Paterson, Calculating fugacity, *Environ. Sci. Technol.*, **15**, 1006-1014 (1981).

3.   D. Mackay and S. Paterson, Fugacity revisited, *Environ. Sci. Technol.* **16**, 654A-660A (1982).

4.   S. Paterson and D. Mackay, *The fugacity concept in environmental modelling*, In *The Handbook of Environmental Chemistry*. (Edited by O. Hutzinger), Vol. 2, Part C, Springer Verlag, Berlin, Heidelberg (1985).

5.   J. Campfens and D. Mackay, Fugacity-based model of PCB bioaccumulation in complex aquatic food webs. *Environ. Sci. Technol.* **31**,577-583 (1997).

6.   Y. Cohen and A. P. Ryan, Multimedia modelling of environmental transport: Trichloroethylene test case. *Environ. Sci. Technol.*, **19**, 412-417 (1985).

7.   Y. Matoba, J. Ohnishi, and M. Matsuo, Indoor simulation of insecticides in broadcast spraying. *Chemosphere* **30**, 345-356 (1995).

8.   W. Stiver and D. Mackay, Linear superposition in modelling contaminant behaviour in aquatic systems. *Water Research.* **29**, 329-335 (1995).

9.   E. E. Kenaga, Predicted bioconcentration factors and soil sorption coefficients of pesticides and other chemicals. *Ecotoxicol. Environ. Safety.* **4**, 26-38 (1980).

10.   K. Ogata, K. *Discrete-Time Control Systems*. Prentice Hall, Englewood Cliffs, New York (1995).

11.   MathWorks, Inc. *The Student Edition of MATLAB*. Prentice Hall, Englewood Cliffs, New Jersey (1992).

12.   O. Yenigün and D. Sohtorink, Calculations with the level II fugacity model for selected organophosphorus insecticides. *Water, Air and Soil Pollution.* 84, 175-185 (1995).

13.   V. Zitko and. D. W. McLeese. In Evaluation of Hazards of Insecticides Used in Forest Spraying to the Aquatic Environment, Canadian Technical Report of Fisheries Aquatic Sciences, Government of Canada (Dec. 1980).