



Unsteady state fugacity model by a dynamic control system

20 Rafael Bru ^{a,*}, José Maria Carrasco ^b, Lourival Costa Paraíba ^{a,c}

^a *Departament de Matemàtica Aplicada, ETSIA, Universitat Politècnica de València, Cami de Vera, s/n, 46022 València, Spain*

^b *Departament de Biotecnologia, ETSEA, Universitat Politècnica de València, València, Spain*

^c *Centro Nacional de Pesquisa de Monitoramento e Avaliação de Impacto Ambiental, CNPMA, EMBRAPA, Jaguariúna, SP, Brazil*

Received 11 November 1997; received in revised form 16 April 1998; accepted 2 June 1998

Abstract

A continuous time dynamic system of an unsteady state fugacity model is presented. Properties of this model as stability are studied. In order to evaluate numerical results a discretization preserving the stability and yielding the positivity property of the model is used. Finally, algorithms to determine the values of the fugacities, the concentrations and the dissipation time are given. The above study is illustrated with numerical results in a three compartmental environmental system. © 1998 Elsevier Science Inc. All rights reserved.

Keywords: Fugacity model; Multiphase environmental model; Unsteady state model; Dynamic control systems; Nonnegative control systems; Fenitrothion

1. Introduction

The thermodynamic concept of fugacity was introduced in 1910 for Lewis [1] in order to explain the behaviour of the real gases with respect to that of ideal gases, in the study of free energy corresponding to an expansion process, isotherm, reversible and infinitesimal.

The fugacity is a thermodynamic magnitude related to the chemical potential and characterized by the leak trend of a substance in a compartment [2,3]. The fugacity express the chemistry activity of a substance and has been applied mainly in thermodynamic problems implicating equilibrium among phases, especially in computations encountered in chemical separation processes such as liquid extraction, distillation and adsorption.

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 advectons (see [4]). '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

* Corresponding author. Tel.: +34 96 387 7660; fax: +34 96 387 7669; e-mail: rbru@mat.upv.es.

linear system of equations when there are reactions, advections, emissions and transfers of the substance among compartments in stationary state [5,6]. 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’, usually is described by a system of differential equations (3) (see [7]).

In this work, we will present a proposal of the multiphase fugacity environmental ‘Level IV’ model for a ecosystem constituted by n compartments where the fugacities change with the time in response to m emissions and they are determined by a continuous time dynamic control system describing the total bulk balance of the substance.

Some non-stationary models for the study of the kinetic of a substance in the environment have been proposed for the analysis of the concentrations changing with the time [8–10]. But, it seems that none of them presents a mathematical formalism through control theory.

The mathematical unsteady state fugacity model of a substance in an ecosystem for continuous time control system permits to analyse the asymptotic stability and the non-negativity of the corresponding discrete system. More precisely, we will see that the fugacity model can be solved as a positive discrete time control system obtained by discretizing the continuous time control system. Further, we will prove that the continuous and the discrete time control systems are both asymptotically stable and that the discrete system is non-negative. The numerical algorithms presented indicate that this control model turns out to be easy to compute. Finally, we illustrate our model by a numerical example studying the insecticide fenitrothion in the fugacity multiphase model constituted by air, water and bottom sediment.

2. Notations and definitions

The distribution of a small quantity of a substance between two compartments denoted by the indices i and j , respectively, under 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 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 $C = Zf$ where C is the concentration in mol m^{-3} , f is the fugacity given in Pascal (Pa) and the constant of proportionality Z is the capacity of fugacity in $\text{mol m}^{-3} \text{ Pa}^{-1}$. 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.

For example, in the atmosphere the fugacity of a substance is equal to the partial pressure, the one that can be expressed in terms of the concentration in the air C_a and by the equation of the ideal gases given by

$$f_a = C_a RT^0, \quad (1)$$

where $R = 8.314 \times \text{Pa m}^3 \text{ mol}^{-1}$ is the gas constant and T^0 is the absolute temperature. By expression (1), the air capacity of fugacity is $Z_a = 1/RT^0$.

The fugacity of a substance dissolved in water is approximated by its partial vapour pressure, the one that is proportional to its concentration in water, that is,

$$f_w = HC_w, \quad (2)$$

where H is the Henry's constant in $\text{Pa m}^3 \text{mol}^{-1}$. Consequently, the capacity of fugacity of water is $Z_w = 1/H$.

For the other compartments, the capacity of fugacity is expressed as the product of the capacity of fugacity in water or in air, by using the density of the compartment and the adsorption coefficient [6,11]. For example, for the bottom sediment the capacity of fugacity is evaluated by expression $Z_s = k_d \rho_s Z_w$, where k_d is the adsorption coefficient and ρ_s in kg m^{-3} is the density of the dry soil, consequently, the fugacity or concentration in this compartment can be calculated by equation

$$C_s = \rho_s k_d Z_w f_s.$$

In an unsteady state, the fugacities are functions of time and they can be determined as a system of ordinary differential equations, describing the total bulk balance during an infinitesimal time interval dt . In this balance, the storage capacity of a substance in a compartment i is given by the product of its volume V_i and by its capacity of fugacity Z_i .

The biological and chemistry reactions are supposed to be a first order process where the rate of reaction is r_i in min^{-1} and the reaction component for each compartment is $r_i V_i Z_i$.

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

The advection 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 $\text{m}^3 \text{min}^{-1}$ entering into compartment i with concentration C_{Bi} and leaving this compartment with concentration C_i .

The emissions in compartment i , as a function of the time in mol 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.

3. Fugacity model of a continuous and discrete time system

Given a compartment i and a compartment j there exist the following excluding possibilities for transferring substance between these two compartments: (a) there is a contact area between compartment i and compartment j , in this case, there is a positive gradient while the equilibrium of the fugacities will not be reached among these two compartments; (b) there is no contact area between compartment i and compartment j , consequently, there is not any possibility of a direct transfer of the substance among these two compartments. These two possibilities are fundamental in the position and in the analysis of the fugacity model for a continuous time control system.

Let $J_i = \{j \in \mathbb{N} : \text{the set of indices } i \neq j \text{ of compartments in which there exists a contact area with compartment } i\}$.

The variation rate of the fugacity in the time, for each one of the compartment, is calculated using the total bulk balance, which is described by the following system of ordinary differential equations:

$$V_i Z_i \frac{df_i}{dt} = E_i + G_i C_{Bi} + \sum_{j \in J_i} d_{ji} f_j - \left(G_i Z_i + r_i V_i Z_i + \sum_{j \in J_i} d_{ij} \right) f_i, \quad (3)$$

where $f_i = f_i(t)$, with $f_i(t) = f_i^0$, for all $i = 1, 2, \dots, n$.

The system expressed by Eq. (3) can be written as the following continuous time control system:

$$\dot{\mathbf{f}} = \mathbf{A}\mathbf{f} + \mathbf{B}\mathbf{u}, \tag{4}$$

where $\dot{\mathbf{f}} = \dot{\mathbf{f}}(t)$ is the fugacity derivative vector of components $[f_i] = df_i/dt$,

$$\mathbf{A} = [a_{ij}] = \begin{cases} a_{ki} = \frac{-(G_i Z_i + r_i V_i Z_i + \sum_{j \in J_i} d_{ij})}{V_i Z_i} & \text{if } k = i, \\ a_{ki} = \frac{d_{ki}}{V_i Z_i} & \text{if } k \in J_i, \\ a_{ki} = 0 & \text{if } k \notin J_i \end{cases}$$

is the $n \times n$ state matrix, $\mathbf{f} = \mathbf{f}(t)$ is the state vector of fugacity of components $[f_i] = f_i(t)$, $\mathbf{B} = \mathbf{I}_n$ is the identity matrix of order n and $\mathbf{u} = \mathbf{u}(t)$ is the control vector of components $[u_i] = (E_i + G_i C_{Bi})/V_i Z_i$.

3.1. Example

For a simple ecosystem constituted by air ($i=1$), water ($i=2$) and bottom sediment ($i=3$), system (3) is determined by the system of ordinary differential equations:

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

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

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

with the initial conditions $f_1(0) = f_1^0$, $f_2(0) = f_2^0$ and $f_3(0) = f_3^0$, or by the continuous time control system (4) where the matrices \mathbf{A} and \mathbf{I}_3 , are respectively,

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

$$\mathbf{I}_3 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

The vectors $\dot{\mathbf{f}} = \dot{\mathbf{f}}(t)$, $\mathbf{f} = \mathbf{f}(t)$, $\mathbf{u} = \mathbf{u}(t)$, $\mathbf{f}_0 = \mathbf{f}(0)$ are, respectively,

$$\dot{\mathbf{f}} = \left[\frac{df_1}{dt} \quad \frac{df_2}{dt} \quad \frac{df_3}{dt} \right]^T, \quad \mathbf{f}(t) = [f_1(t) \quad f_2(t) \quad f_3(t)]^T,$$

$\mathbf{u}(t) = [(E_1 + G_1 C_{B1})/V_1 Z_1 \quad (E_2 + G_2 C_{B2})/V_2 Z_2 \quad (E_3 + G_3 C_{B3})/V_3 Z_3]^T$, and $\mathbf{f}(0) = [f_1^0 \quad f_2^0 \quad f_3^0]^T$. In this example $J_1 = \{2\}$, $J_2 = \{1; 3\}$ and $J_3 = \{2\}$.

Now we return to Eq. (4) which admits the following integral solution in $[0; t]$ (see [12]):

$$\mathbf{f}(t) = e^{At}\mathbf{f}(0) + \int_0^t e^{A(t-\tau)}\mathbf{I}_n\mathbf{u}(\tau) d\tau. \quad (5)$$

Let m be the number of emissions and let T be the time interval between each emission. Discretizing Eq. (5), see [12] for details, for each $t = kT$, where $k = 0, 1, 2, \dots, (m - 1)$ we have

$$\mathbf{f}((k + 1)T) = \mathbf{W}(T)\mathbf{f}(kT) + \mathbf{H}(T)\mathbf{u}(kT), \quad (6)$$

where

$$\mathbf{W}(T) = e^{AT}, \quad \mathbf{H}(T) = \int_0^T e^{A\tau}\mathbf{I}_n d\tau, \quad \tau = T - t.$$

When the time interval T between each emission is fixed, the matrices $\mathbf{W}(T)$ and $\mathbf{H}(T)$ are constants. 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, $\mathbf{u} = \mathbf{u}(kT)$, for $kT \leq t < kT + T$.

Thus, if the emissions $E_i(kT)$ for each compartment i are known, for the corresponding times $k = 0, 1, 2, \dots, (m - 1)$, and consequently the control vectors $\mathbf{u}(kT)$, then, it is possible to compute the fugacities and the respective concentrations in these times for each one of the compartments $i = 1, 2, \dots, n$, using Eq. (6). Note that $\mathbf{u}(t) = 0$, for all $t \geq mT$, and in this case system (4) is determined by

$$\mathbf{f}((k + 1)T) = \mathbf{W}(T)\mathbf{f}(kT) \quad \text{for } k \geq m. \quad (7)$$

We will see below that the discretization (6) has the property of maintaining the stability of Eq. (5).

In the model given by Eq. (4) and the corresponding solution (5), or alternatively the discretized model (6) we suppose that: (i) the volume of each compartment is constant, (ii) the emissions are known for each time kT in the time interval $[0; (m - 1)T]$ and (iii) for the times outside of that interval the emissions are null.

4. Analysis of the model

In this section we deal with some properties of our model. First we study the stability of the continuous time control system described by the matrix equation (4). Later, we will prove that the discrete model (6) is asymptotically stable. In addition, since we are modelling fugacities, it is important to know the non-negativity of the discrete time control system given by matrix equation (6) (i.e. all matrices of (6) has only non-negative entries). In the following theorems we will use the terminology, corresponding to non-negative matrices used by Berman and Plemmons [13].

Theorem 1. *The discrete control system defined by the pair $(\mathbf{W}(T), \mathbf{H}(T))$ is a positive system, that is, the components of the matrices $\mathbf{W}(T)$ and $\mathbf{H}(T)$ are non-negatives.*

Proof. The matrix \mathbf{A} is essentially non-negative since there exists a constant $\delta > 0$ sufficiently large, for example $\delta > \max_{i=1,2,\dots,n} [a_{ii}]$, such that $(\mathbf{A} + \delta\mathbf{I}) > 0$. Then, by Theorem (3.12) of [13], $\mathbf{W}(T) = e^{AT} \geq 0$. By the monotony of the integral we have $\mathbf{H}(T) = \int_0^T e^{A\tau}\mathbf{I}_n d\tau \geq 0$. \square

As a practical consequence of this theorem one can deduce that if we apply non-negative controls and the initial conditions are non-negative then we always obtain non-negative state vectors that in our problem are fugacities. In fact, this is the definition of positive discrete time control systems, and this is equivalent to the matrices $\mathbf{W}(T)$ and $\mathbf{H}(T)$ are non-negatives.

With the following theorem we can assure that system (4) is stable because the matrix \mathbf{A} has eigenvalues with negative real parts (see [14]).

Theorem 2. *Let \mathbf{A} be the matrix of system (4), $-\mathbf{A}$ is positively stable, that is, its eigenvalues have positive real part.*

Proof. First, by the definition of the problem all parameters d_{ij} are positive. Furthermore, it is observed that

$$|a_{ii}| = \left| \frac{G_i Z_i + r_i V_i Z_i + \sum_{j \in J_i} d_{ij}}{V_i Z_i} \right| = \sum_{j \in J_i} \left| \frac{d_{ij}}{V_i Z_i} \right| + \left| \frac{G_i Z_i + r_i V_i Z_i}{V_i Z_i} \right| > \sum_{j \in J_i} \left| \frac{d_{ij}}{V_i Z_i} \right| = \sum_{i \neq j} |a_{ij}|,$$

then $-\mathbf{A}$ is strictly diagonal dominant. Since $-\mathbf{A}$ has positive diagonal elements then the Gerschgorin's disks are in the positive semiplane. From both properties we deduce that the eigenvalues of $-\mathbf{A}$ have positive real part and consequently $-\mathbf{A}$ is positively stable. Then \mathbf{A} has eigenvalues with negative real part. In addition \mathbf{A} is not singular. \square

The discretization (6) maintains the stability of the original continuous time control system, then the point where all fugacities vanish is asymptotically stable for system (6). By completeness, we give the short proof of this result for our particular matrices.

Theorem 3. *The discrete positive control system ($\mathbf{W}(T)$, $\mathbf{H}(T)$) is asymptotically stable, that is, the point where all fugacities are null is an equilibrium stable point.*

Proof. If λ_i are the eigenvalues of \mathbf{A} then, $e^{\lambda_i T}$ are the eigenvalues of $\mathbf{W}(T)$. By Theorem 2 the eigenvalues λ_i have negative real part, then we have $|e^{\lambda_i T}| < 1$ and therefore, $\|\mathbf{W}(T)\|^p \rightarrow 0$, when $p \rightarrow +\infty$. Hence the system ($\mathbf{W}(T)$, $\mathbf{H}(T)$) is asymptotically stable. \square

5. Algorithm to compute the settling time

To determine the needed time to get low concentrations in all compartments, we have to compute the time for which the fugacities vanish, after the emissions finish. This time is called fugacity settling time. The *fugacity settling time* is defined as the time required for the fugacity values stay within a range of the final value. The settling time can be conceived as the time required so that the system arrives and stays within a range of the equilibrium point. It can be computed by the following algorithm whose convergence is guaranteed by Theorem 3.

The computation of the matrices $\mathbf{W}(T)$ and $\mathbf{H}(T)$ when the matrix \mathbf{A} is known can be accomplished by the mathematical scientific package MATLAB [15], which calculates the exponential of a matrix through Padé's approximations with the function `expm` using the command $[\mathbf{W}, \mathbf{H}] = c2d(\mathbf{A}, \mathbf{I}_n, T)$.

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

Begin

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

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

```

 $f((k+1)T) = \mathbf{W}(T)f(kT) + \mathbf{H}(T)\mathbf{u}(kT)$ 
for  $i = 1$  until  $n$  compute
 $C_i(kT) = Z_i f_i(kT)$ 
Let  $\text{tol} > 0$  be a tolerance of the origin.
For  $k > m$  compute
 $f((k+1)T) = \mathbf{W}(T)f(kT) + \mathbf{H}(T)\mathbf{u}(T)$ 
until  $\|f(k+1)T\| \leq \text{tol}$ 
for  $i = 1$  until  $n$  compute
 $C_i((k+1)T) = Z_i f_i((k+1)T)$ 
End;
```

The first value of $k_s = k$, for which the inequality of Algorithm 1 is satisfied, determines the settling time $t_s = k_s T$ for the tolerance tol . The value of tolerance can be established as a function of the limits of chromatography detection of the concentrations of the substance in the compartments.

6. Algorithm to compute the dissipation time

By Eq. (7), for each compartment, it is possible to compute the instant time for which the value of the concentration reduced $p\%$ of the first value of the concentration after the emissions finish. This time is called the *dissipation time* in the compartment i , denoted by t_p^i and calculated by the following procedure:

Algorithm 2 (A pseudo-code algorithm to compute the dissipation time).

```

Begin
Compute matrices  $\mathbf{W}(T)$  and  $\mathbf{H}(T)$  by:  $[\mathbf{W}, \mathbf{H}] = c2d(\mathbf{A}, \mathbf{I}_n, T)$ 
For  $k \geq m$  compute
 $f((k+1)T) = \mathbf{W}(T)f(kT)$ 
 $C_i(kT) = Z_i f_i(kT)$ 
until  $C_i(kT) \leq \{(100 - p)/100 \cdot C_i((m - 1)T)\}$ 
End;
```

The first value of $k_p = k$, for which the inequality is satisfied, determines the dissipation time at level $p\%$, $t_p^i = k_p T$ for the compartment i .

7. Numerical simulation

We have selected the insecticide fenitrothion to verify our model. Fenitrothion is an insecticide frequently used in crops and forest protection. For that, we have considered a hypothetical three compartments environmental system consisting of air, water and bottom sediment with volumes of 1.0×10^6 , 1.0×10^4 and $1.5 \times 10^3 \text{ m}^3$, respectively. The sediment density and content volumetric of carbon are, respectively, $1.5 \times 10^3 \text{ kg m}^{-3}$ and 4.0%. In this system, we apply in the air one mole of the insecticide fenitrothion during 60 min, that is, $E_1(k) = 1/60$ and $E_2(k) = E_3(k) = 0$ for $k = 0, 1, 2, \dots, 59$. According to Zitko and McLeese [16], the constant rate of disappearance in minutes of the fenitrothion in air, water and bottom sediment are respectively 4.76×10^{-4} , 3.80×10^{-4} and 2.85×10^{-5} . Henry's constant for the fenitrothion (see [17]) is $6.65 \times 10^{-2} \text{ Pa m}^3 \text{ mol}^{-1}$. The coefficient of adsorption k_d for this substance in this bottom sediment is $27 \times 10^{-3} \text{ m}^3$

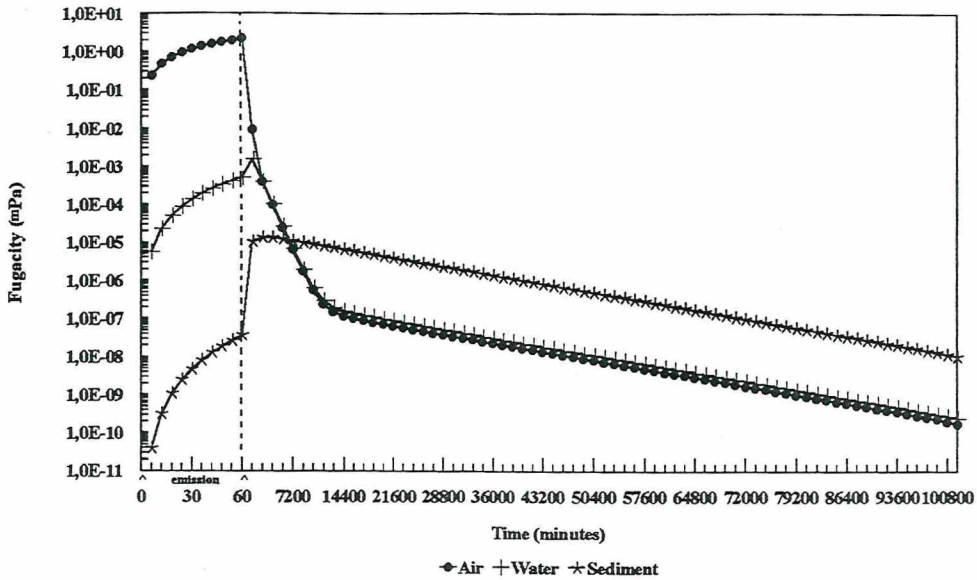


Fig. 1. Fugacities of fenitrothion in air, water and bottom sediment before and after the emissions, obtained by Algorithm 1.

kg⁻¹. The value of T and tol are 1 min and 1.0×10^{-11} Pa, respectively. The exit advection flow in air, water and bottom sediment are, respectively 6.87×10^2 , 5.49 and 6.20×10^{-2} m³ min⁻¹.

With these data we wish to evaluate, during and after the emissions, the values of the concentration and the fugacity of fenitrothion in the air, water and bottom sediment and then to determine the needed time to stabilize the fugacity, that is the fugacity settling time. In this example the air is the only one compartment receiving emissions and we can consider that the advectons are null for all compartments.

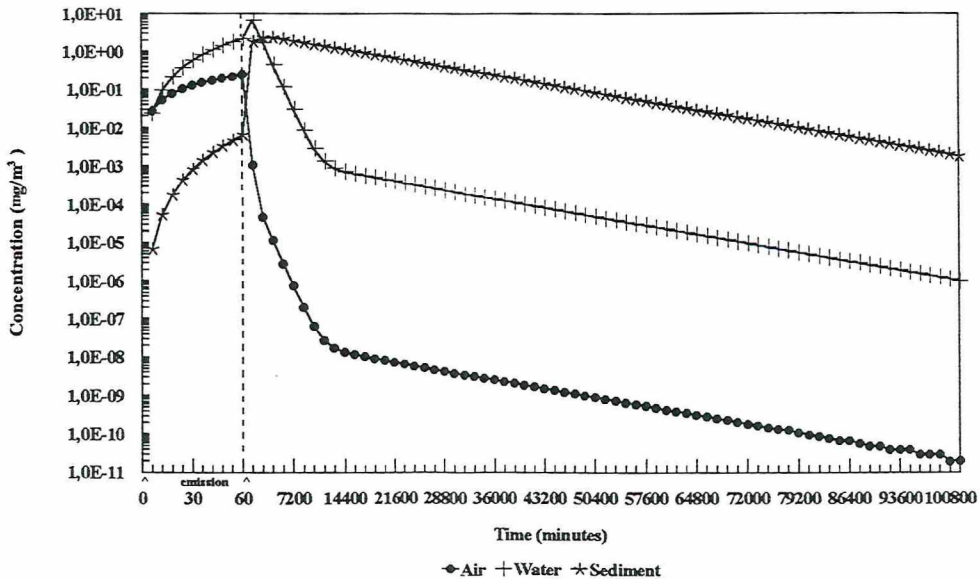


Fig. 2. Concentrations of fenitrothion in air, water and bottom sediment before and after the emissions, obtained by Algorithm 1.

References

- [1] G.N. Lewis, The law of physico-chemical change, *Proc. Am. Acad. Sci.* 34 (1901) 49.
- [2] D. Mackay, S. Paterson, Calculating fugacity, *Environ. Sci. Technol.* 15 (1981) 1006–1014.
- [3] D. Mackay, S. Paterson, Fugacity revisited, *Environ. Sci. Technol.* 16 (1982) 654A–660A.
- [4] J. Koprivnjak, L. Poissant, Evaluation and application of a fugacity model to explain the partitioning of contaminants in the St. Lawrence river valley, *Water, Air and Soil Pollution* 97 (1997) 379–395.
- [5] S. Paterson, D. Mackay, The Fugacity Concept in Environmental Modelling, in: O. Hutzinger (Ed.), *The Handbook of Environmental Chemistry*, vol. 2, Part C, Springer, Berlin, 1985, pp. 121–145.
- [6] J. Campfens, D. Mackay, Fugacity-based model of PCB bioaccumulation in complex aquatic food webs, *Environ. Sci. Technol.* 31 (1997) 577–583.
- [7] D. Mackay, *Multimedia Environmental Models: The Fugacity Approach*, Lewis Publishers, Ann Arbor, MI, 1991, p. 257.
- [8] Y. Cohen, A.P. Ryan, Multimedia modelling of environmental transport: Trichloroethylene test case, *Environ. Sci. Technol.* 19 (1985) 412–417.
- [9] Y. Matoba, J. Ohnishi, M. Matsuo, Indoor simulation of insecticides in broadcast spraying, *Chemosphere* 30 (1995) 345–356.
- [10] W. Stiver, D. Mackay, Linear superposition in modelling contaminant behaviour in aquatic systems, *Water Research* 29 (1995) 329–335.
- [11] E. Bacci, *Ecotoxicology of Organic Contaminants*, Lewis Publishers, Boca Raton, Florida, 1994, p. 165.
- [12] K. Ogata, *Discrete-Time Control Systems*, Prentice-Hall, Englewood Cliffs, NJ, 1995, p. 745.
- [13] A. Berman, R.J. Plemmons, *Nonnegative Matrices in the Mathematical Sciences*, Classics in Applied Mathematics, SIAM, Philadelphia, PA, 1994, p. 340.
- [14] D.G. Luenberger, *Introduction to Dynamic Systems*, Wiley, New York, 1979, p. 446.
- [15] MathWorks Inc., *The Student Edition of MATLAB*, Prentice-Hall, Englewood Cliffs, NJ, 1992, p. 820.
- [16] V. Zitko, D.W. McLeese, Evaluation of hazards of pesticides used in forest spraying to the aquatic environment, *Canadian Technical Report of Fisheries Aquatic Sciences*, Government of Canada, December, 1980. p. 21.
- [17] O. Yenigün, D. Sohtorink, Calculations with the level II fugacity model for selected organophorus insecticides, *Water, Air and Soil Pollution* 84 (1985) 175–185.
- [18] K. Kawata, A. Yasuhara, Determination of fenitrothion and diazinon in air, *Bull. Environ. Contam. Toxicol.* 52 (1994) 419–424.
- [19] National Research Council of Canada, Fenitrothion: The effects of its use on environmental quality and its chemistry, Associate Committee on Scientific Criteria for Environmental Quality, NRCC No. 14104, 1975, p. 162. Ottawa, Canada.