Level IV fugacity model depending on temperature by a periodic control system

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Abstract

A 'Level IV Fugacity Model' depending on temperature, to simulate effects of periodic temperature changes on the dynamic distribution of chemical compounds in environmental systems is presented. This model is a continuous time dynamic and periodic control system of an nonsteady-state 'Level IV Fugacity Model' with capacity of fugacity, substance degradation rate, and substance transfer coefficients depending on temperature. Properties of this model as stability and positivity are studied. In order to evaluate the numerical results a discretization preserving the stability and yielding the positivity of the model is used to simulate and illustrate the dynamic distribution of molinate herbicide in a hypothetical three compartmental environmental system, similar to a paddy field, consisting of air, water and bottom sediment, with four periodic temperature changes. The results show that the discretization preserves the periodicity, stability and the positivity properties. When considering a periodic temperature variation, we observed a significant temperature effect on the capacity of fugacity of compartments of the model. These temperature effect largely affect the dynamic distribution of a chemical compound in environmental systems.
Keywords: fugacity model; dynamic system; nonnegativity; molinate

1 Introduction

We introduce a type of 'Level IV Fugacity Model' to simulate the effects of periodic temperature changes on the dynamic distribution of a chemical compound in an environmental system. In this model the substance partition coefficients, the substance diffusion coefficients, the substance transfer coefficients and the total mass balance equation depend on the temperature changes. The thermodynamic concept of fugacity was introduced by Lewis (1901) in order to explain the behaviour of the real gases with respect to that of ideal gases, in 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 is characterized by the escaping tendency of a chemical substance from a phase or compartment, it is expressed in units of pressure and is linearly proportional to concentration (Mackay and Paterson, 1981; Mackay and Paterson, 1982; Mackay, 1991). The fugacity expresses the chemical 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. Thus, the fugacity is an equilibrium criterion, similar to partial pressure. For a full account of the fugacity approach, see Mackay (1991).

Mathematical models based on the thermodynamic theory of fugacity are outlined frequently by a linear system of equations describing the total mass balance of a chemical substance in an environment constituted by homogeneous compartments, media or phases. 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 degradations and advections (Mackay, 1991; Koprivnjak and Poissast, 1997). 'Level III Fugacity Model' supposes that the fugacities are not
in equilibrium and each fugacity can have different values, which are determined by a linear system of equations when there are degradation, advectons, emissions and transfers of the substance among compartments in stationary state (steady-state) (Paterson and Mackay, 1985; Campfens and Mackay, 1997). In addition, there is another model describing the nonsteady-state behaviour of a substance in the environment, which permits to observe substances whose emission and fugacity vary with time and to determine the time in which the system reaches the steady-state. This last model type, known as 'Level IV Fugacity Model', usually is described by a system of differential equations (Mackay, 1991). Recently, we have described an nonsteady-state fugacity model by a dynamic control system (Bru et al., 1998). Other different fugacity models analysing the concentrations change with time can be found in Cohen and Ryan (1985), Matoba et al. (1995) and Stiver and Mackay (1995). The fugacity approach is appropriate for determining the fate of volatile chemical substances since this approach is based on measurable vapour pressures. The equivalence approach is used for non-volatile chemicals substances such as metals, ions and organo-metallics (Diamond et al. 1992).

The environmental behaviour of persistent organic chemicals, under the effects of temperature changes, was discussed by Mackay and Wania (1995), where the effects of increased condensation from the air to the earth’s surface at low temperature are illustrated by calculations in a 'Level IV Fugacity Model' describing the total mass balance for each of the compartments of a generic environment, resulting in a system of 54 differential equations, solved numerically and yielding estimates of concentrations, masses, transport fluxes, and degradation rates as functions of time. In our previous model (Bru et al. 1998) temperature change and its effects on the chemical parameters were not considered. However, these changes can produce important variations on the model output. According to Mackay and Wania (1995), in the global environment, regions with different ambient temperature are linked by large-scale atmospheric and oceanic movements that might lead to a process of global distillation in which chemicals evaporate from warm regions and condense and accu-
mulate in cold regions. Different chemicals may be subject to this process to various degrees, leading to a distribution of chemicals along with a temperature or latitude gradient.

We will present a proposal from a nonsteady-state fugacity type model of a \( n \) compartmental environmental system, where the fugacities of each compartment are function of the time and varies as a response to \( m \) emissions of the substance and over \( v \) periodic temperature changes. In this model, it is assumed that the temperature affects the capacity of fugacity, substance degradation rate or breakdown process, and substance transfer coefficients among compartments. This overall physical--chemical process will be modeled by a continuous time periodic control system which describes the total mass balance of the substance in an environmental compartmental system, where the state vector variables are the fugacities and the control vector are the emissions. We have selected the pesticide molinate in order to illustrate the use of our model and we have considered a hypothetical three compartment environmental system similar to a paddy field consisting of air, water and bottom sediment.

2 Model development

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. \( K_{ij} \) denotes the partition coefficient controlling the distribution of a substance between these two compartments and is numerically defined as the quotient \( K_{ij} = C_i/C_j \), where \( C_i \) and \( C_j \) are the concentrations of the substance in each one of the compartments. The relationship between the fugacity and concentration is given by \( C_i = Z_i f_i \), where \( C_i \ (mol-m^{-3}) \) is the concentration, \( f_i \) is the fugacity given in Pascal (Pa) and the constant of proportionality \( Z_i \) is the capacity of fugacity \((mol-m^{-3}.Pa^{-1})\). 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. The capacity of fugacity of the compartment expresses the solubility of the compound in the compartment (Mackay and Paterson, 1981; Mackay and Paterson, 1982). 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 the 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 \( f_a = C_aRT \), where \( R = 8.314 \) J \( \cdot \) mol\(^{-1} \cdot K\(^{-1} \) = 8.314 \) Pa \( \cdot \) m\(^3\) \( \cdot \) mol\(^{-1} \cdot K\(^{-1} \) is the universal gas constant and \( T \) (K) is the absolute temperature. Consequently, the capacity of fugacity in the air is temperature dependent and is given by \( Z_a(T) = 1/RT \).

The fugacity of a substance, dissolved in water, is approximated by its partial vapour pressure, which is proportional to its water concentration, that is, \( f_w = K_{aw}C_w \), where \( C_w \) is the concentration in water, and \( K_{aw} = K_{aw}(T) \) (Pa \( \cdot \) m\(^3\) \( \cdot \) mol\(^{-1} \)) is the Henry's constant of the substance or the substance air–water partition coefficient in absolute temperature \( T \). Consequently, the capacity of fugacity of the water is given by \( Z_w(T) = 1/K_{aw}(T) \).

It is generally accepted that both vapour pressure and solubility of pesticides vary inversely in activity as with the temperature changes (Rice et al., 1997). The equation used to correct Henry's constant for the temperature effects is expressed by

\[
K_{aw}(T) = K_{aw}(T_r) \exp \left( \frac{-\Delta H_v}{R} \left( \frac{1}{T} - \frac{1}{T_r} \right) \right)
\]

where \( K_{aw}(T_r) \) is the Henry's constant in an absolute reference temperature \( T_r \) and \( \Delta H_v \) (J \( \cdot \) mol\(^{-1} \cdot K\(^{-1} \)) is the partial molar enthalpy of volatilization of the solution (Weber and DiGiano, 1995).

Not always are \( \Delta H_v \) values known or available in literature or in data bases of organic compounds. Thus, Mackay et al. (1986) applied a factor of 84 (J \( \cdot \) mol\(^{-1} \cdot K\(^{-1} \)) to Trouton's rule (1884) to estimate \( \Delta H_v \) for an organic compound from its normal boiling point (Bacci, 1994). This rule is given by \( \Delta H_v = 84bp \), where \( bp \) is the absolute temperature of the organic
compound at normal boiling point. Goss and Schwarzenbach (1999), from known values of $\Delta H_r$ of almost two hundred organic compounds, suggested the following empiric relation to estimate $\Delta H_r$ values

$$\Delta H_r = -3.82 \ln \left( \frac{P^{293}}{P} \right) + 70.0$$

where $P^{293}$ ($Pa$) is the saturated vapour pressure in the reference temperature ($T_r = 293K$). Knowledge of exact Henry’s constants for a substance under environmentally representative conditions can be very important to understand and predict its fate in aquatic environments. Henry’s constant or the air–water partition coefficient in a reference temperature can be estimated by $K_{aw}(T_r) = P_v^r M_r / S_r$, where $P_v^r$ ($Pa$), $M_r$ ($g\cdot mol^{-1}$) and $S_r$ ($g\cdot m^{-3}$) are the partial vapour pressure, the molar mass of the compound and the substance aqueous solubility in a reference temperature, respectively. Being $K_{aw}$ a partition coefficient, it is expected that this parameter show a significant dependence on the environment temperature. Kavanaugh and Trussel (1980) affirm that the Henry constant increases by 1.6 factor for each $10K$ rise in the average environmental temperature. For a volatile organic substance ($K_{aw}/(RT) \geq 0.04$), when the environment temperature increases $10K$, a triple increase of the Henry constant is produced (LaGrega et al., 1996).

For the capacity of fugacity of the bottom sediment, the substance concentration $C_s$ can be expressed using the substance adsorption coefficient or the substance water–sediment partition coefficient $K_d$ ($m^3\cdot kg^{-1}$), the substance concentration in the water $C_w$ and the density of the bottom sediment $\rho_s$ ($kg\cdot m^{-3}$), such that, $C_s = \rho_s K_d C_w$ (Mackay et al., 1996a; Mackay et al., 1996b). In equilibrium state, the substance fugacity in water $f_w$ is equal to the fugacity of the substance in bottom sediment $f_s$, that is, $f_s = K_{aw}(T) C_w$. Therefore, $f_s$ can be written as $f_s = K_{aw}(T) C_s / (\rho_s K_d)$. Consequently, $Z_s = Z_s(T)$ values for the bottom sediment are given by $Z_s(T) = \rho_s K_d / K_{aw}(T)$. Generally, the water solubility of an organic substance is empirically related to the organic carbon–water partition coefficient $K_{oc}$ ($m^3\cdot kg^{-1}$) by the Kenaga (1980) relationship

$$Log_{10}(K_{oc}) = 3.64 - 0.55Log_{10}(S)$$
where $S$, in this expression, is given in ($kg \cdot m^{-3}$). This relation can be used to determine the value of the $K_d$, by $K_d = \alpha C K_{oc}$, where $\alpha C$ is the volumetric content of organic carbon in the bottom sediment (or soil).

The capacity of fugacity of the other compartments such as soil, fish, plants or aerosols are deduced from the capacity of fugacity of the air or water. For example, the octanol–water partition coefficients $K_{ow}$ can also be used to deduce the capacity of the fugacity of the organic phase (Bacci, 1994). As observed and discussed by Mackay et al. (1996a) and Mackay et al. (1996b), for some types of chemical compounds such as organic pesticides, the capacity of fugacity in a determined temperature, is expressed as function of the capacity of fugacity of the air or water and the substance adsorption coefficient in the compartment. Then, from the above discussion we notice the functional dependency of the capacity of fugacity with the temperature of the air or of the water, and so we will also know the variation of the capacity of fugacity of the other compartments as a function of the temperature. Fugacity capacities vary between compartments of different type, different composition, and different temperature (Wania, 1999).

Furthermore, in the development of a mass balance equation by a fugacity model is fundamental to know the dependence between the substance breakdown process and the temperature, and the transference of the substance among compartments and the temperature. The dependence between the temperature and substance degradation rate on air, water or bottom sediment can be approximated by Arrhenius equation given by (Keen and Spain, 1999)

$$
\mu(T) = \mu(T_r) \exp \left( \frac{-A_e}{R} \left( \frac{1}{T} - \frac{1}{T_r} \right) \right)
$$

where $\mu = \mu(T)$ ($min^{-1}$) is the apparent substance degradation rate at temperature $T$, $\mu(T_r)$ ($min^{-1}$) is the apparent degradation rate in a reference temperature $T_r$, and $A_e$ ($J \cdot mol^{-1} \cdot K^{-1}$) is the Arrhenius activation energy for the degradation process. This energy can be calculated from a plot of $\ln(\mu)$ against $1/T$ (Weber and DiGiano, 1995).

In nonsteady–state fugacity model, the total mass balance can be determined as a system...
of ordinary differential equations where the storage capacity of a substance, in each compartment $i$, is given by $V_iZ_i$, where $V_i$ ($m^3$) is the volume of the compartment $i$. Therefore, in the total mass balance equation, the half-life degradation rate component of the compartment $i$ is given by $\mu_i(T)\dot{V}_iZ_i(T)$ ($mol \cdot min^{-1} \cdot Pa^{-1}$). The flow of the substance between the compartments $i$ and $j$ is the product of the difference $(f_i - f_j)$ by the transfer coefficient $d_{ij}$ ($mol \cdot min^{-1} \cdot Pa^{-1}$). Additionally, we are supposing that the coefficients of transference $d_{ij}$ and $d_{ji}$ are equal. The rate transfer of chemicals $d_{ij}$ between compartments $i$ and $j$ is calculated by

$$d_{ij} = \frac{A_{ij}L_iL_j}{(L_i + L_j)}$$

where $A_{ij}$ is the contact area between the two compartments and the value of $L_i = L_i(T)$ is related to diffusion transport in the boundary layer by Fick's first law and is given by $L_i(T) = D_{c,i}(T)Z_i/\delta$, where the quotient $\delta$ ($m$) is defined as the thickness of the diffusion layer and $D_{c,i} = D_{c,i}(T)$ ($m^2 \cdot min^{-1}$) is the diffusion coefficient of the compound in the $i$th compartment (Zitko and McLeese (1980). Thus, the transfer coefficient $d_{ij}$ can be calculated from diffusion coefficients, fugacity capacities and the thickness of the diffusion layers. Therefore, for all $i$ and $j$, $d_{ij}$ is a function dependence of temperature, that is, $d_{ij} = d_{ij}(T)$. Consequently, it is necessary define expresions to calculate the substance diffusion coefficients to each compartments of the model.

The empirical expresion we have used for estimating the diffusion of the compound in air is given by the empirical formula (Lyman et al., 1995)

$$D_{c,a}(T) = \frac{10^{-3}(T)^{1.75}\sqrt{M_{c,a}}}{p(v_c^{1/3} + v_a^{1/3})^2}$$

(3)

In this equation, $T$ is the absolute temperature, $p$ is the pressure (atm), ($1atm = 9.869 \times 10^{-6} Pa$), $v_c$ is the molar volume of the compound, $v_a$ is the molar volume of the air ($20.1cm^3 \cdot mol^{-1}$) and $M_{c,a}$ is a function of the molar mass of the compound in air given by $M_{c,a} = (m_c + m_a)/(m_cm_a)$ where $m_c$ is the molar mass of the compound and $m_a$ is the molar mass of the air ($28.97g \cdot mol^{-1}$).
The Wilke–Chang expression (Weber and DiGiano, 1995) is frequently used to estimate the diffusion of a compound in water. This empirical formula is given by

$$D_{c,w}(T) = 7.4 \times 10^{-8} \left( \frac{\phi_{sw} m_w}{\mu_w} \right)^{0.3} \frac{T}{v_c^{0.6}}$$  \hspace{1cm} (4)

where $\phi_{sw}$ is a solvent association term (2.6 for water), $m_w$ (g·mol$^{-1}$) is the molar mass of the water, $\mu_w$ is water viscosity (centipoise), $T$ is the absolute temperature and $v_c$ (cm$^3$·mol$^{-1}$) is the molar volume of the compound. The expressions (3) and (4) are in (cm$^2$·s$^{-1}$) therefore, it was multiplied by $6.0 \times 10^{-3}$ to be transformed to (m$^2$·min$^{-1}$), the unity used in this model.

The diffusion of the compound in bottom sediment, $D_{c,s}$ (m$^2$·min$^{-1}$), is defined as (Wu and Gschwend, 1988)

$$D_{c,s} = D_{c,w}(T) \left( \frac{\eta^2}{(1 - \eta) \rho_s K_d + \eta} \right)$$  \hspace{1cm} (5)

where $\eta$ is the sediment intraaggregate porosity or the volumetric fraction of the pore space, and all other terms have already been defined.

We notice the important properties of diffusion by the inspection, for example, of equation (4). Diffusion increases directly with temperature and decreases with the viscosity of the fluid (air or water). These effects are intuitively reasonable. Diffusion should increase with temperature because the kinetic energy of a molecule increases with temperature. Consequently, the total mass balance of substance by the expression of the fugacity is affected by the change of temperature. To understand the quantitative treatment of these phenomena we require a model that is global in scope and takes into account the variability of temperature, where the substance emissions in the $i$th compartment, as a function of the time (min) are denoted by $E_i = E_i(t)$ (mol·min$^{-1}$). In this position we are supposing that there is no effect of dilution, that is, the volume $V_i$ of each one of the compartments remains constant.
2.1 Level IV fugacity model by a periodic control system

In order to construct the total mass balance equation, we recall that for two neighbour compartments $i, j$ there will be a positive gradient of fugacity until the equilibrium of fugacities is reached. Let $J_i = \{ j \in N : j \neq i \}$ of compartments in which there exists a contact area with compartment $i$, where $i, j = 1, 2, \ldots, n$. Additionally, we suppose that in the time interval $I$, in which we wish to simulate the distribution of the chemical compound, the temperature is a periodic function of period $\omega \in I$, that is, $T_{x+i+\omega} = T_x$. Furthermore, we suppose that $T_x$ is known, as a result of given or collected temperature data, for a finite number of integer values and $T_X = \{ T_{x_i} : x_i \in I, T_{x_i+\omega} - T_{x_{i-1}}, l = 1, 2, \ldots, v \}$ the respective set of known temperatures as a result of given on collected temperature data.

Then for each $T \in T_X$ the total mass balance is given by the following system of ordinary differential equations

$$V_i Z_i(T) \frac{df_i}{dt} = E_i(t) + \sum_{j \in J_i} d_{ij}(T)f_j - \left( \mu_i(T) V_i Z_i(T) f_i + \sum_{j \in J_i} d_{ij}(T)f_i \right) \quad (6)$$

where $f_i = f_i(t)$ and $f_i(0) = f_i^0$, for all $i = 1, 2, \ldots, n$. Note that $Z_i$ and $d_{ij}$ are variables depending on the temperature. Thus, the concentrations are calculated by expression $C_i(t) = Z_i(T)f_i(t)$ for all $i = 1, 2, \ldots, n$. The equation (6) gives the explanation of total mass balance components: emissions, intermediate inputs, degradation rate, and outputs. If the temperature is constant, the model described by the differential system equations (6) is reduce the to 'Level IV Fugacity Model'.

The system expressed by equation (6) can be written as the following periodic continuous time control system where the control vector represents the substance emissions and the state variables vectors are the fugacities

$$\dot{f} = A(T)f + Bu$$

$$C - Z(T)f$$

(7)
where $\dot{f} = \dot{f}(t)$ is the fugacity time derivative vector of components $[f_i] = \frac{df_i}{dt}$.

$$A(T) = \begin{cases} 
\alpha_{k,i}(T) = \frac{-\left(\mu_i(T) V_i Z_i(T) + \sum_{j \in J_i} d_{ij}(T)\right)}{V_i Z_i(T)} & \text{if } k = i \\
\alpha_{k,i}(T) = \frac{d_{k,i}(T)}{V_i Z_i(T)} & \text{if } k \in J_i \\
\alpha_{k,i}(T) = 0 & \text{if } k \notin J_i 
\end{cases}$$

$f = f(t)$ is the state fugacity vector of components $[f_i] = f_i(t)$, $B = I_n$ is the identity matrix of order $n$, $u = u(t)$ is the control vector of components $[u_i(t)] = E_i(t)/V_i Z_i(T)$, $C$ is the temporal measurement of concentration vector of components $[C_i] = Z_i(T) f_i(t)$ and $Z$ is a diagonal matrix of order $n$ whose diagonal entries $[Z_i] = Z_i(T)$ that represents the capacity of fugacity of the $i$th compartment.

### 2.2 Discretization of the periodic control system

For each temperature $T \in T_\Lambda$, the equation (7) admits the following integral solution in $[0 \ t]$.

$$f(t) = e^{A(T)t} f(0) + \int_0^t e^{A(T)(t-\tau)} I_n u(\tau) d\tau \quad (8)$$

Discretizing the equation (8) for each $t$, by the method presented in Ogata (1995), and considering that the value of time increment between two emissions is the time unity, we have

$$f(T,(k+1)) = W(T)f(T,k) + G(T)u(k)$$

$$C(T,(k+1)) = Z(T)f(T,(k+1))$$

where $W(T) = e^{A(T)t}$, $G(T) = \int_0^1 e^{A(T)\tau} I_n d\tau$ and $\tau = 1 - t$.  

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Therefore, we have $v$ systems of equations of the type (9), one for each temperature $T_{x_l} \in T_N$, that is, the discrete-time periodic control system is given by

\begin{align}
    f(T_{x_l}, (k + 1)) &= W(T_{x_l})f(T_k) + G(T_{x_l})u(k) \\
    C(T_{x_l}, (k + 1)) &= f(T_{x_l}, (k + 1))Z(T_{x_l})
\end{align}

(10)

For each temperature $T_{x_l}$, $l = 1, 2, \ldots, v$, we rewrite the control system equation (10) like a discrete-time periodic control system

\begin{align}
    f(k + 1) &= W_l f(k) + G_l u(k) \\
    C(k + 1) &= Z_l f(k + 1)
\end{align}

(11)

where $k \in \mathbb{Z}_+$, $f, C$ and $u \in \mathbb{R}_+^n$. $W_l = W(T_{x_l})$, $G_l = G(T_{x_l})$ and $Z_l = Z(T_{x_l})$ are $n \times n$ periodic matrices with period $\omega$. The computation of the matrices $W(T_l)$ and $G(T_l)$ when the matrices $A(T_l)$ are known can be accomplished by the mathematical package MATLAB (1992), which calculates the exponential of a matrix through Padé’s approximations with the function $\text{expm}$ using the command $[W_l, G_l] = \text{expm}(A(T_l), I_n, 1)$.

## 3 Simulations and results

medskip Molinate (S-ethyl hexahydro-1-H-azepine-1-carbothioate) is an herbicide commonly used in rice culture (Deudel et al., 1978; Imai and Kuwatsuka, 1986; Tjeerdema and Crosby, 1988a, Tjeerdema and Crosby, 1988b). It is usually applied to control graminaceous weeds, particularly barnyardgrass (Echinochloa spp.) (Weed, 1983; Worthing, 1991). About 1 million pounds of molinate are used annually in California (Soderquist et al., 1977; Cornacchia et al., 1984). Rice culture implies a flow between the fields and surrounding natural waters and after treatment of rice fields the presence of molinate has been reported in agricultural drains, rivers, deltas and lakes (Cornacchia et al. 1984; Carrasco et al., 1987).

At short exposure times, molinate has a low toxicity to common carp (Cyprinus carpio; $48h \text{LC}_{50} = 34mg \cdot l^{-1}$) (Nishiuchi and Yoshida, 1972) and striped bass (Morone saxatilis;
96h LC_{50} = 12.1 \text{ mg} \cdot \text{ l}^{-1} \) (Finlayson and Faggella, 1986). With longer exposure, it is highly toxic to Japanese carp (C. carpio, var. Yamamoto Koi; 20 days LC_{50} = 0.18 \text{ mg} \cdot \text{ l}^{-1} \) (Kawatsu, 1977) and to common carp (28 days LC_{50} = 0.21 \text{ mg} \cdot \text{ l}^{-1} \) (Finlayson and Faggella, 1986). The greater toxicity of molinate to common carp, compared with other species, after prolonged exposure, may be due to greater bioconcentration, slower depuration and less efficient metabolic deactivation (Tjeerdema and Crosby, 1988).

In California, molinate discharge into agricultural drains flowing into the River Sacramento has regularly been followed by high fish losses, mainly of common carp (Tjeerdema and Crosby, 1988a; 1988b). Molinate concentration in Lake Albufera (Valencia, Spain), after herbicide treatment of rice fields, is in the range 1 to 20 ppt (Carrasco et al., 1987), below fish toxicity levels. However, in some channels outfall into the lake, concentrations as high as 80 ppt have been measured (Carrasco et al., 1987) and the death of several thousands of fish reported.

Figure 1: Graphical representation of a hypothetical three compartment environmental system consisting of air, water and bottom sediment.

Thus, we have selected the pesticide molinate in order to illustrate the use of our model. For that, we have considered a hypothetical three compartment environmental system to a similar a paddy field consisting of air, water and bottom sediment (Fig. 1.) with volumes of $1.0 \times 10^3 m^3$, $1.5 \times 10^3 m^3$ and $3.0 \times 10^2 m^3$, respectively. The contact area between compartments is $1.0 \times 10^4 m^2$ (one hectare). The thickness of the diffusion layer was estimated
as $1.0 \times 10^{-3}$, $1.0 \times 10^{-4}$ and $1.0 \times 10^{-5}m$ in air, water and bottom sediment, respectively. The sediment density, porosity and volumetric content of carbon are $1.5 \times 10^3 kg \cdot m^{-3}$, 0.31 and 0.04, respectively.

In this illustration, the period is 1440 minutes (one day) and we take into account that the temperature changes every 360 minutes (six hours). The temperatures were 278, 273, 208 and 288K at 0, 6, 12 and 18 hours, respectively. The reference temperature in equation (1) was 293K and the Henry's constant for this temperature is $9.7 \times 10^{-2} Pa \cdot m^3 \cdot mol^{-1}$. According to Staudinger and Roberts (1996) the partial molar enthalpy of volatilization of molinate is $30240 J \cdot mol^{-1}$.

The air, water and sediment activation energy, estimated from data of Johnson et al. (1994), are 65750, 39610 and 29960 J \cdot mol^{-1}, respectively. The molinate degradation rate in reference temperature is $1.92 \times 10^{-9} \text{min}^{-1}$. The water solubility of molinate in a reference temperature is $800 g \cdot m^{-3}$. The sediment adsorption coefficient, molar mass, and molar volume of molinate are $35.2 \times 10^{-3} m^3 \cdot kg^{-1}$, $187.3 g \cdot mol^{-1}$ and $224.5 cm^3 \cdot mol^{-1}$, respectively.

In this hypothetical environmental system, on the first day of simulation at 12 : 00h, we apply in the air $18 \text{mol}$ (agronomic recommendation by hectare) of the herbicide molinate during 120 minutes, that is, $E_1(k) = 0.15 \text{mol} \cdot \text{min}^{-1}$ and $E_2(k) = E_3(k) = 0$ for $k = 0, 1, 2, \ldots, 119 \text{min}$. After the finished emission ($k \geq 120 \text{min}$) $E_1(k) = E_2(k) = E_3(k) = 0$.

The temperature dependent 'Level IV Fugacity Model' by a periodic control system was written in MATLAB code. The next step in this simulation is the generation of the matrices $W(T_x)$ for $l = 1, 2, \ldots, v$. With these data, it is only necessary to specify the matrices $A(T_x)$ to calculate the matrices $W(T_x)$ of (11). In consequence the matrices $W(T_x)$, for each temperature and each hour are, respectively,

\[
W(278_{00:00h}) = \begin{bmatrix}
6.6088 \times 10^{-1} & 3.3888 \times 10^{-1} & 3.3618 \times 10^{-5} \\
5.4156 \times 10^{-4} & 9.9920 \times 10^{-1} & 1.8552 \times 10^{-4} \\
5.0913 \times 10^{-9} & 1.7581 \times 10^{-5} & 9.9998 \times 10^{-1}
\end{bmatrix}
\]
\[
W(273_{06:00h}) = \\
\begin{bmatrix}
6.5617 \times 10^{-1} & 3.4359 \times 10^{-1} & 3.4075 \times 10^{-5} \\
4.5814 \times 10^{-4} & 9.9929 \times 10^{-1} & 1.8527 \times 10^{-4} \\
4.3058 \times 10^{-9} & 1.7557 \times 10^{-5} & 9.9998 \times 10^{-1}
\end{bmatrix}
\]

\[
W(298_{12:00h}) = \\
\begin{bmatrix}
6.9396 \times 10^{-1} & 3.0580 \times 10^{-1} & 3.0263 \times 10^{-5} \\
9.4608 \times 10^{-4} & 9.9880 \times 10^{-1} & 1.8642 \times 10^{-4} \\
8.8727 \times 10^{-9} & 1.7667 \times 10^{-5} & 9.9998 \times 10^{-1}
\end{bmatrix}
\]

\[
W(288_{00:00h}) = \\
\begin{bmatrix}
6.482 \times 10^{-1} & 3.2494 \times 10^{-1} & 3.2216 \times 10^{-5} \\
7.3128 \times 10^{-4} & 9.9901 \times 10^{-1} & 1.8599 \times 10^{-4} \\
6.8710 \times 10^{-9} & 1.7625 \times 10^{-5} & 9.9998 \times 10^{-1}
\end{bmatrix}
\]

In this example the entry values of the matrices \(W(T_{x_t})\) change very little as a consequence of the change of temperature; however, the respective entries \(Z(T_{x_t})\) change significantly. The results of these two effects are observed computing the concentrations. For each temperature and hour, the respective diagonal entries of the matrices \(Z(I_{x_t})\) of (11) are

\[
Z(278_{06:00h}) = \text{diag } [4.3266 \times 10^{-4} \ 1.8048 \times 10 \ 9.5228 \times 10^2]
\]

\[
Z(273_{06:00h}) = \text{diag } [4.0458 \times 10^{-4} \ 2.2028 \times 10 \ 1.1622 \times 10^3]
\]

\[
Z(278_{12:00h}) = \text{diag } [4.1764 \times 10^{-4} \ 0.8697 \times 10 \ 4.5889 \times 10^2]
\]

\[
Z(278_{24:00h}) = \text{diag } [4.1764 \times 10^{-4} \ 1.2371 \times 10 \ 6.5273 \times 10^3]
\]

By the stability test, we can observe that the value of the left hand side equation (12) is 0.9999557 and the right hand side is 1.0001935. Consequently, we see that the simulation is asymptotically stable. This stability assures that after a long time the fugacities tend to an equilibrium point.

Figs. 2 and 3 show the evolution of the fugacity and concentration of molinate, respectively. In this simulation, the fugacity settling time (see Bru et al., 1998), or the time required for the fugacity values to stay within a range of the equilibrium final value, is over 10 days. After this
time we are able to begin with the distribution analysis of the molinate, in the air, water and bottom sediment compartments using a steady state fugacity model. The emissions having finished after 120 initial minutes, we observe from Fig. 2. that the fugacities decrease in an uniform way in all compartments until reaching levels of equilibrium with fugacity values around $10^{-4}\mu Pa$.

![Diagram of molinate fugacities](image)

Figure 2: Fugacities of herbicide molinate obtained by a periodic model, before and after the emissions in an hypothetical three compartmental environmental system.

From Fig. 3, we can observe that the concentration of molinate in air decreases abruptly while it increases in water and bottom sediment. We observe the periodicity of the results in the water and sediment compartments. This is the effect of the periodic change of the temperature yielding quite different matrices $Z(T_t)$. The simulation conditions and the properties of molinate can explain the slope of the curves and we can observe that the concentration of this compound presents maximum values in bottom sediment.

Furthermore, the accumulation of molinate in bottom sediment is related to the adsorption
Figure 3: Concentrations of herbicide molinate obtained by a periodic model, before and after the emissions in an hypothetical three compartmental environmental system.

properties of this herbicide. The compound is applied only in the air and then slowly is transfered from the air to the water and finally to the bottom sediment.

4 Conclusions

This model does not require a powerful computer to achieve short computing times and accurate numerical value; these are the advantages presented by a periodic dynamic system of control. With a MATLAB code, it is not necessary to programme the model using a numerical method by a system of differential equation. The main numerical calculations for a periodic control system given by system equations (9) are the determinations of exponential matrices $W_I$ and integral matrices $G_I$, but these calculations are accounted for by an efficient numerical MATLAB command.
In our numerical simulations of molinate, the numerical value of the matrices $W_i$ changes relatively little as consequence of the changes of absolute temperature. But the effect of the periodic changes of temperature upon the concentration of molinate in air, water and sediment can be better observed in Fig. 3. These results are the consequence of the numerical values of concentrations in the different compartments as an effect of the temperature on the component values of matrices $Z_i$.

The spatial variability in compartmental fate modelling has been explained by Wania (1996), linking fugacity models and geographical information systems (GIS). The model presented in this work may also be effective in situations where there are geographical temperature differences suggesting the link among fugacity model and GIS. In these situations the partition coefficients and the consequent component of the matrices $Z_i$ constituted by $Z_i(T)$ values for air, water and bottom sediment and most other compartments variate considerably with the temperature changes (Mackay and Wania, 1995).

Some chemical compounds have approximately zero solubility in water and others are not volatile; in both these cases, an equilibrium criterion analogous to fugacity is preferred and the calculations follow the same approach as for chemicals having a distribution into all environmental media (Mackay et al., 1996a; Mackay et al., 1996b; Diamond et al., 1990; Diamond et al., 1992). Equivalence $Q \, (mol \cdot m^{-3})$, is substituted for fugacity ($Pa$) and is directly related to concentration $C \, (mol \cdot m^3)$ through a dimensionless proportionality constant, or $Z$ value, i.e. $C_i = Q_i Z_i$. If the solubility of a substance in water is zero, we first define $Z_a(T) = 1/RT$ in air and the other $Z_i$ values are deduced using, conveniently, partition coefficients with respect to air, that is, $K_{ia}$; thus $Z_i = K_{ia} Z_a(T)$. Consequently, the formalisms developed in this work for temperature dependent 'Level IV Fugacity Model' by a periodic control system, can be applied in a suitable equilibrium criterion model.

We have modelled the temperature dependent 'Level IV Fugacity Model' by a periodic control system, where the state vectors are the fugacities, the control vectors are the emissions and the periodicity is a consequence of the temperature changes. The corresponding
discrete time model, described by equation (10), permits the outline of a very simple numerical solution without losing the coherence with the real physical problem. These results suggest how this model can be used in the determination of the more vulnerable environmental compartment to a chemical compound over the effect of temperature changes. The thermodynamic parameters of the model with the enthalpy of volatilization, and activation energy, are not frequently encountered in literature or in databases on chemical organic compound and this difficulty could harden the use of the model presented in this work. However, when these values are experimentally known or determined we can make valuable estimations on the behavior and fate of chemical organic compounds.

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Appendix

In this section we deal with some properties of our model. First we study the positivity of the discrete time periodic control system described by the matrix equation (11). Later, we will present a test of the stability by this model, that is, we will prove that the discrete periodic system (11) is asymptotically stable. Since we are modeling fugacities, it is important to know the nonnegativity of the discrete time periodic control system given by matrix equation (11) (i.e. that all matrices of (11) have only nonnegative entries). It is well-known that the properties of periodic systems are studied by the monodromy matrices $\prod_{t=1}^{v} W_t$ and $\prod_{t=1}^{v} G_t$, see Bru and Hernández (1989) for details.

**Theorem 1** The discrete-time periodic control system (11) defined by the pair

$$\left( \prod_{t=1}^{v} W_t, \prod_{t=1}^{v} G_t \right)$$
is a positive system, that is, the components of those matrices are nonnegative. Consequently, the fugacity and concentrations are nonnegatives.

Proof.: This is a consequence of that each matrix in both products are nonnegative, see Theorem 1 of Bru et al. (1998).

Thus, the solutions of these periodic systems are nonnegative provided that the inputs and the initial conditions are nonnegative as well.

The study of stability of the discrete–time periodic system (11) reduces to assure that the spectral radius of the monodromy matrix \( \prod_{i=1}^{n} W_i \) is less than one. Since this matrix is the product of matrices it is not easy to prove. However, we know that, by Bru et al. (1998), each matrix \( W_i \) has spectral radius less than one. With this knowledge we recall a result of Johnson and Bru (1990), which permits to check whether or not the discrete periodic system is stable, that is, verifying if the spectral radius of \( \prod_{i=1}^{n} W_i \) is less than one. We denote by \( \rho(\cdot) \) the spectral radius of a \( n \times n \) matrix and

\[
\left( \frac{y_p}{y_q} \right)_{\text{max}} = \max \left\{ \left( \frac{y_{p,i}}{y_{q,i}} \right), i = 1, 2, \ldots, n \right\}
\]

where \( p \neq q = 1, 2, \ldots, n \) and \( y_p \) is the eigenvector of the matrix \( W_i \) of components \( y_{p,i} \) associated with the eigenvalue \( \rho(W_i) \), that is, \( W_i y_p = \rho(W_i) y_p \). The following result given in Theorem 1 of Johnson and Bru (1990)

\[
\rho \left( \prod_{i=1}^{n} W_i \right) \leq \left( \frac{y_1}{y_2} \right)_{\text{max}} \left( \frac{y_2}{y_3} \right)_{\text{max}} \cdots \left( \frac{y_{n-1}}{y_n} \right)_{\text{max}} \left( \frac{y_n}{y_1} \right)_{\text{max}} \prod_{i=1}^{n} \rho(W_i) \tag{12}
\]

can be used as a test of the stability of positive periodic discrete–time systems.

References


