Development of a numerical model to predict pesticide volatilisation from agricultural soil

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Abstract

A numerical model is described to predict the subsurface transport and volatilisation of pesticides incorporated in a soil. For this work, an analytical model, «the behaviour assessment model (BAM)» developed by Jury [1] was used as the starting point. Calculated volatilisation fluxes are compared with experimental data obtained with \(^{14}\)C-ring-labeled trifluralin from a volatilisation chamber. When the soil moisture is kept constant and when no water evaporation occurs, instantaneous equilibrium and simple linear adsorption isotherms between concentrations in the solution and adsorbed phases are assumed, but when water evaporation occurs it is necessary to include in the model kinetic rate equations to describe the adsorption-desorption process. After these modifications, the equations become too complex and no analytical solution can be found. Thus, the use of a numerical technique is required to solve the equations.

1 Introduction

Volatilisation is one of the major pathways for pesticide losses into the atmosphere. To predict the importance of this phenomenon, it is necessary to
to understand the mechanisms involved in the transport of pesticides through the soil and their transfer into the atmosphere. Various examples of mathematical models exist in the literature. They are based on equations describing the rate of movement of the pesticides towards the soil surface and through the air boundary layer. These movements occur by diffusion and/or by convection. Generally, they assume instantaneous adsorption equilibrium and a linear relationship between the concentrations in both the solution and the adsorbed phases (Kay and Elrick,[2]; Lindstrom et al.[3]; Spencer et al.,[4]; Mayer et al.,[5]; Jury et al.,[6]). However, in some situations, particularly those involving dispersive-convective-adsorptive flow process, it is necessary to add to the model equations representative of the adsorption dynamics. Under such circumstances, the resulting differential equation describing pesticide transport becomes more complex and no analytical solution can be found. A method of approximation must be used and numerical techniques provide the only useful alternative in modelling the transport and the volatilisation of the pesticides incorporated in a soil.

The purpose of this paper is to describe the transport and the volatilisation of pesticides incorporated in a soil using a model including adsorption/desorption kinetic terms and to check the efficiency of the model with experimental data obtained from a volatilisation chamber with trifluralin (alpha,alpha,alpha-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine).

2 Methods

2.1 Apparatus and materials

Experimental data were obtained from a volatilisation chamber described by Cherif [7] using \textsuperscript{14}C-ring- labelled trifluralin (Amersham). The pesticide was adsorbed on an Alsatian soil (the loess-France) which was air-dried, passed through a 50 \( \mu \text{m} \) sieve and sterilised prior to use. The soil parameters are described in details in Table 1. The volatilisation chamber allows simulation of field conditions and controls all the parameters which influence the volatilisation process. These parameters consist of micro-climatic factors such as temperature, soil and air humidity (which controls the water flux), as well as wind speed.

During the experiments, the soil moisture is measured by a daily weighing of the entire system (soil/pesticides and volatilisation chamber). To keep constant the soil moisture level, the missing water is added by means of the water feeding tube. The flux of water evaporation is controlled by the humidity of the air stream sweeping the surface of the soil. To avoid external pesticide contamination and the dispersal of soil particles, a pure and laminar air flow sweeps over the surface of the soil throughout the experiments and carries the volatilised pesticides towards an XAD-2 resin trap. The air above the soil surface is kept at a relative humidity (RH) of either 100\% or 0\% and the air flow velocity is fixed at about 0,7 \( \text{L.min}^{-1} \). The experiment was carried out at 30°C (\( \pm 1^\circ\text{C} \)) using the soil described in Table 1. The constants of adsorption and the kinetic rate coefficients of
trifluralin adsorbed on the Alsatian soil are determined experimentally using the batch technique [8].

Table 1. Properties of the Alsatian soil (loess) used in the experimental studies.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Organic Carbon</th>
<th>pH (water)</th>
<th>Bulk density</th>
<th>Clay &lt;2 μm</th>
<th>Silt 2-50 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alsatian loess (50 μm)</td>
<td>0.17 %</td>
<td>8.42</td>
<td>1.27 g.cm⁻³</td>
<td>16 %</td>
<td>64 %</td>
</tr>
</tbody>
</table>

3. Theory

The model used to characterise the subsurface transport and the loss of the pesticides by volatilisation into the atmosphere is based on various simplifying assumptions. Because those assumptions are described in detail by Jury [1], only a brief description and necessary extensions of the model will be described here. The unsteady-state, one-dimensional convective-dispersive mass transport equation which describes the concentration distribution of a chemical undergoing adsorption in an unsaturated or saturated soil is expressed as follow (using continuity relationships of mass over space and time):

\[
\frac{\partial C_T}{\partial t} = -\frac{\partial J_T}{\partial x}
\]  

where \( C_T \) (μg.cm⁻³), is the total pesticide concentration in all phases (liquid, gas, adsorbed); \( J_T \) (μg.30 cm².day⁻¹) is the total pesticide flux through the 30 cm² of the surface of the soil in the volatilisation chamber; \( t \) (day) is the time and \( x \) (cm) is the height of the soil \([x=0 \text{ at the base of the volatilisation chamber}].

The total concentration of the pesticide, \( C_T \), is the sum of contributions of each phase and can be expressed as:

\[
C_T = \rho C_s + \theta C_w + a C_a
\]

where \( C_s \) is the adsorbed concentration (μg.cm⁻³); \( C_w \) is the liquid concentration (μg.cm⁻³); \( C_a \) is the gas concentration (μg.cm⁻³); \( \rho \) is the volumetric solid content (cm³.cm⁻³); \( \theta \) is the volumetric water content (cm³.cm⁻³) and \( a \) is the volumetric gas content (cm³.cm⁻³).

The total solute flux, \( J_T \) (μg.30 cm².day⁻¹), can be written as follows:
The first term of the equation represents gaseous diffusion, the second term liquid diffusion and the last term describes the convection of the solute induced by the mass flow of the soil solution, where \( F_w \) (cm.day\(^{-1}\)) represents the water flux; \( D_{als} \) and \( D_{wls} \) (cm\(^2\).day\(^{-1}\)) are respectively the soil-gas diffusion coefficient and the soil-water diffusion coefficient. They are calculated from Millington-Quirk’s equation [9].

The liquid-gas partition is described by Henry’s law:

\[
C_a = K_H \cdot C_w
\]  

where \( K_H \) is the constant of Henry’s law (dimensionless).

Equations (3) and (4) give a rewrite of the differential equation as follows:

\[
\frac{\rho \partial C_w}{\theta \partial t} + \frac{\partial C_w}{\partial t} + \frac{a K_H \partial C_w}{\theta \partial t} = \frac{D_{als} K_H \partial^2 C_w}{\theta \partial x^2} + \frac{D_{wls} \partial^2 C_w}{\theta \partial x^2} - \frac{F_w \partial C_w}{\theta \partial x}
\]

\[
\left(1 + \frac{a K_H}{\theta}\right) \frac{\partial C_w}{\partial t} = \frac{\partial^2 C_w}{\partial x^2} \left[\frac{D_{als} K_H + D_{wls}}{\theta}\right] - \frac{\partial C_w}{\partial x} \left[\frac{F_w}{\theta}\right] - \frac{\partial C_a}{\partial t} \left[\frac{\rho}{\theta + a K_H}\right]
\]

where: \( D_E \) is the effective diffusion coefficient:

\[
D_E = \left[\frac{D_{als} K_H + D_{wls}}{\theta + a K_H}\right]
\]

and \( V_E \) is the effective solute convection velocity:

\[
V_E = \left[\frac{F_w}{\theta + a K_H}\right]
\]

### 3.1 Boundary Conditions

#### 3.1.1 Initial conditions

At the soil surface (\( x=L \)) we can assume that the pesticides volatilise through a stagnant air boundary layer of thickness \( d \), that at \( t=0 \) the pesticides are uniformly incorporated in the soil and that the gas concentration in the boundary layer is zero.

\[
C_f(x,0) = C_0 \quad \text{if} \ 0<x<L \quad \quad \quad \quad \quad \quad \quad C_f(x,0) = 0 \quad \text{if} \ x=L
\]

where \( C_0 \) (µg.cm\(^{-3}\)) is the uniform initial concentration; and \( L \) the height of the soil.

#### 3.1.2 Upper boundary condition
According to Hartley and Graham-Bryce [10], in laminar conditions, the transport of pesticides across the air layer above the soil surface is controlled by the diffusion phenomenon and can be defined in terms of an effective thickness \( d \) which gives the following expression:

\[
J_x(0,t) = h_\delta C_u(0,t)
\]  

where \( h_\delta = D_{air}/d \) and is the transport coefficient across the diffusion boundary layer above the surface of the soil. The upper surface of the diffusion boundary layer is located where the horizontal air flux velocity is equal to the velocity of the pesticide’s diffusion. This reasoning, combined with Einstein-Smoluchowski’s equation [11], gives the following calculations:

1. The square of the distance \((x^2)\) travelled by a diffusing molecule at time \( t \) is given by:

\[
x^2 = 2D_{air}t
\]  

2. The molecule’s velocity can be deduced from the above relation:

\[
v_p = (2D_{air}/t)^{1/2}
\]

3. Based on the assumption that the horizontal air flux velocity is equal to the velocity of the pesticide’s diffusion on the upper surface of the diffusion boundary layer \((v_p = V)\), the thickness \( d \) can be expressed, according to equation (8), as follows:

\[
d = 2D_{air}/V \quad \text{and} \quad h_\delta = D_{air}/d = V/2
\]

### 3.1.3 Lower boundary condition

\[C_T(\infty, t) = 0\]

### 3.2 Adsorption equations

The manner in which the adsorption equations are included in the differential equation (5), depends mainly on the nature of the experimental information available on the pesticides. A general relationship, established by Lapidus and Amundson [12] describes the adsorption-desorption phenomenon as follows:

\[
\frac{\partial C_s}{\partial t} = f(C_u, C_s)
\]

#### 3.2.1 Equilibrium conditions

The adsorption model, is derived from the Freundlich equation, generally used to describe the relationship at equilibrium between the amount in solution \( (C_u) \) and the amount adsorbed \( (C_s) \). The Freundlich equation is as follows:
$C_s = K_p C_w^n$  \hfill (11)

Where: $K_p$ (cm$^3$.g$^{-1}$) is the adsorbed-liquid partitioning coefficient. This equation was used by Jury [1] assuming that $n=1$ and thus the pesticides are subject to a linear equilibrium adsorption

### 3.2.2 Kinetic conditions

In non-equilibrium conditions, equation (10) can be expressed as follows:

$$\frac{\partial C_s}{\partial t} = k^d D^d \left[ \frac{k_a \theta}{k_d \rho} C_w^n - C_s \right]$$  \hfill (12)

Equation (12) is a first-order kinetic rate equation, where: $k_a$ and $k_d$ (day$^{-1}$) are respectively the adsorption and desorption rate constants; and $n$ is the Freundlich exponent. $K$, the linear adsorption isotherm can be expressed as follows (assuming the isotherm linearity with $n=1$):

$$K = \frac{k_{ads} \theta}{k_{det} \rho} = K_p \frac{\theta}{\rho}$$  \hfill (13)

### 4 Solution procedure

The differential equation is converted into a finite difference equation, where the physico-chemical processes are carried out over small intervals of time and space. The discretisation of space and time is selected in such manner that the solution is approached with a reasonable degree of accuracy. This procedure was used by Van Genuchten and Wierenga [13] in order to describe the movement of pesticides through porous media using various models of kinetic adsorption.

#### 4.1 Conversion into finite difference equations

Equation (5) is solved by dividing the total depth of the soil ($L$) into $N$ compartments of size $\Delta x$ cm. Indices with $i$ are used to indicate sequences in quantities for these compartments. Time is divided into intervals of $\Delta t$ days. Much attention is given to set out numerical solutions involving the calculation of concentrations in the soil at time $t + \Delta t$ by using the distribution of these concentrations at time $t$. Changes in the amount of pesticide per compartment, resulting from diffusion, mass flow transport and adsorption, are calculated by the fluxes over a short intervals of time $\Delta t$.

Differential equation (5) is converted into the corresponding finite difference form by using the rectangular integration method. It represents the flux of pesticides between the depth $i$ and $i+1$ during the time period $\Delta t$ and is written as follow:
\[
C_{i}^{t+\Delta t} \cdot S \cdot \theta \cdot \Delta x - C_{i}^{t} \cdot S \cdot \theta \cdot \Delta x = \left[ \frac{C_{i}^{t+\Delta t} + C_{i-1}^{t+\Delta t}}{2} \right] V_{E} \cdot S \cdot \theta \cdot \Delta t - \left[ \frac{C_{i+1}^{t+\Delta t} + C_{i}^{t+\Delta t}}{2} \right] V_{E} \cdot S \cdot \theta \cdot \Delta t
\]
\[
+ \left[ \frac{C_{i-1}^{t+\Delta t} - C_{i}^{t+\Delta t}}{\Delta x} \right] D_{E} \cdot S \cdot \theta \cdot \Delta t - \left[ \frac{C_{i}^{t+\Delta t} - C_{i+1}^{t+\Delta t}}{\Delta x} \right] D_{E} \cdot S \cdot \theta \cdot \Delta t
\]
\[
- \left[ C_{s,i}^{t+\Delta t} \cdot S \cdot \Delta x - C_{s,i}^{t} \cdot S \cdot \Delta x \right] \theta \left[ \frac{\rho}{\theta + a K_{H}} \right] \tag{14}
\]

where: \( C_{i} \) is the concentration of the pesticides in each layer at time \( t \); and \( S \) is the cross-sectional area of the volatilisation chamber. In this case, the stabilisation condition is: \( \frac{V_{E} \cdot \Delta x}{D_{E}} \leq 2 \)

5 Results and discussion

Figure 1 shows the measured volatilisation fluxes obtained from the volatilisation chamber with \(^{14}\)C-ring-labeled technical trifluralin. The volatilisation fluxes are represented for different experimental conditions. During the first twenty days of the volatilisation experiment the soil moisture is kept constant at a relative humidity (RH) of 10.3% and the air above the soil surface is maintained at a relative humidity (RH) of approximately 100% so that no water evaporation occurs. Then for three days, the air above the soil is kept at 0% of relative humidity and the soil moisture remains at the same relative humidity (RH) of 10.3%. During the ten last days of the experiment, the air above the soil is kept dried and the soil is let progressively to drain. The parameters used in the simulations are presented in Table 2. Some assumptions are made regarding the characteristics of the experimental set-up: the pesticide is incorporated uniformly in the soil at time \( t = 0 \), the physico-chemical properties of the pesticide are constant during the volatilisation experiments, and the soil parameters are uniform when the soil remains in a steady-state (soil moisture constant, no water evaporation).

The calculated volatilisation curves are presented in figures 2. In the absence of water evaporation (\( F_{w} = 0 \)) the model assumes that the three phases of the soil system (solid, liquid and gaseous) are in equilibrium and fit reasonably the experimental data. Thus, under these conditions, a model such as the one developed by Jury [1] is sufficient to describe the pesticide volatilisation rate. In fact, during the experiment, slight water evaporation occurs (about 1.5 mL.day\(^{-1}\)) but this phenomenon has no effect on the model outputs probably because of the low solubility of trifluralin in water (0.19 mg.L\(^{-1}\)). On the other hand, when the system is not in equilibrium i.e. when an important water flow evaporation occurs (about 6 mL.day\(^{-1}\)), kinetic terms (\( k_{A} \), the adsorption rate constant, \( k_{D} \), the desorption rate constant and \( K \), the linear adsorption isotherm) are included in the model to describe the sorption-desorption process.
Figure 1: Measured volatilisation flux obtained with trifluralin on the alsatian loess.

Figure 2: Observed and computed fluxes of trifluralin volatilisation.
In this particular case, the kinetic approach is the most appropriate to describe the sorption process contrary to the model based on a linear adsorption equilibrium which overestimates the volatilisation flux of trifluralin as it is observed in figure 2. We note that the overestimation is moderate for trifluralin. So, to confirm the better simulation obtained using the kinetic terms, additional studies on other pesticides are necessary but we could imagine that the overestimation will increase for more soluble pesticides such as atrazine. The kinetic approach cannot be conducted using analytical resolution because the solutions of the differential equations become to complex and cannot be calculated.

Table 2. Selected parameters used in the simulations for the trifluralin

<table>
<thead>
<tr>
<th>Invariable parameters</th>
<th>value</th>
<th>dimension</th>
<th>origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil porosity(O)</td>
<td>0.52</td>
<td>cm^3/cm^3</td>
<td>measured</td>
</tr>
<tr>
<td>Solid phase content(ρ)</td>
<td>0.48</td>
<td>cm^3/cm^3</td>
<td>measured</td>
</tr>
<tr>
<td>Depth of pesticide incorporation(L)</td>
<td>10</td>
<td>cm</td>
<td>defined</td>
</tr>
<tr>
<td>Initial concentration(C_0)</td>
<td>6.9(±0.68)</td>
<td>μg/cm³</td>
<td>measured</td>
</tr>
<tr>
<td>Constant of Henry’s law(K_H)</td>
<td>1.10^2</td>
<td>###</td>
<td>literature</td>
</tr>
<tr>
<td>Transport coefficient across the air boundary layer(h₅)</td>
<td>0.0049</td>
<td>cm</td>
<td>calculated from Eq (13)</td>
</tr>
<tr>
<td>Air diffusion coefficient (D_{air}) (30°C)</td>
<td>1667.52 (±69.12)</td>
<td>cm^2.day⁻¹</td>
<td>adapted from Fuller and Giddings[14] and Fuller et al. [15, 16]</td>
</tr>
<tr>
<td>Water diffusion coefficient (D_{water}) (30°C)</td>
<td>0.389 (&lt;0.043)</td>
<td>cm^2.day⁻¹</td>
<td>adapted from Hayduk and Minhas[17]</td>
</tr>
<tr>
<td>Adsorbed-liquid partitioning coefficient(K_p)</td>
<td>108.7</td>
<td>###</td>
<td>measured</td>
</tr>
</tbody>
</table>

1-20 (days) - Time step : 1.00sec.

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
<th>dimension</th>
<th>origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air content(a)</td>
<td>0.417</td>
<td>cm^3/cm^3</td>
<td>measured</td>
</tr>
<tr>
<td>Soil/air diffusion coefficient (D_{air,s})</td>
<td>334.08 (±13.85)</td>
<td>cm^2.day⁻¹</td>
<td>calculated from Eq.4</td>
</tr>
<tr>
<td>Water content(θ)</td>
<td>0.103</td>
<td>cm^3/cm³</td>
<td>measured</td>
</tr>
<tr>
<td>Soil/water diffusion coefficient (D_{w,s})</td>
<td>1.6.10^{-3} (&lt;1.77.10^{-4})</td>
<td>cm^2.day⁻¹</td>
<td>calculated from Eq.5</td>
</tr>
<tr>
<td>Water flux(F_w)</td>
<td>0.0 (0.05)</td>
<td>cm.day⁻¹</td>
<td>measured</td>
</tr>
</tbody>
</table>

21-31 (days) - Time step : 4.32sec

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
<th>dimension</th>
<th>origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption kinetic rate(k_A)</td>
<td>24.0</td>
<td>day⁻¹</td>
<td>measured</td>
</tr>
<tr>
<td>Desorption kinetic rate(k_D)</td>
<td>0.221</td>
<td>day⁻¹</td>
<td>measured</td>
</tr>
<tr>
<td>Water flux(F_w)</td>
<td>0.005-0.25</td>
<td>cm.day⁻¹</td>
<td>measured each day</td>
</tr>
<tr>
<td>a, θ, D_{air,s}, D_{w,s}</td>
<td>****</td>
<td>****</td>
<td>recalculate each day</td>
</tr>
</tbody>
</table>
References


