

Solute transport in the top soil zone under non-isothermal field conditions

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Abstract

The effects of field conditions on chemical migration in the top soil were examined using a deterministic modeling approach. A complete water and volatile organic compound transport model for the unsaturated soil zone under non-isothermal conditions has been developed and implemented in a numerical model. The mass balance equation for water considers liquid and vapor fluxes generated by temperature and capillary pressure gradients. In addition to the classical transport mechanisms (diffusion, dispersion and convection) and equilibrium relations between soil phases (Henry's law constant and partition with the soil organic phase) the transport model for the organic compound takes into account the vapor-solid sorption process and its dependence with temperature and soil moisture content. Simulation results for different VOC transport under non-isothermal conditions agree well with experimental results reported in the literature for soils that dry progressively. Test cases for 3 compounds of

different volatility (benzene, 1,3-dichlorobenze and lindane) and 2 soil scenarios (a wet and a dry one) are presented. Results suggest that the effects of daily temperature and water moisture oscillation on the chemical transport are stronger for those compounds with relatively low Henry's law constant and for dry soil conditions. Chemical gas and liquid fluxes contribute to the volatilization flux to varying degrees depending on the hour of the day. For volatile compounds like 1,3-dichlorobenzene, the dominant transport mechanisms are diffusion and dispersion in gas phase while for less volatile compounds like ethanol and lindane, dispersive and convective liquid flux governs the transport process. In the case of 1,3-dichlorobenzene changes in the adsorption affinity caused by daily temperature and moisture variations affects its migration and volatilization flux with differences on mass remaining in soil as high as 12% after a period of 5 days simulation.

1.- Introduction

The growing concern about the environmental impact of contaminant presents in soils has increased the number of deterministic transport models for contaminant migration and volatilization in the vadose zone. These simulation models have been widely used as an effective tool to understand the different mechanisms that influence chemical transport in the unsaturated soil as well to design and asses different remediation techniques.

In many cases, however, these simulation models assume that an isothermal description of the soil is adequate. This assumption may lead to important errors when these models are used to predict chemical migration and volatilization fluxes from contaminated soils under natural field conditions. Different authors have shown that simultaneously temperature and soil moisture daily oscillations, conditions usually encountered in the environment, may affect the migration and volatilization fluxes of organic compounds present in soil [*Parmele et al.*, 1972; *Harper et al.*, 1983; *Lindberg et al.*, 1995; *Haenel and Siebers*, 1995; *Baker et al.*, 1996]. The effect of temperature and moisture content in contaminant migration is expressed not only through the water dynamic generated by temperature and moisture content gradients, but also through the temperature and water moisture dependence of the different organic transport parameters and equilibrium coefficients that fix the chemical partitioning between soil phases.

Although *Piver and Lindstrom* [1991] discussed the use of different modeling techniques for contaminant transport in field conditions, the first work devoted to the study of the effect of simultaneously temperature and moisture content profile variations on pollutant transport seems to correspond to *Cohen and Ryan* [1989]. Using a one-dimensional numerical model for chemical transport and a site specific temperature and moisture data set from a previous work made by *Jackson* [1973], the authors studied the role of daily moisture and temperature gradients on chemical transport in the top soil zone. Although the authors acknowledged that water vapor flux could be important in air-dry soils, their model didn't include this flux. Their results indicated that for relatively moist soils, where transport of liquid phase was possible, the effect of dispersion on chemical volatilization was important. The authors also showed the influence of daily temperature cycle on the volatilization flux. In a later work, *Grifoll*

and Cohen [1996] focused in the coupling effect between pollutant transport and water movement subjected to raining and evaporation episodes under isothermal conditions. The aim of the work was to show, via a deterministic model, the effect of transient water movement on contaminant volatilization. Their results suggested that transport contaminant mechanisms such as diffusion, dispersion and convection could all be significant to varying degrees during various parts of the year. These studies made evident that in order to correctly predict the contaminant transport near the soil surface, an accurate description of temperature and moisture profiles as well as liquid and vapor water fluxes is needed. Unfortunately, and as *Cahill and Parlange* [1998] pointed out, "there has never been a satisfactory comparison of the theory [*Philip and de Vries*, 1957] for water vapor movement in soils with short term field observation". The lack of an appropriate theoretical framework capable of accurately predicting the temperature and moisture profiles variations in soils has been a limiting factor in the study of the effects of dynamic natural field conditions on contaminant transport.

Different authors have also focused on the influence of chemical vapor sorption on the transport of volatile organic compounds (VOC) as affected by temperature and water moisture content. Results obtained considering a fix moisture and temperature profile, have demonstrated the importance of including vapor phase sorption when modeling VOCs migration and volatilization to the atmosphere [*Shoemaker et al.*, 1990; *Culver et al.*, 1991]. Other authors have explored the effects of fluctuations of relative humidity and temperature on vapor sorption and the release of organic compounds from contaminated soil [*Shonnard and Bell*, 1993; *Batterman et al.*, 1995; *Thoma et al.*, 1999]. In this later study, *Thoma et al.* [1999] focused on the effect of dynamic competitive sorption, modulated through fluctuating relative humidity, on the chemical diffusive flux in soil columns. The authors found that the flux varied by a factor of up to

2 during 24 hours cycle when the experimental system was subjected to humidity fluctuations of $\pm 40\%$.

In this paper a complete water and organic compound transport model for the unsaturated soil zone under non-isothermal dynamic conditions has been developed and implemented in a numerical code. In addition to the classical mechanisms and processes that govern the chemical transport (convection, dispersion, diffusion, solid organic sorption and partition between liquid and gas phases) the model also includes chemical vapor/mineral surface adsorption as an equilibrium process, which depends on water vapor pressure and temperature. Model simulations will be used to study the coupling effect between energy, water and organic compound transport under dynamic field conditions. These conditions are usually found in a soil drying episodes. Special attention will be given to identify the dominant transport mechanisms in each phase. Simulation results will show that variations in the adsorption affinity caused by this dynamic conditions can be responsible of differences on organic compound mass remaining in soil as high as 12% after a period of 5 days simulation.

2.- Basic equations

The chemical transport model includes four different mass balance equations: one for the liquid water, one for the vapor water, one for the gaseous phase as a whole and, finally, one for the organic compound as well as an energy balance. The liquid water movement is modeled by means of Richards' equation subject to dynamic surface boundary conditions. The water vapor movement is modeled considering the dependence of the vapor pressure with temperature and the decrease of vapor pressure with capillary pressure of the liquid water. No empirical enhancing factors were used

for the water vapor diffusion process. The movement of the gaseous phase as a whole is due mainly to liquid water displacement and change of gas density with temperature. The energy balance equation considers conductive, convective and dispersive heat fluxes inside the porous matrix. The top boundary condition for the water considers evaporation controlled by capillary head at surface and rain infiltration. The top boundary condition for the energy equation is expressed through an energy balance that takes into account downward and upwards radiative fluxes, convective heat flow to the atmosphere, sensible heat flux and the heat flux generated by other transport mechanisms that goes deep into the soil. The mass and energy balance equations are coupled and therefore must be solved together. The chemical concentrations values in soils are sufficiently low to ensure that its presence doesn't affect the energy fluxes and other mass fluxes. This condition allows the chemical compound balance equation to be solved independently from the other four mass balance equations. A more detailed explanation about the model formulation is given by *Gastó et al. [2002]*.

2.1 Organic transport under non isothermal conditions

The one-dimensional (vertical) organic compound transport in the porous matrix can be described using the following equation for each phase [*Griffoll and Cohen, 1996*]:

$$\frac{\partial \theta_i C_i}{\partial t} = \frac{\partial}{\partial z} \left[\theta_i \left(\frac{D_i}{\tau_i} + D_{vi} \right) \frac{\partial C_i}{\partial z} - q_i C_i \right] + \sum_{\substack{j=1 \\ j \neq i}}^M a_{ij} N_{ij} \quad (1)$$

$i = 1, \dots, M$

where C_i (kg/m^3) is the organic compound concentration in phase i and q_i (m/s) is the volumetric flux for that phase. The molecular diffusion coefficient for the organic

compound in phase i , D_i (m^2/s) depends on temperature in a similar way as the diffusion coefficient for the water gas phase [Bird *et al.*, 1960]. D_{vi} is the dispersion coefficient and τ_i is the tortuosity factor evaluated according to the model presented in Gastó *et al.* [2002]. It is worth noting that in equation (1) it doesn't appear the chemical reaction rate, term that accounts for bio- and chemical transformations. This reaction term depends (in addition to the chemical concentration) on the specific soil characteristics and its microorganism community [Lyman *et al.*, 1990; Mackay *et al.*, 1992]. In absence of specific data, it is usually common to neglect this degradation term. In equation (1) the chemical flux mass from phase j to phase i is equal to N_{ij} , and a_{ij} is the interfacial area per unit volume of soil matrix between phases i and j . The model assumes local-equilibrium condition between phases. Earlier studies by Cohen and Ryan [1989] and Gierke *et al.* [1990] suggested that the local equilibrium assumption for air-water mass transfer is reasonable for volatile chemicals. Subject to the restriction of local phase equilibrium, the mass transfer equations as expressed in equation (1) can be written in terms of the overall chemical concentration in the soil matrix:

$$\frac{\partial C_{sm}}{\partial t} = \frac{\partial}{\partial z} \left(D_{ap} \frac{\partial \left(\frac{C_{sm}}{\zeta} \right)}{\partial z} - V_{eff} C_{sm} \right) \quad (2)$$

where C_{sm} (mass of compound /soil volume) is the total soil matrix chemical concentration given by

$$C_{sm} = \zeta \cdot C_l \quad (3)$$

where

$$\zeta = (\theta_l + \theta_g H_{GL} + (1-\phi)H_{SL}) \quad (4)$$

where the sub scripts S, G and L refer to the soil-solids, soil-water and soil-air phases

respectively, and H_{ij} is the partition coefficient between soil phases i and j defined as:

$$H_{ij} = \frac{C_i}{C_j} \quad (5)$$

The temperature dependence of the different partition coefficients are presented in table 1. The effective convective velocity is denoted by V_{eff} and can be expressed as:

$$V_{eff} = \frac{1}{\zeta} \left(q_l + q_g H_{GL} + \theta_g \left(\frac{D_g}{\tau_g} + D_{vg} \right) \frac{\partial H_{GL}}{\partial T} \frac{\partial T}{\partial z} \right) \quad (6)$$

this equation includes part of the effects of temperature gradient on the dispersive flux.

The apparent chemical diffusion coefficient, in the soil matrix, D_{ap} , can be calculated as:

$$D_{ap} = \left[\theta_g \left(\frac{D_g}{\tau_g} + D_{vg} \right) H_{GL} + \theta_l \left(\frac{D_l}{\tau_l} + D_{vl} \right) \right] \quad (7)$$

The longitudinal dispersion coefficient in each phase appearing in equation (1), D_{vg} and D_{vl} were estimated as $D_{vi} = \alpha_{Li} \cdot q_i / \theta_i$ ($i=g,l$) where α_{Li} , longitudinal dispersivity in phase i , has been evaluated using the correlation presented in Gastó et al. [2002].

The evolution of the concentration profiles is obtained by solving equation (2), given V_{eff} , D_{ap} and ζ as a function of time and depth, and subject to the appropriate initial and boundary conditions. In this work the volatilization boundary condition was set at the soil-atmosphere interface. Accordingly, the chemical surface volatilization flux, J_0 , is given by:

$$J_0 = -k_{atm} (C_{atm} - C_g) \quad @ \quad z = 0 \quad (8)$$

where k_{atm} is the atmospheric-side mass transfer coefficient between soil and atmosphere evaluated using the same correlation proposed by Brutsaert [1975] with modifications proposed by Grifoll and Cohen [1994]. C_{atm} is the bulk organic compound concentration in the atmospheric phase. In all simulations the depth of the soil was

selected in order to be sufficiently large to ensure that the chemical concentration front did not reach the bottom boundary over the length of the simulation. Therefore, the bottom boundary can be conveniently set as $\delta C_{sm}/\delta z = 0 @ z = L$.

2.2 Time and space discretization

For the range of simulations conducted in this work, the soil depth was set equal to 1 m and was divided into two zones. The first zone ($0 < z < 0.05$ m) has a constant step size equal to 0.001 m. In the second zone ($0.05 \text{ m} < z < 1 \text{ m}$) the step size increases progressively from 0.001 m to 0.1 m such that $\Delta z_i = r \cdot \Delta z_{i-1}$ with r equal to 1.1. A variable time step was selected between a minimum of 1s and a maximum of 3600 s to ensure enough numerical description of the temporal variations of the different dependent variables. In all cases the local compliance of the classical restrictions when solving numerically linear transport equations (Courant and Péclet number limits) was monitored. Moreover, in all simulations was checked that further decreases of the grid and time steps did not change appreciably the results.

3.- Simulation set up

The model ability to accurately predict chemical transport in unsaturated soils under field conditions has been confirmed through the simulation and comparison of three different experimental works. [*Parmele et al.*, 1972, *Baker et al.*, 1996, *Jin et al.*, 1994]. The correct simulation of these works will prove the model capacity to qualitatively describe and reproduce the main mechanisms and processes that govern the migration of organic compounds in soils under field conditions.

Once the simulation model has been checked and in order to illustrate the effect of simultaneously temperature and moisture variations on chemical transport, different test cases will be designed and simulated. Three organic compounds of different volatility (ethanol, 1,3-dichlorobenzene and lindane) and two soil scenarios will be used.

The temperature and moisture content profiles corresponding to the two soil scenarios have been obtained previously from the simulation of a well documented experimental work concerning water transport in natural field conditions [*Jackson, 1973*]. A more detailed explanation about that simulation is given by *Gastó et al. [2002]*.

The soil scenarios selected represent different stages of the drying process of a bare soil initially saturated under natural field conditions. The wet soil scenario coincide with the first days of the process. These initial days are characterized by relatively high water content values for the first 20 cm depth. These conditions favors convective water liquid fluxes. On the other hand, the dry soil scenario is characterized by low water content values with high volumetric water content and temperature gradients during the hottest hours of the day. This extreme conditions favor gas over liquid phase water transport.

The simulations tests were carried out for three chemicals: ethanol, 1,3-dichlorobenzene and lindane. These chemicals were selected to provide a self-consistent set of physicochemical parameters that span a reasonable range of three orders of magnitude for the Henry's law constant. Ethanol was chosen as an example of highly water soluble compound with a strong tendency to partition into the liquid water phase and relatively low tendency into partition to the gas phase. 1,3-dichlorobenzene represents the case of a volatile compound with a strong tendency to partition to the gas phase and finally lindane represents the case of a less volatile compound with a strong tendency to persist in soils. In all simulation cases, the soil was initially contaminated down to a depth of 0.1 m. Below 0.1 m the soil was free of contaminant. The initial concentration

was restricted to the case of residual contamination (no free-phase of contaminant was present in the soil). The pertinent physicochemical properties for these and other substances used for the rest of studies simulated are given in table 5 and 6.

4.- Results and discussion

4.1 Field validation

Simulation results corresponding to the experiments of Baker, Parmele and Jin are presented in figure 1, 2 and 3 respectively. In Baker's study, [1996], a well known herbicide, EPTC ($C_9H_{19}NOS$), was artificially incorporated to a maximum depth of 5 to 10 cm into a Waukegan silt loam soil. The experiment was conducted in May 1993 at Minnesota and during seven days herbicide concentration as well as other important parameters were measured. Both the temperature and VMC corresponding to the soil surface exhibited a dynamic behavior imposed by large diurnal cycle of radiant energy, with variations similar to those found in Jackson's work. The initial temperature and VMC soil profiles for the simulation process have been obtained from measured values provided by Baker. The hydraulic functions as well as the adjusted parameters used in the simulation are given in table 3 and 4.

The measured and simulated volatilization fluxes of EPTC corresponding to the first 36 hours are shown in figure 1. Both the simulated and measured values exhibit a high initial volatilization flux value followed by a rapid decline. A similar behavior was observed by Cliath et al. [1980] when they measured EPTC volatilization from a flood-irrigated field. It is interesting to observe that both the measured and simulated values describe a similar increment during the latest hours of day 132 and initial hours of day

133. This increase coincides with the hours of the day when the moisture water content near surface rises. The relationship between water content and flux volatilization has been experimentally observed by different authors [*Fang et al.*, 1961; *Gray and Weierich*, 1965] and can be attributed to differences in the way molecules sorb to surfaces in wet or in dry systems. When the moisture content increases, the chemical gas adsorption over the solid inorganic surface decreases due to the competitive sorption of water molecules. As a consequence, both the gas chemical concentration as well as the diffusion and volatilization fluxes increases. In our case these effects have been considered through the water content and temperature dependence of the sorption coefficient. In absence of specific data for EPTC, temperature and moisture content dependence parameters corresponding to a similar compound, diethyl ether, have been employed [*Goss*, 1993]. Later and coinciding with the hours of the day when the soil temperature increases most, the simulated volatilization flux exhibits a new increment that can be attributed to the temperature effects on the absorption coefficient k_{oc} . It is worth noting that the chemical volatilization flux simulated is sensible to the Henry's law constant value employed. The use of experimental values obtained under laboratory conditions, conditions far from those normally encountered in field conditions, implies an important simplification that can be responsible of the flux discrepancies observed specially during the initial hours.

The complex relationship between water, energy and chemical transport processes has been made evident in Baker's experiment. Only a complete simulation model that accounts for the different transport processes will be therefore able to describe with detail experimental results obtained under field conditions.

The second work that will be simulated is an experimental study concerning dieldrin volatilization [*Parmele et al.*, 1972]. The experimental work was realized in a

cultivation area under field conditions. The experiment site was located at Coshocton (Ohio) and $5.6 \cdot 10^{-4} \text{ kg/m}^2$ of dieldrin was disced into the soil to a depth of 7.5 cm on the 30 April 1969. The experimental results were measured on the 26th of June 1969, 57 days after the beginning of the experiment. Using the same soil characteristics data employed in Jackson's simulation for the water transport under non-isothermal conditions, the contaminant volatilization period that goes from 30 April to 26 June has been simulated. Although no specific meteorological information data is provided, the simulated volumetric moisture content (VMC) and soil temperature profiles are similar to those described in Parmele's work. The initial contaminant profile considers a constant dieldrin concentration in liquid phase equal to $2.8 \cdot 10^{-6} \text{ kg/m}^3$ for the first 7.5 cm.

Figure 2 shows the measured and simulated volatilization flux corresponding to 26 June. The measured values describe a strong daily variation cycle with a ratio between the maximum ($900 \cdot 10^{-6} \text{ ng/cm}^2\text{s}$) and minimum ($50 \cdot 10^{-6} \text{ ng/cm}^2\text{s}$) volatilization flux greater than an order of magnitude. Simulation results obtained under isothermal ($T = 288 \text{ K}$) and non-isothermal soil conditions are presented together. Volatilization fluxes for non-isothermal conditions follow a daily variation cycle similar to the experimental values measured. Discrepancies as high as 30% for the maximum volatilization flux are found between simulated and experimental measures.

Daily strong temperature oscillations with maximum values around 40°C and minimum values around 10°C have been observed in the simulation results. This strong temperature oscillations are responsible of the flux volatilization cycles. The absence of liquid flux convection after a long dry period together with the low water solubility of dieldrin implies that gas diffusion is the main transport mechanism. When the soil temperature rises the dieldrin vapor pressure also rises incrementing the gas phase

concentration as well as the chemical volatilization flux. Although the lack of temperature and VMC soil profiles negate a quantitative comparison of model predictions to field data, the measured and simulated flux volatilization are of similar magnitude and both exhibit a similar behavior. This qualitative agreement between field data and simulation results makes evident the model capacity to accurately describe the transport dynamics of a volatile compound in field conditions characterized by strong thermal oscillations. It is also important to note that different volatilization results are obtained when different values for atmospheric factors like wind speed or relative humidity are used. This sensibility implies that the use of adequate values for this and other atmospheric variables may lead to a closer comparison with simulation values.

The strong daily oscillation found for measured volatilization fluxes contrast with simulation results obtained for isothermal conditions. In this case, a constant volatilization flux value is observed with discrepancies as high as 100% between simulated and measured values during midday. These results make evident that the use of isothermal conditions not only limits the model ability to describe the complex dynamics observed but it may induce to important errors when constant volatilization values, far from those measured, are used to assess the pollutant impact of a contaminant soil scenario.

The last experimental work that has been simulated is the toluene transport and biodegradation study made by Jin et al. [1994]. In this case the experiment was realized under fixed laboratory conditions and soil columns were used. Both the temperature and the volumetric water content inside the column were maintained constant being the values equal to 0.14 and 273.15 K respectively. The column depth is 20 cm and the initial toluene concentration is equal to 0.14 kg/m³.

The absence of convective water flux together with the high volatility of toluene

implies that gas diffusion is the only significant mass transport mechanism. This condition allows a qualitative comparison between experimental and simulated results. The measured toluene volatilization fluxes along with the simulation results are presented in figure 3. Both measured and simulated results describe a similar behavior with an strong flux reduction during the initial hours. Discrepancies observed can be explained in terms of differences on the tortuosity model employed to calculate the effective diffusion coefficient for toluene. After a 48 hours period the difference observed are less than a 6%. These results make evident the model ability to correctly describe the chemical transport mechanisms in unsaturated soils.

3.3 Temperature and water dynamics effects on chemical volatilization

In order to determine the effect of temperature and moisture content variations in chemical migration and volatilization from soils, several test cases for three different chemical compounds and two soil scenarios have been simulated. In all cases simulation results obtained considering isothermal (295 K) as well as non-isothermal conditions are presented. The soil was initially contaminated with an uniform soil concentration to a depth of 10 cm.

Under non isothermal field conditions, the chemical volatilization flux for the three compounds considered describes a characteristic daily sinusoidal oscillation with maximum values during midday and minimum values at night. This behavior is similar to that observed in Parmele's work. The daily volatilization maximum coincide with the hour of the day when the soil temperature near surface reach their maximum value. The presence of important temperature and capillary pressure gradients during these hours modify the gas phase concentration profile through the temperature and moisture

content dependence of the gas/solid sorption coefficient, as well as the temperature dependence of the Henry's law constant and the octanol/water partition coefficient. The combined effects of temperature and water moisture variations on the different equilibrium parameters provoke an increase in chemical gas concentration affecting both the diffusion flux and the volatilization flux at the top surface. These hours coincides also with the daily moment when the water dynamics near surface reaches its maximum value due to the high evaporative demand at surface. The effect of water transport on contaminant migration is more significant during these hours and contributes to the chemical transport near surface. This behavior strongly contrasts with results obtained when isothermal conditions are considered. Under isothermal soil conditions the chemical volatilization flux has a similar behavior to that observed in Jin's work [1994].

The evolution of the percentage of initial mass remaining in soils for the three compounds and the two soil scenarios is depicted in figure 4. Results considering isothermal (22°C) and non-isothermal soil conditions are shown. In the case of volatile compounds like ethanol and 1,3-dichlorobenzene their volatilization fluxes are much higher than that for lindane and therefore the mass remaining in soil after the 5 days simulation period is less than in the case of lindane.

Results for ethanol clearly show that wet soil conditions favors volatilization. These results make evident the importance of convective liquid fluxes in the volatilization process in the case of compounds like ethanol with a high tendency to partition into the liquid water phase. After 5 days simulation period, the differences in mass remaining between isothermal and non-isothermal conditions are more noticeable for soil dry conditions (4.3% in the case of dry soil vs. 0.7% in the case of wet soil). This result suggests that temperature effects on ethanol volatilization are more significant for those

soil conditions that favor mass transfer in gas phase. On the other hand, results for 1,3-dichlorobenzene clearly show that dry soil conditions favor volatilization (66% of the initial mass volatilized for dry soil conditions versus 58% for wet soil after a simulation period of 5 days). These results are coherent with the high tendency of 1,3-dichlorobenzene to partition into the gas phase. The volatilization process will be enhanced in soil conditions that favor gas phase transport.

Compared to ethanol and 1,3-dichlorobenzene, lindane shows a much lower tendency to volatilize from soils. In all cases the volatilized mass at the end of the simulation period represents less than the 5% of the initial mass present in soil. This result is consistent with the low volatilization flux found for this compound. The air/water partition coefficient for lindane is much lower than that of ethanol and 1,3-dichlorobenzene, while at the same time the sorption coefficient is much higher. This explains the relatively high tendency of lindane to persist in soil. Higher volatilization percentages obtained for wet soil conditions suggests the important role of water liquid fluxes in lindane migration and volatilization from soil. Results obtained for dry soil scenario indicate that differences in mass remaining values at the end of the simulation period can be as high as 50% between isothermal and non isothermal conditions. These results, similar to those found for ethanol, suggest that temperature effects on volatilization process are more important for slightly volatile compounds and for dry soil scenarios that favor gas over liquid transport.

3.4 Importance of the different transport mechanisms

In order to determine and assess the importance of the different mass transport mechanisms that contribute to the chemical volatilization and migration from the inner

soil to the soil surface, a contribution index, γ_{ij} , for every mechanism (i) and phase (j) is proposed. This contribution index can be defined as follows:

$$\gamma_{i,j} = \frac{\int_{z_{inf}}^0 \mathbf{J}_{i,j} dz}{\sum_{j=1}^2 \sum_{i=1}^3 \left[\int_{z_{inf}}^0 \mathbf{J}_{i,j} dz \right]} \quad (9)$$

where \mathbf{J}_{ij} is the mass flux generated by mechanisms i in phase j and z_{inf} is the depth where the total chemical flux that contributes to volatilization flux is equal to 0. The mass transfer mechanisms considered are: diffusion, dispersion and convection in liquid and gas phase.

The temporal evolution of the contribution index for the most significant mass transport mechanisms in liquid and gas phase for ethanol, 1,3-dichlorobenzene and lindane are given in figure 5. The figure also presents the total contribution for each phase (obtained from the sum of the different contribution mechanisms in each phase). Ethanol results correspond to the dry soil scenario while for 1,3-dichlorobenzene and lindane, results presented are obtained from the wet soil scenario. These soil scenarios have been selected in order to provide for each compound a representative case where both the liquid and gas phases contribute to a different extent to the chemical transport. In all cases, simulation results presented were obtained for non-isothermal conditions.

Ethanol's results demonstrate that mass fluxes in liquid phase clearly dominates the transport process, being dispersion the main transport mechanism in liquid phase. The gas phase fluxes contribute also up to 10% to the total ethanol transport during the hottest hours of day. The dominant mass transport mechanisms in gas phase is diffusion. Both the liquid and, to a minor extent, the ethanol gas flux describe a daily oscillation cycle similar to the one observed for the volatilization flux in Parmele's work. These results implies that the daily maximum liquid and gas flux contribution to the ethanol

transport are found at different hours of the day. In the liquid phase, the daily highest flux value is located around midday and coincides with the moment of the day when the evaporative demand is greatest. This coincidence implies a strong coupling effect between water and chemical transport in the case of compounds like ethanol. These compounds tend to partition into the liquid water phase due to their high water solubility, low octanol/water coefficient and relatively low Henry's law constant. Later and coinciding with the hours of the day when the soil surface dries as a consequence of the high evaporative demand, the convective liquid water flux decreases due to the extreme low soil hydraulic conductivity values encountered near surface. It is interesting to note that when the liquid contribution decreases, the gas contribution increases due to the presence of important concentration gradients in gas phase. This concentration gradients can be explained in terms of the presence of (1) high temperature values and (2) important concentration gradient in liquid phase. These concentration gradients in liquid phase are consequence of the ethanol accumulation caused by the absence of convective liquid fluxes near surface. These two factors augments the chemical concentration in gas phase thus incrementing the diffusion and dispersion gas fluxes. A kind of relief mechanism is therefore observed between transport phases responsible of the chemical migration and volatilization.

Contrary to the assertions found for ethanol, results for 1,3-dichlorobenzene confirms the important contribution of the gas phase to the chemical volatilization process even for wet soil conditions (conditions that favor liquid water flows). These results are consistent with the 1,3-dichlorobenzene high tendency to partition into the air phase. The total gas phase contribution increases with time as long as the soil dries, with values ranging from 70% for the first day to 90% for the last day. The total gas contribution describes also a daily oscillation cycle similar to the one observed for ethanol with

maximum values centered around midday, when the soil temperature is maximum. The presence of high temperature values during the hours of the day when the sun incident radiation is higher, increases the gas concentration due to the rise of the Henry's law constant. It is instructive to observe the complementary behavior described by the diffusive and dispersive gas phase contribution index. Results corresponding to liquid phase show that dispersion is the main transport mechanism.

Results obtained for lindane are similar to those obtained for ethanol and show the important contribution of the liquid phase to the chemical volatilization process specially during the initial hours. Later and as the soil gradually dries, the gas phase contribution increases with daily maximum contribution that range from values near 10% the second day to values greater than 20% the last day. This results implies that the soil drying process favors and increments the gas flux contribution to the total chemical transport being dispersion the dominant transport mechanism in gas phase. Contrary to the previously findings obtained for ethanol and 1,3-dichlorobenzene, results obtained for lindane show the importance of dispersive and convective transport mechanism in liquid phase. The unexpected high contribution index for liquid convection can be explained in terms of lindane low liquid concentration values. The absence of important concentration gradients in liquid phase, except during the initial hours, reduces the influence of the diffusive and dispersive transport mechanisms compared to the convective flux. Similar to the results obtained for ethanol, for lindane the daily minimum liquid flux contribution coincides with the moment when the soil surface is at its lowest moisture content. This soil conditions favor the gas flux contribution.

3.5 Chemical sorption effects on volatilization process

Depending on the sorption process considered, (absorption, adsorption or both processes together) different values are obtained for the total mass volatilized at the end of the simulation period. In order to distinguish and assess the effect of simultaneously temperature and moisture content variation on the adsorption coefficient and its implications into the volatilization flux, the coefficient partition between the solid and liquid phase, H_{SL} , will be evaluated depending on the different sorption mechanisms considered. If we consider that adsorption and absorption processes are additive, the partition coefficient between the solid and liquid phase, H_{SL} , can be expressed as:

$$H_{SL} = \frac{C_S^I + C_S^O}{C_L} = K \rho_S a H_{GL} + k_{oc} f_{oc} \rho_S \quad (10)$$

where C_S^I and C_S^O are the inorganic and organic chemical concentration values in the solid phase and C_L is the chemical concentration in liquid phase respectively. K is the adsorption coefficient (m) and a is the soil specific surface area (m^2/g). k_{oc} is the octanol/water partition coefficient and f_{oc} is the organic content soil fraction. In our case a is equal to 8,18 (this value correspond to a sandy loam soil type). In equation 10 the first term accounts for the gas phase adsorption into the inorganic solid surface while the second term accounts for the absorption process between the organic solid part and the liquid phase.

Only results for 1,3-dichlorbenzene are presented. Figure 6 shows the evolution of the initial mass remaining in soils for this compound and for the wet soil scenario.

In the case of ethanol the differences founded depending on the type of sorption considered are low and less than a 3% of the total initial mass at the end of the simulation period. These results suggest that in the case of soluble compounds like

ethanol, compounds with a relatively low Henry's law value and a strong tendency to partition into the water phase, the effects of dynamic temperature and moisture conditions on the adsorption coefficient don't modify to a great extent the transport and volatilization process. Different results are obtained for 1,3-dichlorobenzene. In this case differences in the total volatilized mass at the end of the simulation period can be as high as high as 12% depending on the sorption process considered. This results show that in the case of compounds like 1,3-dichlorobenzene, compounds with a relatively high Henry's law constant, low water solubility and a strong tendency to partition into the gas phase, the effects of temperature and moisture content on the adsorption process can substantially alter the volatilization process.

These effects are expressed through the temperature and moisture content dependence of the partition coefficient H_{SL} . It would be therefore illustrative to show the evolution of the H_{SL} for 1,3-dichlorobenzene located at the soil surface. Figure 7 shows how H_{SL} describes a daily variation cycle with minimum values during the hottest hours of day when absorption is the only sorption process considered. This behavior is consistent with the exothermic value of the solution's enthalpy for this compound. The absorption process is therefore thermodynamically enhanced at low temperatures. A different pattern is observed when adsorption is included into the sorption process. Not only the value of H_{SL} is higher and increases progressively as the soil surface dries but also the daily cycle pattern changes. The figure shows how the extreme low moisture soil values usually encountered during midday increases the chemical competition for the adsorptive surface sites increasing therefore the adsorption coefficient. This inverse relationship between K and moisture has been demonstrated by different authors [Thibodeaux *et al.*, 1991; Goss and Schramm, 1991; Goss, 1992]. When adsorption and absorption are considered together, the low moisture content values observed during the

hottest hours of the day increases the chemical tendency to adsorb into the soil surface surpassing the inverse tendency exhibited by absorption. The net effect implies a noticeable reduction of the volatilization process at the end of the simulation period.

4.- Conclusions

A new simulation model for the transport of organic volatile compounds in the unsaturated zone under natural field condition has been developed. The model has been validated against experimental data concerning chemical transport. Results obtained for different soil scenarios have shown that the effect of water dynamics on chemical transport is higher for those compounds like ethanol with a strong tendency to partition into the water phase. The effect of daily temperature and moisture content variations on chemical transport and volatilization is more important for slightly volatile compounds and for dry soil scenarios that favor gas transport. The liquid and gas fluxes contribution to the compound volatilization can be all significant to varying degrees, during different hours of the day. For compounds like ethanol, with high solubility and relatively low Henry's law constant dispersion mechanism dominates the transport in the liquid phase, while for compounds with a higher tendency to volatilize like, 1,3-dichlorobenzene, diffusion and dispersion dominates the gas phase transport. In the case of compounds like lindane, with a high tendency to partition to the solid phase and thus to remain in soils, convection and dispersion plays an important role in liquid phase transport.

The model takes into account the adsorption process and its dependence with temperature and moisture content. The effect of daily temperature and moisture content variations on the adsorption coefficient can be important and can reduce the volatilization flux in the case of volatile compounds like 1,3-dichlorobenzene.

5.- References

- Bear, J. and Bachmat, Y., 1991. *Introduction to modeling of transport phenomena in porous media*. Kluwer academic publishers. Dordrecht.
- Bear, J., 1972. *Hydraulics of Groundwater*, pp 569, McGraw Hill, New York.
- Biggar, J.W. and Nielsen, D.R., 1976. Spatial variability of the leaching characteristics of a field soil. *Water Resour. Res.* 1, pp 78-84.
- Bird, R.B., Stewart, W.E. and Lightfoot, E.N., 1960. *Transport Phenomena*. John Wiley & Sons. New York.
- Bras, R.L., 1990. *Hydrology an introduction to hydrologic science*. Addison-Wesley publishing company. Massachusetts.
- Broadbridge, P. and White, I., 1988. Constant rate infiltration. A versatile nonlinear model, 1. Analytic solution. *Water Resour. Res.* 24, pp. 145-154.
- Brutsaert, W., 1975. A theory for local evaporation (or heat transfer) from rough and smooth surfaces at ground level. *Water Resour. Res.* 4, pp. 543-550.
- Cahill, A.T. and Parlange, M.B., 1998 a. On water vapor transport in field soils. *Water Resour. Res.* 34, pp.731-739.
- Cahill, A.T. and Parlange, M.B., 1998 b. Review of heat and water movement in field soils. *Soil&Tillage Research.* 47, pp. 5-10.
- Cahill, A.T. and Parlange, M.B., 2000. Reply on the comment made by Dani Or and Jon Wraith. *Water Resour. Res.* 36, pp. 3107-3110.
- Campbell, G.S., 1994. *Soil physics with BASIC*. Elsevier Science B. V. Amsterdam.
- Cary, J.W., 1965. Water flux in moist soil: thermal versus suction gradient. *Soil Sci.*, 100. pp. 168-175.
- Cohen, Y. and Ryan P.A., 1989. Chemical transport in the top soil zone-the role of moisture and temperature gradients. *Journal of Hazardous Materials.* 22, pp. 283-304.
- Fuller, E.N., Schettler, P.D. and Giddings, J.C., 1966. A new method for predicting binary gas-phase diffusion coefficients. *Ind. Eng. Chem.*, 58, pp. 19-27.
- Gastó J.M. and Grifoll J., Simulation and analysis of water transport and evaporation under non-isothermal field conditions, in preparation to submit to *Water Resour. Res.*
- Grant, S.A. and Salehzadeh A., 1996. Calculation of temperature effects on wetting coefficients of porous solids and their capillary pressure functions. *Water Resour. Res.* 32, pp. 261-270.
- Gehlar, L.W., Mantoglou, A., Welty, C. and Rehfeldt, K.R., 1985. *A review of field-scale physical solute transport processes in saturated and unsaturated porous media*. Electric Power Research Institute EPRI EA-4190 Project 2485-5, 116p.
- Gierke, J.S., Hutzler, N.J. and Crittenden, J.C., 1990. Modeling the movement of volatile organic chemicals in columns of unsaturated soil. *Water Resour. Res.*, 26, pp.

1539-1547.

Goss, K.U. and K.W. Schramm, Determination of effective diffusion coefficients for gaseous and dissolved organic substances in soil materials using "stopped elution" method with HPLC and GC, *J. Soil Sci.*, 42, 47-58, 1991.

Goss, K.U., Effects of temperature and relative humidity on the sorption of organic vapors on quartz sand, *Environ. Sci. Technol.*, 26, 2287-2294, 1992.

Grifoll, J. and Cohen, Y., 1994. Chemical volatilization from the soil matrix: Transport through the air and water phases. *J. Hazard. Mater.* 37, pp. 445-457.

Grifoll, J. and Cohen, Y., 1996. Contaminant migration in the unsaturated soil zone: the effect of rainfall and evapotranspiration. *Journal of Contaminant Hydrology.* 23, pp. 185-211.

Grifoll, J. and Cohen, Y., 1999. A front-tracking numerical algorithm for liquid infiltration into nearly dry soils. *Water Resour. Res.*, 35, pp. 2579-2585.

Haga, D., Niibori, Y. and Chida, T., 1999. Hydrodynamic dispersion and mass transfer in unsaturated flow. *Water Resour. Res.* 35, pp. 1065-1077.

Hayduk, W., Minhas, B.S. and Lan, J., 1982. Correlations for prediction of molecular diffusivities in liquids. *Can. J. Chem. Eng.*, 60, pp. 295-299.

Jackson, R.D., 1973. Diurnal changes in soil water content during drying. En R. R. Bruce et al. (ed.) Field soil water regime. Special Pub. 5. Soil Sci. Soc. Amer. Proc. pp. 37-55.

Jin, Y. and Jury, W.A., 1996, Characterizing the Dependence of Gas Diffusion Coefficient on Soil Properties, *Soil Sci. Soc. Am. J.* 60, pp. 66-71.

Jury, W.A. and Letey, J. Jr., 1979. Water vapor movement in soil: reconciliation of theory and experiment. *Soil Sci. Soc. Amer. Jour.*, 43, pp. 823-827.

Kucklick, J.R., Himckley, D.A. and Bidleman, T.F., 1991. Determination of Henry's law constants for hexachlorocyclohexanes in distilled water and artificial seawater as a function of temperature. *Mar. Chem.*, 34, pp. 197-209.

Leighton, D. and Calo, J., 1981. Distribution coefficients of chlorinated hydrocarbons in dilute air-water systems for groundwater contamination applications. *J. Chem. Eng. Data*, 26, pp 382.

Mackay, D., Shiu, W.Y. and Ma, K.C., 1992. Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organics Chemicals, Vol I. Lewis. Chelsea. MI.

Millington, R.J. and Quirk, J.P., 1960. Transport in porous media. pp. 97-106. In F.A. Van Beren et al. (ed.), *Trans. Int. Congr. Soil Sci.* 7th, Vol. 1. Madison, WI.14-24, Elsevier, Amsterdam.

Milly, P.C., 1982. Moisture and heat transport in hysteretic, inhomogeneous porous media: a matric head-based formulation and a numerical model. *Water Resour. Res.* 18, pp. 489-498.

Montgomery, J.H., and Welkom, L.M., 1990. *Groundwater Chemicals Desk Reference*, Lewis Publishers, Chelsea, Michigan.

Olson, R.L and Davis, A., 1990. Predicting the fate and transport of organic compounds in groundwater. *Hazard. Mater. Control.*, 3, pp. 40-64.

Patankar, S.V., 1980, *Numerical heat transfer and fluid flow*, McGraw-Hill, New York.

Philip, J.R. and deVries, D.A., 1957. Moisture movement in porous materials under temperature gradients. *Transactions American Geophysical Union*. 38, pp. 222-231.

Press, W.H., Flannery, B.P., Teukolsky, S.A. and Vetterling, W.T., 1989. *Numerical Recipes*. Cambridge University Press, Cambridge.

Rose, C.W., 1967. Water transport in soil with a daily temperature wave. I Theory and experiment, II Analysis. *Australian Journal of soil research*, 4, pp. 31-57.

Sahimi, M., Heiba, A. Davis, H. and Scriven, L., 1986. Dispersion in flow through porous media, II. Two phase flow. *Chem. Eng. Sci.* 41, pp. 2123.

Sander R., 1999, Compilation of Henry's Law constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry. Version 3. <http://www.mpch-mainz.mpg.de/~sanders/res/henry.html>

Scanlon, B.R. and Milly, P.C., 1994. Water and heat fluxes in desert soils: 2 numerical simulations. *Water Resour. Res.* 30, pp. 721-733.

Schwarzenbach, R.P., Gschwend, P.M and Imboden D.M., 1993. *Environmental Organic Chemistry*. John Wiley&Sons. New York.

Sophocleous, M., 1979. Analysis of water and heat flow in unsaturated-saturated porous media. *Water Resour. Res.* 5, pp. 1195-1206.

Tyndall, J.A. and Kunkel, J.R., 1999. *Unsaturated zone hydrology for scientists and engineers*. Prentice-Hall, New Jersey.

Thibodeaux, L.J, Nadler, K.C., Valsaraj, K.T. and D.D. Reible, The effect of moisture on volatile organic chemical gas-to particle partitioning with atmospheric aerosols: Competitive adsorption theory predictions, *Atmos. Environ.*, Part A, 25, 1649-1656, 1991.

U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry (ATSDR), Atlanta, Georgia.

van Genuchten, M. Th., 1981. Analytical solutions for chemical transport with simultaneous adsorption, zero-order production, and first-order decay. *J. Hydrol.* 49, pp. 213-233.

Wescot, D.W. and Wierenga, P.J., 1974. Transfer of heat by conduction and vapor movement in a closed soil system. *Soil Sci. Soc. Am. Proc.* 38, pp. 9-14.

Yamanaka, T., Takeda, A. and Shimada, J., 1998. Evaporation beneath the soil surface: some observational evidence and numerical experiments. *Hydrological Processes*. 12, pp. 2193- 2203.

TABLES

Table 1. Temperature and moisture content dependence for the different partition coefficients, H_{ij} .

Partition coefficient H_{GL} ^a	$H_{GL} = H_{GL_ref} \left[\exp \left(\frac{\Delta_{sol}H}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right) \right]^{-1}$
Partition coefficient H_{SL}	$K_{OC} = K_{OC_ref} \cdot \exp \left[\frac{\Delta H_s^e}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right]$
Absorption ^b	$\Delta H_s^e \cong -RT \ln x_w + T \cdot \Delta S_s^e$
Adsorption ^c	$K = A \exp \left(\frac{B}{T} - C \cdot RH \right)^c$

^a Sander (1999) ($T_{ref}=298K$)

^b K_{OC} is the octanol/water partition coefficient, x_w is the aqueous solubility (mol/mol) and ΔS_s^e is the solution entropy for liquids (approx. -57 J/molK) at $T=298K$, Schwarzenbach et al. (1993)

^c K is the adsorptive vapor/solid surface parameter, RH is the relative air humidity and A , B and C are specific parameters for each compound.

Table 2. Temperature and relative humidity dependent parameters for the adsorption coefficient [Goss, 1992].

Coefficient	Ethanol	1,3-diclorbenzene
A ^a	$3.561 \cdot 10^{-10}$	$1.251 \cdot 10^{-9}$
B	5689	4571
C	0.0367	0.0313

Table 3. Hydraulic functions

	$\theta_l(\psi)$	$k_r(\psi)$
Brooks and Corey ^a	$\theta_l = \left(\frac{\psi_b}{\psi} \right)^\lambda \cdot (\varepsilon - \theta_{wr}) + \theta_{wr} \quad ; \quad \psi < \psi_b$ $\theta_l = \varepsilon \quad ; \quad \psi > \psi_b$	$k_r = \left(\frac{\psi_b}{\psi} \right)^\eta \quad ; \quad \psi < \psi_b$ $k_r = 1 \quad ; \quad \psi > \psi_b$
Haverkamp et al.	$\theta_l = \frac{\alpha(\theta_s - \theta_r)}{\alpha + \psi ^\beta} + \theta_r$ ^b	$k_r = a \psi ^b$ ^c

^a Where ψ is the matric potential. ψ can be related with P_l through, $\psi = P_l / \rho \cdot g$. ψ_b is the the bubbling pressure and $\eta=2+3 \cdot \lambda$, [Brooks and Corey, 1964].

^b [Haverkamp et al., 1977].

^c Supposed relationship.

Table 4. Hydrological parameters.

	Jackson	Baker
θ_{sat} (m ³ /m ³)	0.388	0.501
θ_{res} (m ³ /m ³)	$5 \cdot 10^{-3}$	$7.5 \cdot 10^{-3}$
K_s (m/s)	$1.98 \cdot 10^{-6}$	$9.167 \cdot 10^{-7}$
ψ_b (m)		-0.472
λ		0.328
α	3.953	
β	0.398	
a	$6.664 \cdot 10^{-3}$	
b	-2.09	

^a Calculated value with T=298K and RH=50%

Table 5. Physicochemical properties for EPTC and dieldrin.

	EPTC	Dieldrin
Molecular diffusion in air, D_g (m ² /s)	$5.8 \cdot 10^{-6}$ ^a	$4.3 \cdot 10^{-6}$ ^b
Molecular diffusion in water, D_l (m ² /s)	$5.5 \cdot 10^{-10}$ ^b	$5 \cdot 10^{-10}$ ^b
Aqueous solubility, (kg/m ³)	0.37 ^c	$1.4 \cdot 10^{-4}$ ^b
Partition coefficient Gas/Liq H_{GL}	$6.948 \cdot 10^{-4}$ ^d	$4.524 \cdot 10^{-4}$ ⁱ
Partition coefficient Sol/Liq H_{SL} ^j	41.42	258
Partition coefficient Organic Carbon /Water, K_{oc}	1563 ^c	9736 ^h
Solution enthalpy, $\Delta_{\text{sol}}H/R$ (K)	4464 ^f	5000 ⁿ

^a Using the correlation of *Fuller et al.* [1966]

^b Using the correlation of *Hayduck et al.* [1982]

^c *Freed et al.* [1967]

^d *Ericson* [1991]

^e *Kenaga et al.* [1980]

^f *Breiter et al.* [1998]

^g *Cohen and Ryan* [1989]

^h *Jury et al.* [1984c]

ⁱ *Mackay i Shiu.* [1981]

^j Where $H_{SL} = K_{oc} \cdot f_{oc} \cdot \rho_{\text{bulk}}$ ($\rho_{\text{bulk}} = 2.65 \text{ g/cm}^3$ and $f_{oc} = 0.01$)

^k *Griffoll i Cohen* [1994]

^l *Schwarz et al.* [1980]

^m *Karickhoff et al.* [1979]

ⁿ *Bissonette et al.* [1990]

Table 6. Physicochemical properties for ethanol, 1,3-dichlorbenzene and lindane.

	Ethanol	1,3-dichlorbenzene	Lindane
Molecular diffusion in air, D_g (m ² /s)	$1.02 \cdot 10^{-5}$ ^a	$6.9 \cdot 10^{-6}$ ^c	$5.8 \cdot 10^{-6}$ ^c
Molecular diffusion in water, D_l (m ² /s)	$1.24 \cdot 10^{-9}$ ^b	$7.9 \cdot 10^{-10}$ ^f	$5.5 \cdot 10^{-10}$ ^f
Aqueous solubility, (kg/m ³)	1000	$123 \cdot 10^{-3}$ ^g	$7.3 \cdot 10^{-3}$ ⁱ
Partition coefficient Gas/Liq H_{GL}	$2.151 \cdot 10^{-4}$ ^c	0.146 ^h	$1.485 \cdot 10^{-4}$ ^m
Partition coefficient Sol/Liq H_{SL} ^j	$1.06 \cdot 10^{-2}$	7.314	102.3
Partition coefficient Organic Carbon /Water, K_{oc}	0.2 ^d	138 ⁱ	1930 ⁿ
Solution enthalpy, $\Delta_{\text{sol}}H/R$	6600 ^c	2400 ^k	5500 ^l

^a *Reid et al.* [1977]

^b *Landolt-Börnstein* [1969]

^c *Snider and Dawson* [1985]

^d *Karickhoff et al.* [1981]

^e Using the correlation of *Fuller et al.* [1966]

^f Using the correlation of *Hayduck et al.* [1982]

^g *Mackay et al.* [1982]

^h *Mackay i Shiu* [1981]

ⁱ *Lee et al.* [1989]

^j Where $H_{SL} = K_{oc} \cdot f_{oc} \cdot \rho_{\text{bulk}}$ ($\rho_{\text{bulk}} = 2.65 \text{ g/cm}^3$ and $f_{oc} = 0.02$)

^k *USEPA* [1982]

^l *Montgomery et al.* [1990]

^m *Kucklick et al.* [1991] a 298K

ⁿ U.S. Department of Health and Human Services

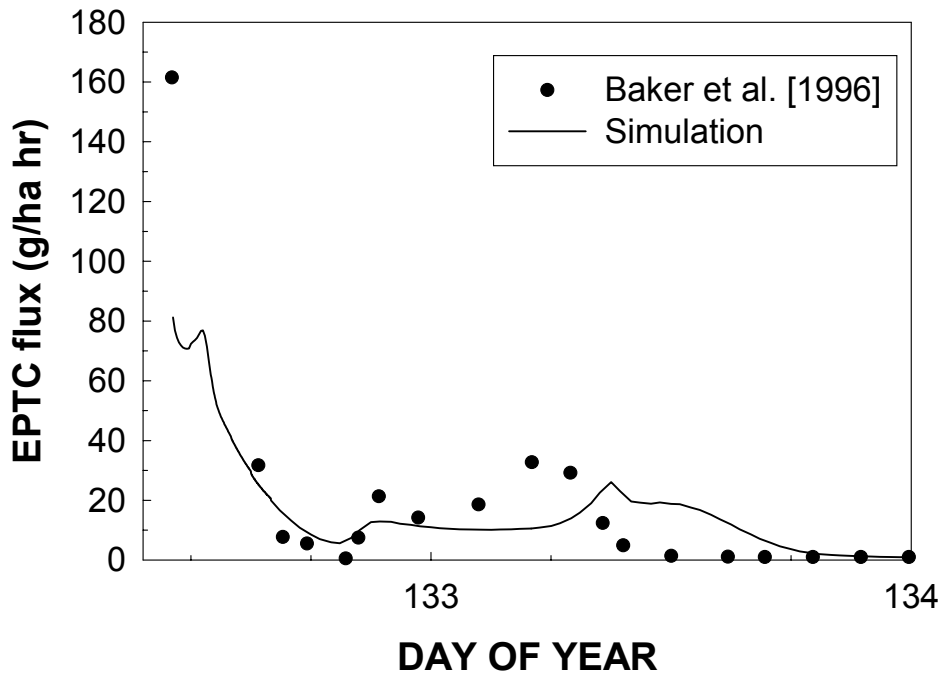


Figure 1

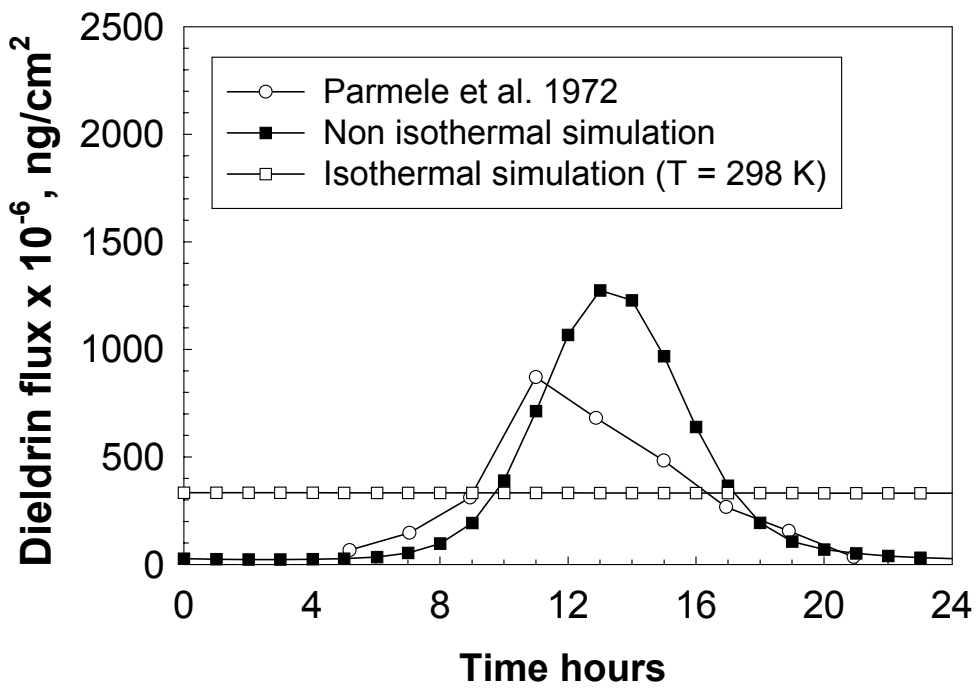


Figure 2

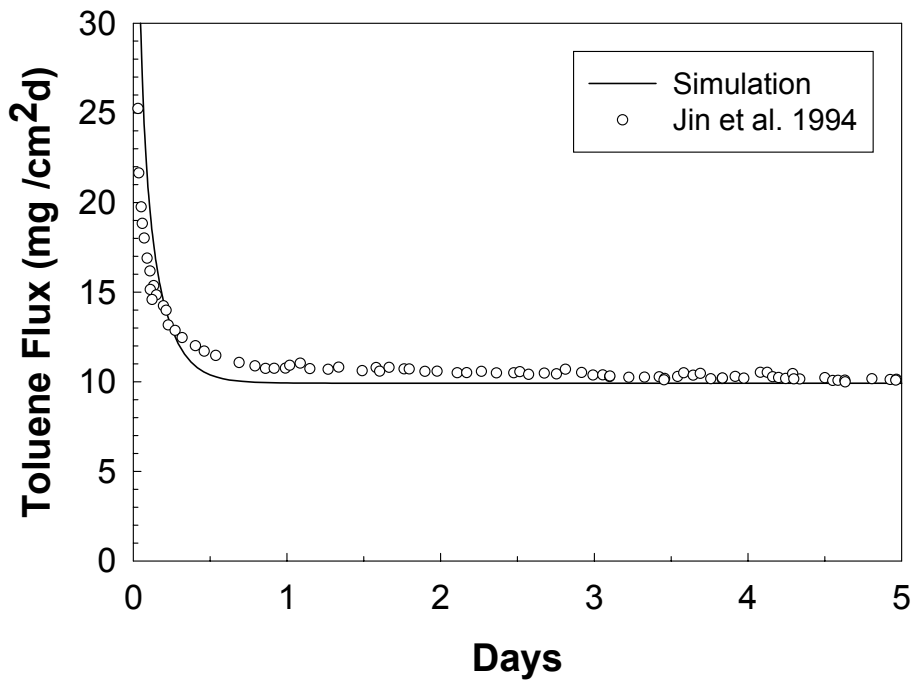


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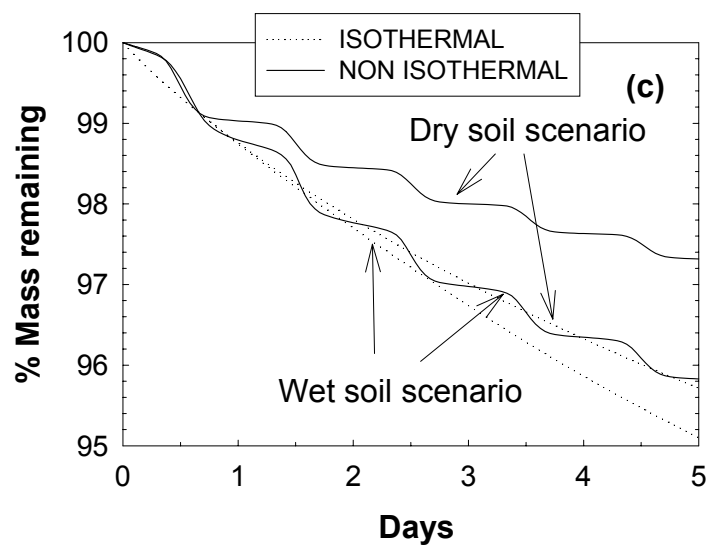
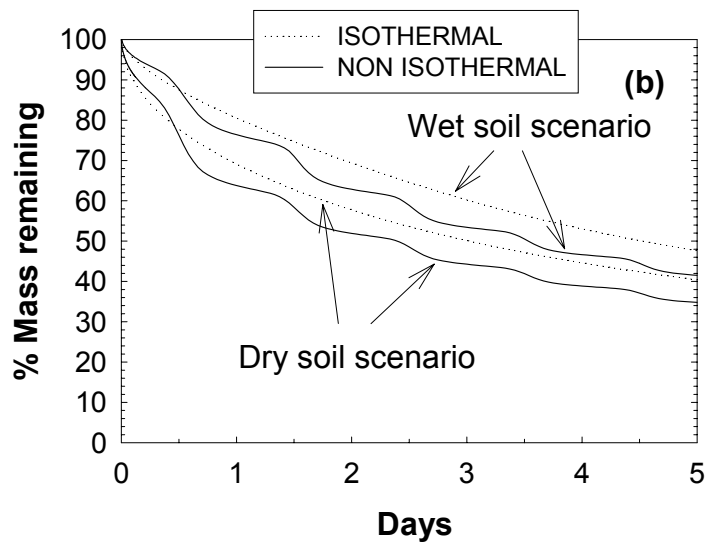
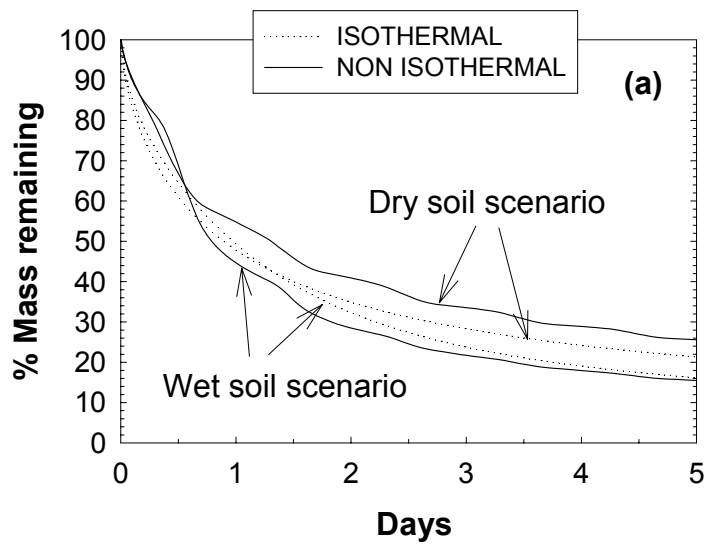


Figure 4

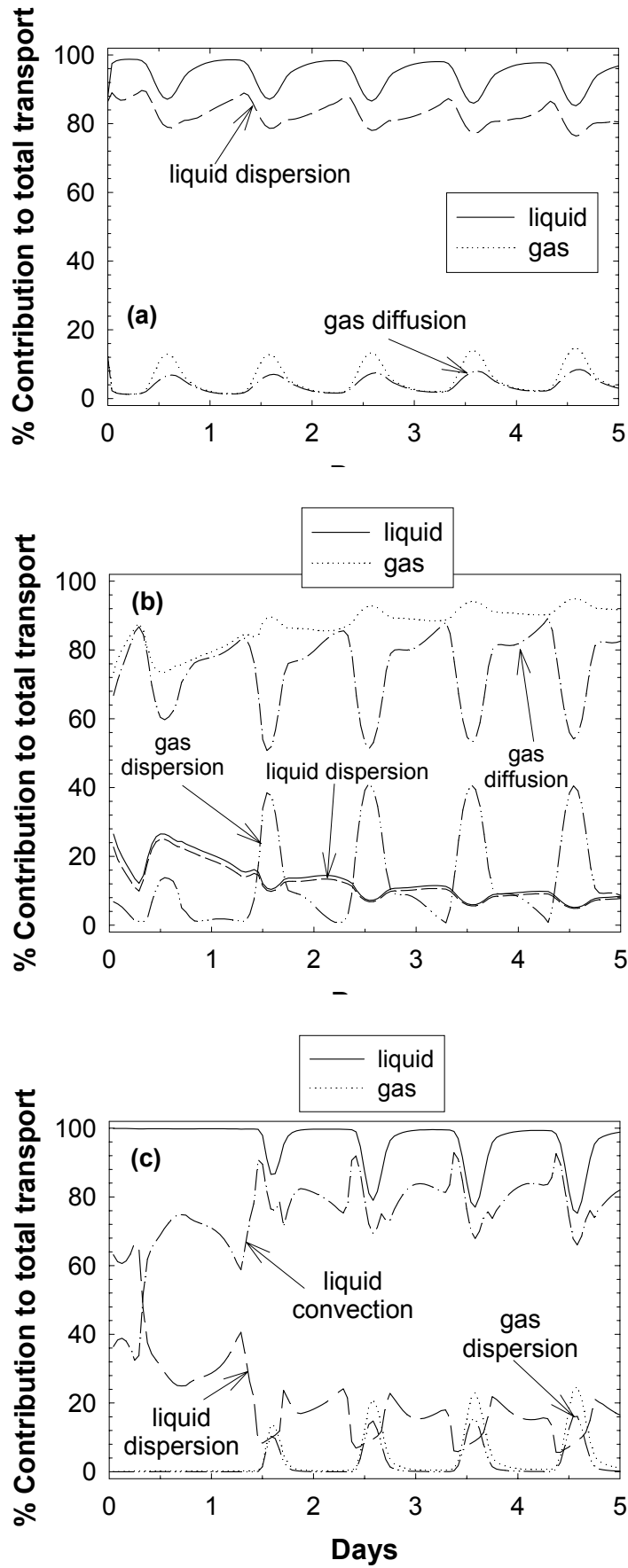


Figure 5

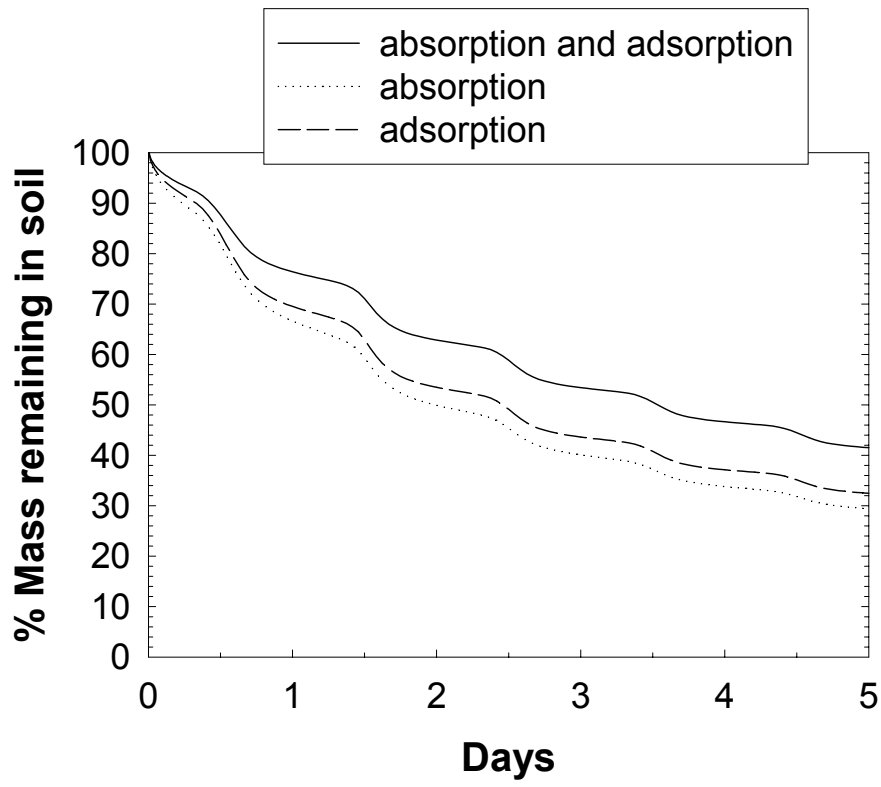


Figure 6

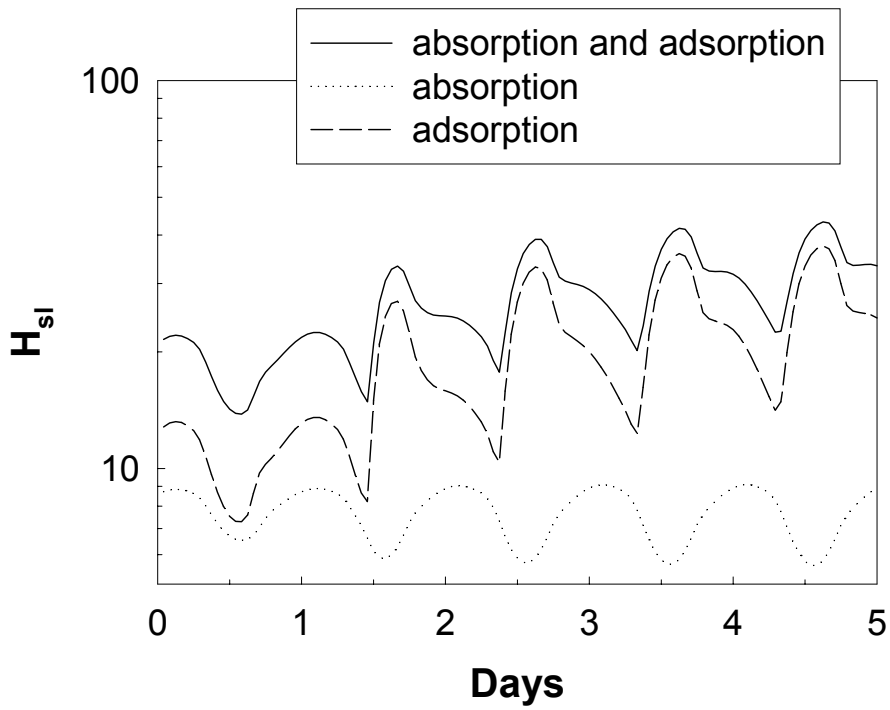


Figure 7