

The Fate of Non-Volatile Organic Chemicals in The Agricultural Environment

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Abstract: Multimedia dynamic model of the fate of non-volatile organic chemicals (NVOC) in the agricultural environment is described. The modeled environment, consisting of up to three major surfaces environmental compartments, includes air, agricultural soil, and surface water. This model is based on the equivalence approach suggested by Mackay and co-workers in 1989. As the movement of chemicals in the environment is closely associated with the movement of air, water and organic matter, the complete steady state mass budgets for air, water and particulate organic carbon (POC) between the model compartments are described. All of the model equations, which are expressed in equivalence notation, the mass balance for NVOC in the environmental surfaces compartments at dynamic state, and equations for the calculation of partitioning, overall persistence, total amount, total concentrations at dynamic state and intermedia fluxes of organic chemicals between air, water, and soil at steady-state are provided.

Keywords: Non-volatile organic chemicals; Equivalence; Multimedia model; Dynamic; Partitioning

INTRODUCTION

Organic pollutants from the agricultural environment can enter the atmosphere by a variety of different routes, particularly from direct discharges, wind erosion of soil or volatilization from soil or water^[1,2]. Upon entry into the atmosphere, pollutants are transported and distributed over long distances, through wet and dry processes^[3,4]. However, if the pollutants enters the environment, two groups of processes affect its fate: (i) transport and transfer processes that move a chemical among ecosystem compartments and away from the emission point, include sorption, volatilization^[5], runoff^[6], and leaching^[7], and (ii) degradation processes that convert chemical to transformation products^[8] include photo, chemical and microbial degradation^[9]. Predicting the fate of organic pollutants released into the environment is necessary to anticipate, and thereby minimize, adverse impacts away from the point of emission. This means that we must understand what happens to a chemical once it has been emitted, and we must be able to forecast its behavior in the environment. Using this

information, the probable adverse impacts on the environment and on human health can then be estimated.

The multimedia fate and transport models (MFTMs) have been developed and used for many years to simulate the fate of such contaminants, such as the influence of forests on the overall fate of semivolatile organic compounds^[10]; urban area model^[11]; the great lakes region (CHEMGL)^[12]; coastal zone model for persistent organic pollutants (CoZMo-POP 2)^[13]. These models are fugacity-based, which are valid for most volatile organic pollutants and very hydrophobic compounds.

Many of the chemicals used in agricultural activities are considered environmentally non-volatile (e.g., glyphosate; paraquat; bentazon) that is, they do not partition appreciably into air. The fate and transport processes of non-volatile organic chemicals (NVOC) in the agricultural environment at dynamic or even at steady-state conditions are not obvious yet. The purpose of this paper is to develop multimedia fate and transport model of NVOC in the agricultural environment at

dynamic conditions. In the following context model description is provided.

MODEL STRUCTURE

Current model is based on the dynamic Level IV equivalence model developed by Mackay and co-workers^[14]. The basic concept of the equivalence approach are fully described elsewhere^[14-18], and are only briefly summarized here. This approach is used to estimate NVOC fate on a various scales. Below we describe modifications to the Level IV model to allow its application to agricultural environment for NVOC.

Model compartments: A typical MTFM divides the environment into a number of boxes or compartments, which are considered well-mixed and homogeneous with respect to both environmental characteristics and chemical contamination^[18]. These environmental compartments are then linked by a variety of inter-compartmental transfer processes^[13]. Current model comprise three bulk compartments (Fig. 1): air (A), surface water (W), and agricultural soil (S). These compartments are linked by up to seven transport processes from X to Y medium (D_{XY} , m^3/h). Chemical can enter air and water through advection. Chemical can also enter each medium X through a direct emission, E_X (mol/h). Each bulk compartment consists of pure and particulate-phases of specified volume. Chemicals are assumed to be in equilibrium between these phases within each bulk compartment (e.g., between dissolved and suspended particulate-phases within water). Chemical can transfer among compartments and can be lost from all compartments through various transformation processes^[11].

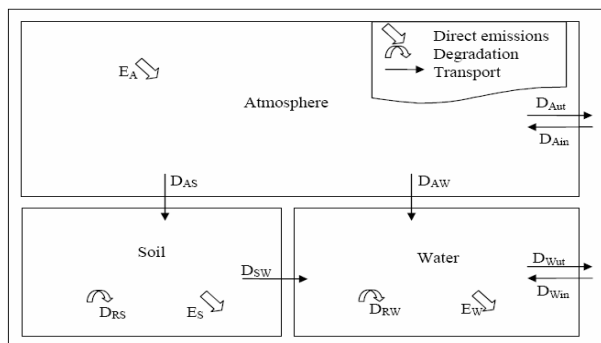


Fig. 1: Schematic representation of the environmental compartments and contaminant fate processes

Transfer fluxes of contaminants: The movement of chemicals in the environment is closely associated with

the movement of air, water and organic matter. In the current model, advective inter-compartmental transfer fluxes for the contaminants are calculated as the product of a flux of a carrier phase G in units of m^3/h , namely air (G_a), water (G_w), and particulate organic carbon (G_p), and a contaminant concentration (C) in that phase in units of $moles/m^3$. Solving the contaminant mass balance thus requires the construction of mass balances for air, water and particulate organic carbon (POC) within the modeled system. In contrast to the fluxes of the contaminants, the fluxes of these carrier phases were assumed by to be constant in time. In the following, details are provided for the construction of mass balances for air, water, and POC at a steady state situation.

Mass balance of air: With only one atmospheric compartment and one advection rate in and out of the model region, the mass balance for air, (m^3/h) is calculated using Eq. (1) in Table 1. In this equation, V_A is the volume of atmospheric compartments in m^3 ; τ_A is the atmospheric residence time in h, which calculated

$$\text{as: } \tau_A = \frac{L_A}{WS} \quad (1)$$

where L_A is the length of atmospheric compartment, m, and WS is the wind speed, m/h.

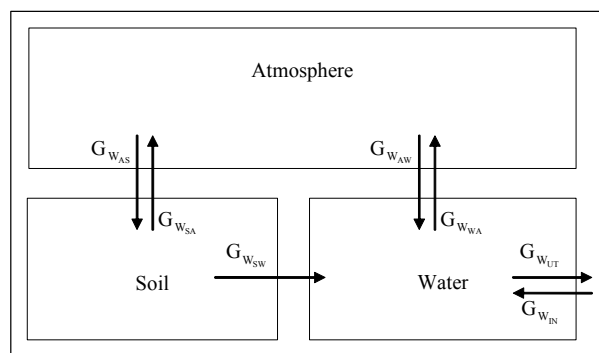


Fig. 2: Water fluxes between the model compartments

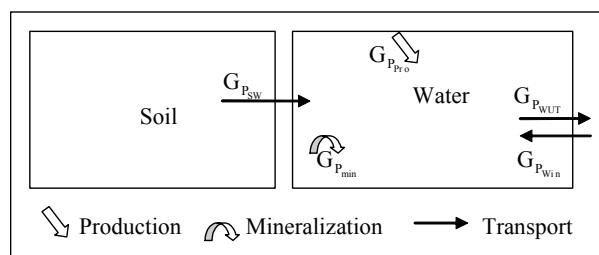


Fig. 3: POC budget for the soil and water compartments

Mass balance for water: A complete steady state water balance is formulated for the model region, i.e. a consistent set of up to 7 inter-compartmental water fluxes, G_W , between modeled compartments (Fig. 2). The water flux to soil compartment by precipitation, $G_{W_{AS}}$ in m^3/h (Eq. (2) in Table 1), is estimated from rain rates for the terrestrial environment (U_S , m/h), and the surface area of terrestrial compartment A_S , m^2 . By analogy with $G_{W_{AS}}$, the water flux to aquatic compartment by precipitation, $G_{W_{AW}}$ in m^3/h (Eq. (3) in Table 1), is a product of the rain rates for the aquatic compartment, U_W in m/h, and its surface area, A_W in m^2 . Evaporation loss from soil compartment, $G_{W_{SA}}$ in m^3/h (Eq. (4) in Table 1) is estimated employing fractions ϕ_S of the total water flow to soil compartment that evaporates from that compartment. Thus, by analogy with $G_{W_{AW}}$, the evaporation from water compartment, $G_{W_{WA}}$ in m^3/h (Eq. (5) in Table 1) in this equation, ϕ_W is the fraction of the total water flow to water compartment that evaporates from that compartment. The inter-compartmental water fluxes are then derived as the balance of input by precipitation and run-off and loss by evaporation. Thus, the run-off flux from soil compartment, $G_{W_{SW}}$ in m^3/h is calculated using Eq. (6) in Table 1. The net flow between water compartment and outside, $G_{W_{NUT}}$ in m^3/h is calculated using Eq. (7) in Table (1). Finally, in the water compartment, ϕ_W is defined as the fraction of net water input to a downstream compartment that evaporates from that compartment, whereas $\phi_{G_{W_{UT}}}$ is a factor by which the water flux in the water compartment is increased by inflow from the soil compartment. However, the water flows from water compartment to outside, $G_{W_{UT}}$ in m^3/h is calculated using Eq. (8) in Table 1, and the water flow from outside to water compartment, $G_{W_{IN}}$ in m^3/h is calculated using Eq. (9) in Table 1.

Mass balance for particulate organic carbon: Both within the soil and water compartments, many organic contaminants attach themselves preferentially to organic material, and transport of contaminants between virtually all environmental media can be mediated through organic matter^[13]. In the current model, a complete steady state mass balance for organic matter is formulated for the model region, i.e. a consistent set of up to five POC production, transport and mineralization rates, G_p , (m^3 POC/h) (Fig. 3).

Specifically, the concentration of POC in the water compartment, C_{PW} in g/m^3 is calculated from the balance of these processes. Even though they are not required for the contaminant mass balance, rates of primary production and POC mineralization are also calculated to complete and assure the consistency of the mass balance. Required parameters for construction of these mass budgets are: (i) the water fluxes, G_W , (ii) the concentration of POC in the water flowing into the model domain in g/m^3 , C_{PIn} , and (iii) the mineralization rate in the water compartments as fraction of the primary productivity in h^{-1} , ϕ_{min} . Wania et al. 2006 have derived the POC concentrations and fluxes as following:

The inflow of POC from soil to water (Eq. (10) in Table 1), $G_{P_{SW}}$ in units of m^3/h is calculated as a product of the run-off flux from soil compartment $G_{W_{SW}}$, and the volume fraction of solids in soil run-off, v_{SS} . The volume fraction of solids in soil run-off is calculated from the mass fraction of organic carbon using:

$$v_{SS} = \frac{1}{1 + \frac{(1 - m_s) \cdot \rho_{OC}}{m_s \cdot \rho_{mm}}} \quad (2)$$

where m_s is the mass fraction of organic carbon in solids of soil compartment, ρ_{OC} , ρ_{mm} are the density of organic carbon and mineral matter in units of g/m^3 .

The primary POC production in the aquatic compartment, $G_{P_{Pro}}$ in units of m^3/h is calculated using Eq. (11) in Table 1. In this equation, P_W is the primary productivity in the aquatic compartment, g POC/ $(m^2 a)$, A_W is the surface area of aquatic compartment, m^2 . The POC mineralization in the aquatic compartment (Eq. (12) in Table 1), $G_{P_{min}}$ in units of m^3/h is calculated as a fraction of the primary productivity. The calculation of the POC fluxes in and out of the aquatic compartment, followed by simultaneous solution of the POC mass balance over this water compartment to yield concentrations of POC in water (C_{PW}), which calculated using Eq. (13) in Table 1. In this expression, C_{PIn} is the concentration of POC in the water flowing into the model domain in units of g/m^3 . C_{PW} will be needed in the later calculation to calculate the phase partitioning in the aqueous system.

Description of contaminant fate: Unsteady-state conditions give differential equations in time. The simplest method of sitting up the equation is to write:

$$\frac{d(\text{contents})}{dt} = \text{total input rate} - \text{total output rate} \quad (3)$$

Table 1 Equations used to calculate the air, water, and particulate organic carbon fluxes between the model compartments in m³/h

Mass balance	Fluxes equations
Air	1. $G_A = V_A / \tau_A$
Water	2. $G_{W_{AS}} = U_S \cdot A_S$
	3. $G_{W_{AW}} = U_W \cdot A_W$
	4. $G_{W_{SA}} = \phi_S \cdot G_{W_{AS}}$
	5. $G_{W_{WA}} = \phi_W \cdot (G_{W_{AW}} + G_{W_{SW}})$
	6. $G_{W_{SW}} = (1 - \phi_S) \cdot G_{W_{AS}}$
	7. $G_{W_{NUT}} = (1 - \phi_W) \cdot (G_{W_{AW}} + G_{W_{SW}})$
	8. $G_{W_{UT}} = G_{W_{NUT}} \cdot (1 + \phi_{G_{WUT}})$
	9. $G_{W_{IN}} = G_{W_{NUT}} \cdot \phi_{G_{WUT}}$
	POC
11. $G_{P_{Pro}} = P_W \cdot A_W / (\rho_{OC} \cdot 8760)$	
12. $G_{P_{min}} = G_{P_{Pro}} \cdot \phi_{min}$	
13. $C_{PW} = (G_{P_{SW}} + G_{P_{Pro}} - G_{P_{min}} + (G_{W_{IN}} \cdot C_{Pin} / \rho_{OC})) / (G_{W_{UT}} / \rho_{OC})$	

Table 2: Mass balance equations for each phase

Medium	Mass balance equations
1. Air	$d(V_A Z_{BA} Aq_A) / dt = E_A + D_{AIN} \cdot Aq_{AUT} - Aq_A \cdot (D_{AS} + D_{AW} + D_{AUT})$
2. Water	$d(V_W Z_{BW} Aq_W) / dt = E_W + D_{AW} \cdot Aq_S + D_{SW} \cdot Aq_S + D_{WIN} \cdot Aq_{WUT} - Aq_W \cdot (D_{RW} + D_{WUT})$
3. Soil	$d(V_S Z_{BS} Aq_S) / dt = E_S + D_{AS} \cdot Aq_A - Aq_S \cdot (D_{RS} + D_{SW})$

Table 3 Equation used to calculate the dimensionless Z-values^a

Phase	Equation
Pure	
1. Air	$Z_A = Z_W \cdot K_{AW}$ (probably zero)
2. Atmospheric particles	$Z_Q = Z_W \cdot K_{QW}$
3. Water	$Z_W = 1$
4. Water suspended particles	$Z_P = Z_W \cdot \rho_P \cdot K_P / 1000$
5. Soil	$Z_S = Z_W \cdot \rho_S \cdot K_{SW} / 1000$
6. Bulk	
7. Air	$Z_{BA} = Z_A + v_{QA} \cdot Z_Q$
8. Rain water	$Z_{BR} = Z_W + v_{QA} \cdot Z_Q \cdot Q$
9. Water	$Z_{BW} = Z_W + Z_P \cdot (C_{PW} / \rho_{OC})$
10. Soil	$Z_{BS} = v_{AS} \cdot Z_A + v_{WS} \cdot Z_W + \left\{ (1 - v_{WS} - v_{AS}) \left[1 + \left(\frac{(1 - m_S) \rho_{OC}}{(m_S \cdot \rho_{MM})} \right) \right] \right\} \cdot Z_P$

Table 4: Equation used to calculate the D-values in units of m³/h

Compartments		Process	Equation
From	To		
Air	Water	1. Total	$D_{AW} = D_{WWD} + D_{WDD}$
		2. Wet deposition of gases and particles	$D_{WWD} = G_{WAW} \cdot Z_{BR}$
		3. Dry particle deposition	$D_{WDD} = U_{DW} \cdot v_{QA} \cdot Z_Q \cdot A_W$
Air	Soil	4. Overall deposition	$D_{AS} = U_{DS} \cdot v_{QA} \cdot Z_Q \cdot A_S + G_{WAS} \cdot Z_{BR}$
Soil	Water	5. Water and solid runoff	$D_{SW} = G_{WSW} \cdot Z_W + G_{PSW} \cdot Z_S$
Losses		6. Degradation	$D_{DRX} = V_X \cdot Z_{BX} \cdot k_{RX}$
Advections		7. Advection of air into model domain	$D_{AIN} = Z_{BAIN} \cdot G_A$
		8. Advection of air out of model domain	$D_{AOUT} = Z_{BA} \cdot G_A$
		9. Advection of water into model domain	$D_{WIN} = Z_{BWIN} \cdot G_{WIN}$
		10. Advection of water out of model domain	$D_{WUT} = Z_{BW} \cdot G_{WUT}$

The input and output rates should be in units of amount/time, e.g., mol/h or g/h. The “contents” must be in consistent units, e.g., in mol or g, and dt, the time increment, in units consistent with the time unit in the input and output terms, e.g., h. The differential equation can then be solved along with an appropriate initial or boundary condition to give algebraic expression for concentration as a function of time^[18].

Based on the (Eq. 3), contaminant fate in the current model is expressed with the help of one dynamic mass balance equation for each of the three model compartments. These equations are formulated in terms of equivalence^[16], in units of mol/m³, i.e. employ the concepts of Z-values, (dimensionless) to describe phase partitioning and D-values, in units of m³/h to describe contaminant fate processes. They thus take the generic form:

$$\frac{d(V_X BZ_X Aq_X)}{dt} = E_X + \sum_Y D_{YX} \times Aq_Y - \left(\sum_Y D_{XY} \times D_{RX} \right) \times Aq_X \quad (4)$$

In this equation, V_X , Z_{BX} , Aq_X are the volume, bulk Z-value and equivalence of compartment X, D_{XY} and D_{YX} are the D-values describing the transport processes delivering contaminant from compartment Y to compartment X, and vice versa, E_X is the emission rate into compartment X in mol/h, and D_{RX} is the D-value describing the degradation loss in compartment X. The three differential mass balance equations are solved using a stepwise approach, with a finite difference approximation. The expressions for phase partitioning,

inter-media transport and degradation build upon those from previous fugacity/aquivalence models^[13,16,18-19].

In the following context, details are provided for the calculation of the mass balance equations for each model compartment. These calculations are based on equation 4 and figure 1.

The mass balance equation for Air: With two input rates to the atmospheric compartment (1) emission rate into air compartment, E_A in mol/h, and (2) advection of air into model region, D_{AIN} in m³/h, and three loss rates (1) deposition of contaminant to terrestrial compartment, D_{AS} in m³/h, (2) deposition of contaminant to aquatic compartment, D_{AW} in m³/h, and (3) advection of air out of model region, D_{AOUT} in m³/h, the mass balance equation for atmospheric compartment is calculated using Eq. (1) in Table 2.

The mass balance equation for water: With four input rates to the aquatic compartment (1) emission rate into water compartment, E_W in mol/h, and (2) advection of water into model region, D_{WIN} in m³/h, (3) water runoff from soil compartment, D_{SW} in m³/h, and (4) deposition of contaminant from atmospheric compartment, D_{AW} in m³/h, and two loss rates (1) degradation in water, D_{RW} in m³/h, and (2) advection of water out of model region, D_{WUT} in m³/h, the mass balance equation for aquatic compartment is calculated using Eq. (2) in Table 2.

The mass balance equation for soil: With two input rates to the terrestrial compartment (1) emission rate into terrestrial compartment, E_S in mol/h, and (2) deposition of contaminant from atmospheric compartment, D_{AS} in m^3/h , and two loss rates (1) water run-off to aquatic compartment, D_{SW} in m^3/h , and (2) degradation in soil, D_{RS} in m^3/h , the mass balance equation for terrestrial compartment is calculated using Eq. (3) in Table 2.

These mass balance equations are needed to evaluate the partitioning of chemicals in the agricultural environment, and to calculate the overall persistence, concentration, and amount of chemicals in each environmental phase.

In the following, details are provided for how the various Z and D-values are calculated in the current model.

Description of phase partitioning: As ideal for fugacity/aquivalence models^[20], equilibrium phase partitioning in the current model is expressed in terms of Z-values or the compartment capacities. The Z-values for NVOC are calculated using the equivalence approach. As discussed previously, this approach was developed by Mackay and co-workers^[14]. The derivation of equivalence approach as a criterion of equilibrium are fully described elsewhere^[18] and are only briefly summarized here.

Mackay et al. 1996b have described that the capacity of water compartment (Z_W) for all NVOC is first defined as 1.0 and all other Z-values, including that for aerosols, are deduced as:

$$Z_X = K_{XW} \cdot Z_W \quad (5)$$

It is desirable to calculate a Z-value for bulk phase consisting of other phases at equilibrium. The use of bulk Z-values helps to simplify calculations by reducing the number of compartments^[18]. The bulk Z-value for a compartment j , (Z_{Bj}), (Eq. 2) is an average of the compartment capacity, Z_j , of the various gaseous, aqueous and solid sub-phases making up this compartment, weighted by the volume fraction of these sub phases.

$$Z_{Bj} = \sum v_{ij} \cdot Z_j \quad (6)$$

where v_{ij} is the volume fraction of sub-phase i in phase j , m^3/m^3 , and Z_j is the dimensionless capacity of phase j .

In the subsequent, details are provided for the phase partitioning in each of three model compartment.

Phase partitioning in the aqueous system: As discussed previously, the capacity of pure water Z_W is

defined as 1.0. Particulate organic carbon (POC) in water is important, like aerosols in the atmosphere; it serves as a vehicle for the transport of contaminants from the bulk of the water to bottom sediment^[18]. The Z-value for POC, Z_P (Eq. (4) in Table 3), is a product of the POC to water partition coefficient, K_P in (L/kg), and the capacity of pure water^[21]. The bulk Z-value for water compartment (Z_{BW}) is calculated using Eq. (10) in Table 3, where C_{PW} is the concentration of POC in the water column, were previously derived as part of the POC mass balance.

Phase partitioning in the air phase: Based on Eq. (5), the capacity of atmospheric compartment, Z_A is calculated from air-water partition coefficient (K_{AW}) (Eq. (1) in Table 3). Definition of a zero K_{AW} , which results in Z_A being zero, is acceptable. The Z-value for atmospheric particles, Z_Q , is calculated using Eq. (2) in Table 3. In this equation, K_{QW} is the (hypothetical) aerosol-water partition coefficient. Mackay et al. 1996b have suggested a value for (hypothetical) K_{QW} of 100, causes the entire chemical in the atmosphere to be associated with aerosol particles. Changing this value of 100 has no significant effect on chemical fate. The bulk Z-value for the atmosphere is calculated using Eq. (8) in Table 3. In this equation, v_{QA} represent the volume fractions of aerosol in air. If the concentration of aerosols or total suspended particulates is TSP ng/m^3 , this corresponds to 10^{-12} TSP kg/m^3 and to a volume fraction of

$$v_{QA} = \frac{10^{-12} \text{TSP}}{\frac{\rho_Q}{1000}} \quad (7)$$

where ρ_Q is the aerosol density in kg/m^3 ^[18]. The rain bulk Z-value is calculated using Eq. (9) in Table 3, where Q is the particle scavenging ratio.

Phase partitioning in the soil phase: The capacity of soil compartment, Z_S is calculated from soil-water partition coefficient (K_{SW}) (Eq. (5) in Table 3). Soil is a composite of air, water and solids. The non-organic fraction of the solids is assumed to make a negligible contribution to the bulk Z-value for soils. Thus, the soil bulk Z-value is calculated using Eq. (11) in Table 3. In this equation, v_{AS} , v_{WS} , and the term in wavy brackets are the volume fraction of air, water, and particulate organic carbon in bulk soil, respectively, where ρ_{mm} , ρ_{OC} is the density of mineral matter, and organic carbon, respectively in g/m^3 , and m_S is the mass fraction of organic carbon in solids of soil compartment.

Description of chemical fate processes: Transport and degradation processes in equivalence-based models are described with the help of D-values in units of m^3/h ^[16]. The group G Z, and other like it, appear so frequently in later calculations that it is convenient to designate them as D-values, i.e.,

$$D = U \cdot A_X \cdot Z_X \quad (8)$$

where U is the intermedia transport parameter, i.e., mass transfer coefficient in m/h, A_X is the surface area of compartment X in m^2 , and Z_X is the dimensionless capacity of compartment X.

Description of air-surface exchange: In air-surface exchange, there can be deposition by the parallel processes of (1) dry particle deposition, (2) wet particle deposition, (3) rain dissolution, i.e. the dissolution of contaminant in the falling rain drops (wet gaseous deposition), and (4) diffusive absorption-volatilization. Since the current model is fairly applicable to NVOOC that have a negligible or zero vapor pressure, the model thus neglects the absorption-volatilization process.

Aerosol particles have a very high surface area and thus sorb many pollutants, especially those of a very low vapor pressure. Dry particle deposition occurs when gases and aerosol particles are intercepted by the earth's surface under the influence of gravity in the absence of precipitation. Deposition velocity, is quite slow and depends on the turbulent condition of the atmosphere; size and properties of the aerosol particle; the nature of the ground surface. Typical velocity is about 0.3 cm/s or 10.8 m/h.

Rain is often highly contaminated with substances, and often much more contaminated than surface water. Wet particle deposition is by washout of contaminant sorbed onto particles by precipitation. It is directly proportional to the concentration of pollutant in the rain phase. The concentration of pollutants in wet deposition is due to two important effects with quite different physical mechanisms: aerosol particle scavenging, and gas scavenging^[22]. Wet deposition is about twice the dry deposition.

Description of air-water exchange: Wet deposition of gaseous and particle-bound substances is treated as an advective transport process, and the D-value is calculated using Eq. (2) in Table 4. In this equation, G_{wAw} is the product of the rain water flow to the water surface in m^3/h (Eq. (3) in Table 1), and Z_{BR} is the dimensionless bulk Z-value of rain (Eq. (9) in Table 3). The D-value for dry particle deposition, D_{wDd} is calculated using Eq. (3) in Table 4, where A_w is the

water compartment surface area, m^2 , and U_{DW} is the dry particle deposition velocity to water compartment in m/h. This velocity is volumetric rate of particle transport:

$$U_{DW} = \frac{G_Q}{A_w} \quad (9)$$

where G_Q is the flow of aerosol deposited to water compartment, m^3/h . Thus, summing of the D-values for wet deposition of gaseous and particle and dry particle deposition (Eqs. (2) and (3) in Table 4) yields the overall D-values for atmospheric deposition to water (Eq. (1) in Table 4).

Description of air-soil exchange: By analogy with the overall D-value for atmospheric deposition to soil is calculated using Eq. (4) in Table 4. In this equation, A_S is the soil compartment surface area, m^2 , G_{wAs} is the product of the rain water flow to the soil surface in m^3/h (Eq. (2) in Table 1), and U_{DS} is the dry particle deposition velocity to soil compartment in m/h, which calculated similar to U_{DW} , (Eq. 9) with considering the surface area for soil but not for water.

Description of soil-water exchange: Contaminants may be transferred from soil to water through solids or water runoff. The D-values for these processes are calculated using Eq. (5) in Table 4. In this equation, G_{wSw} is the run-off flux from soil to water in m^3/h (Eq. (6) in Table 1), and G_{pSw} is the inflow of POC from soil to water in m^3/h (Eq. (10) in Table 1).

Description of loss processes: The loss or removal processes for a contaminant are the reaction (degradation). Mackay, 2001 has used a simple first-order kinetic expression for all reactions. The basic rate equation is:

$$\text{Rate } N = V \cdot C \cdot k = M \cdot k \quad \text{mol/h} \quad (10)$$

where V is the phase volume in m^3 , C is the concentration of the chemical in mol/m^3 , M is the amount of chemical, and k is the first-order rate constant with units of reciprocal time.

Reaction rates increase with increasing temperature. Svante Arrhenius determined the relationship between the reaction rate constant and temperature

$$k = A \cdot \exp \frac{AE}{RT} \quad (11)$$

where A is a constant that is characteristic of the reaction, AE is the activation energy of the degradation

reaction in J/mol, T is the absolute temperature in K, and R is the ideal gas constant in J/(K·mol).

Occasionally, it is desirable to convert a rate constant from a known or reference temperature to a second temperature. In this case, Eq. (11) can be used for two different temperatures, the equations for k equated, and the constant A drops out^[22].

$$k_{T_1} = k_{T_2} \cdot \exp \frac{AE}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (12)$$

In the current model, all degradation rates are calculated as a function of compartment temperature using a contaminant-specific degradation rate k_{DRX} at the reference temperature 25°C and activation energy AE_X . Thus,

$$k_{RX} = k_{DRX} \cdot \exp \frac{AE_X}{R} \left(\frac{1}{T} - \frac{1}{T_X} \right) \quad (13)$$

This degradation rate is assumed to include all degradation processes that the chemical can undergo, including biodegradation, hydrolysis, and photolysis. Thus, the D-values describing degrading reactions in each model compartments are calculated using Eq. (8) in Table 4. In the later expression, the D-values are calculated using the bulk-phase Z-values, degradation rates for the bulk compartment and not for a specific phase.

Description of advection processes: The D-values for advected air into/out of model domain, (Eqs. (7), (8) in Table 4) is the product of the transfer rate of the air G_A , (Eq. (1) in Table 1) in units of m³/h, and its dimensionless bulk Z-value, Z_{BA} (Eq. (8) in Table 3). The D-values for advected water into/out of model domain, (Eqs. (9), (10) in Table 4) is the product of the water flow from outside to model domain and vice versa, (Eqs. (8), (9) in Table 1) in units of m³/h, and its dimensionless bulk Z-value, Z_{BW} (Eq. (10) in Table 3).

Overall persistence, concentration, and total amount: Environmental persistence is an important criterion when assessing chemical contaminants^[23]. The overall environmental persistence may be predicted as the total amount of chemical in the environment at steady state divided by the total loss rate^[24]. In the current, the overall persistence τ (h) is calculated using the following expression:

$$\tau = \frac{\sum_X Aq_X \cdot V_X \cdot Z_{BX}}{\sum_X Aq_X \cdot D_{RX}} \quad (14)$$

where Aq_X is the equilibrium criterion (aquivalence) in mol/m³, V_X is the volume of compartment X in m³, Z_{BX}

is the dimensionless bulk Z-value for compartment X, and D_{RX} is the degradation in compartment X in m³/h.

The concentration of chemical (mol/m³) in compartment X is the product of the dimensionless compartment capacity Z_X , and its relative aquivalence Aq_X in units of mol/m³.

The total amount of chemical in compartment X in mol is the product of dimensionless bulk compartment capacity Z_{BX} , compartment volume in m³, and its relative aquivalence Aq_X in units of mol/m³.

RESULTS AND DISCUSSION

The use of this model, intermedia fluxes of organic chemicals between air, water, and soil at steady-state, partitioning, overall persistence, total amount, and total concentrations at dynamic conditions can be calculated. The results of these calculations are useful to decision makers because this model provides an appropriate quantitative framework to evaluate our understanding of the complex interactions between chemicals and the agricultural environment. It is introduced to set clean-up standards, to assess the relative importance of chemical emissions, to evaluate the partitioning, persistence, long-range transport of non-volatile organic pollutants, and set priorities in agricultural pollution prohibition.

CONCLUSION

A MFTM at non-steady state conditions has been developed that incorporates mechanisms of NVOC transport and transformation in the agricultural environment. The model, an adaptation of Mackay's Level IV aquivalence model, includes the air, surface water, and agricultural soil compartments. Current model aimed to evaluate the fate of NVOC in the major surfaces compartments for agricultural environment. In addition to the model usage benefits mentioned above, we believe that the model is a useful first step towards improving our understanding of the influence of the built environment on chemical fate.

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