

ASSESSING THE FATE OF PESTICIDES IN GROUNDWATER BY COMBINING BATCH AND SOIL COLUMN EXPERIMENTS WITH NUMERICAL MODELING

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Summary. *The risk assessment of groundwater pollution by pesticides may be based on pesticide sorption and biodegradation kinetic parameters that may be estimated with inverse modeling of datasets from either batch or continuous flow soil column experiments. In the present work, a chemical non-equilibrium and non-linear 2-site sorption model is incorporated into solute transport models to invert the datasets of batch and soil column experiments, and estimate the kinetic sorption parameters for two pesticides: N-phosphonomethyl glycine (glyphosate) and 2,4-dichlorophenoxy-acetic acid (2,4-D). When coupling the 2-site sorption model with the 2-region transport model, except of the kinetic sorption parameters, the soil column datasets enable us to estimate the mass-transfer coefficients associated with solute diffusion between mobile and immobile region.*

1 INTRODUCTION

The widespread application of pesticides in agriculture has led to their infiltration in soil and groundwater pollution. The fate of pesticides in subsurface is governed by the interaction of physical / chemical / biological processes as for instance: the sorption in soil grains, the volatilization, the degradation through biotic and abiotic mechanisms, etc¹. Computational numerical codes are commonly used to map the spatial and temporal evolution of pesticide concentration in groundwater². Occasionally, continuous soil column tests or batch experiments are combined with inverse modeling approaches to estimate the kinetic

parameters of pesticide sorption and/or biodegradation processes³. A discrepancy may exist between the values of parameters estimated by the aforementioned two types of experiments⁴. The modeling of solute sorption in soils is often based on the local equilibrium assumption (LEA). However, in some cases the equilibrium is not reached rapidly enough with respect to advective transport, and sorption is limited by some chemical reaction rate or physical mass-transfer resistance⁵. In the present work, a non-linear Freundlich isotherm is coupled with a 2-site sorption model⁶ to invert datasets of soil column and batch experiments for glyphosate and 2,4-D, and estimate the kinetic sorption parameters. In order to decouple the mass-transfer resistance from the sorption kinetics, a two region model⁷ is combined with the 2-site sorption model.

2 MATERIALS AND METHODS

2.1 Soil column and batch experiments

An organophosphorus herbicide (glyphosate, solubility=11.6 g/L at 25°C) and a chlorinated herbicide (2,4-D, solubility=790 mg/L at 25°C) were selected. Feed solutions, that are representative of polluted groundwater, were prepared by dissolving each pesticide in synthetic groundwater at concentrations 100mg/L (glyphosate) and 50mg/L (2,4-D), respectively. A mineral soil with porosity 40% and composition: sand= 83%, silt=4%, clay=13% was used. Continuous flow experiments were performed on stainless steel and long soil columns placed inside a thermostatted incubator at 15°C. Effluent samples were collected from column outlet and the concentration of each pesticide was measured with ion chromatography. More details of the experimental procedure, analytical techniques and results are reported elsewhere⁸.

Batch experiments were performed at 15°C to estimate the sorption isotherm (equilibrium) and (non-equilibrium) kinetics for each pesticide. Equal quantities of soil and triple distilled water were placed in glass vials which were kept in a thermostatted chamber with continuous end-over-end mixing for 24hr until equilibration was established. In kinetic studies, after the equilibration step, equal quantities of pesticide solution were added in the vials so that the initial concentration and the ratio of soil to liquid were kept constant. The vials were placed again under end-over-end mixing, and at various times the aqueous solution was separated with filtration and analyzed with ion chromatography. In equilibrium tests, after the equilibration step, different volumes of pesticide solution were added in the vials so that the initial concentration was varying whereas the ratio of solid to liquid was kept constant. The suspensions were mixed for 48hrs, then they were removed from the vials, centrifuged and filtered, and the pesticide concentration was measured with ion chromatography.

2.2 Sorption models and parameter estimation

The equilibrium sorption isotherm of pesticides is usually described by the Freundlich model⁴

$$S = K_d C_{eq}^n \quad (1)$$

where K_d ($\text{Kg}^{(1-n)}\text{m}^{-2}\text{L}^n$) is the Freundlich sorption coefficient, the exponent n is a measure of the energy heterogeneity of sorption sites, S (Kg/Kg) is the concentration of pesticide adsorbed per unit mass of solid phase, C_{eq} (Kg/m^3) is the equilibrium concentration of pesticide in the aqueous phase. The values of parameters K_d and n are estimated with non-linear fitting of Eq.(1) to equilibrium sorption data of batch tests.

Under the local equilibrium assumption (LEA), equilibrium is assumed to exist at each point in space between the dissolved solute, associated with the liquid phase, and the solute associated, through sorption, with the solid phase of the medium. In general, sorption appears to be limited by some chemical reaction rate or physical mass transfer resistance and non-equilibrium models are required to describe the transient response of solute concentration in aqueous phase. In the non-equilibrium two-site model, type 1 sorption occurs at sites governed by an equilibrium expression, while type 2 sorption occurs at sites governed by a non-equilibrium equation^{5,8}. Assuming that the concentration of sorbed solute on sites of type 1 is S_1 , and f is the fraction of all sites that are of type 1, then, according to Eq.(1) we obtain

$$\frac{\partial S_1}{\partial t} = fK_d n C^{n-1} \frac{\partial C}{\partial t} \quad (2)$$

Assuming a linear rate for desorption rate, the concentration of solute on sites of type 2, S_2 , is described by the expression

$$\frac{\partial S_2}{\partial t} = a[(1-f)K_d C^n - S_2] \quad (3)$$

where a (s^{-1}) is a sorption rate constant. The solute mass balance in a batch reactor yields

$$\frac{\partial C}{\partial t} = -\frac{\rho_b}{\varphi} \frac{\partial (S_1 + S_2)}{\partial t} \quad (4)$$

where ρ_b (Kg/m^3) and φ are the soil density and porosity, respectively. By incorporating Eqs.(2) and (3) into Eq.(4) and after some manipulation we get

$$\frac{\partial C}{\partial t} = -\frac{\rho_b}{\varphi} a \frac{(1-f)K_d C^n - S_2}{1 + \frac{\rho_b}{\varphi} fK_d n C^{n-1}} \quad (5)$$

The numerical solution of Eqs. (3) and (5) provides the transient response of pesticide concentration in the aqueous solution of batch reactor.

The 1-dimensional transport of a pesticide through a homogeneous soil column includes advection, dispersion, sorption, biodegradation and any other potential abiotic mechanism⁸, and can be described by the following mass balance

$$\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} - u_0 \frac{\partial C}{\partial x} - \frac{\rho_b}{\phi} \frac{\partial S}{\partial t} - r_B - r_A \quad (6)$$

where x is the axial distance from the inlet port (m), D_L is the longitudinal dispersion coefficient ($\text{m}^2 \text{s}^{-1}$), u_0 is the mean pore velocity (m s^{-1}), r_B is the rate of pesticide biodegradation ($\text{kg m}^{-3} \text{s}^{-1}$), and r_A is the rate of abiotic transformation (e.g. hydrolysis). By ignoring biodegradation and abiotic transformation, Eq.(6) in conjunction with Eqs.(2) and (3) yield the following dimensionless relationships

$$\left(1 + \frac{\rho_b}{\phi} f K_d^n C_0^{n-1} C^{*n-1}\right) \frac{\partial C^*}{\partial \tau} = \left(\frac{D_L}{L u_0}\right) \frac{\partial^2 C^*}{\partial \xi^2} - \frac{\partial C^*}{\partial \xi} - \left(\frac{\rho_b L a}{\phi u_0 C_0}\right) \left[(1-f) K_d C_0^n C^{*n} - S_2\right] \quad (7)$$

$$\frac{\partial S_2}{\partial \tau} = \left(\frac{a L}{u_0}\right) \left[(1-f) K_d C_0^n C^{*n} - S_2\right] \quad (8)$$

where $\tau = t u_0 / L$, $\xi = x / L$, $C^* = C / C_0$. The numerical solution of Eqs. (7) and (8) produces the transient response of the axial distribution of the pesticide concentration in the aqueous solution of the soil column.

5 RESULTS AND DISCUSSION

The input parameter values of soil columns are shown in Table 1. It's worth mentioning that the hydrodynamic dispersion coefficient, D_L , and mean pore velocity, u_0 , were estimated by fitting the breakthrough curves of a conservative tracer (Br-) with the analytical solution of the advection-dispersion equation⁸.

Parameter	Soil Column A (glyphosate)	Soil Column C (2,4-D)
Diameter, D	0.05 m	0.05 m
Length, L	0.795 m	0.785 m
Porosity, ϕ	0.42	0.45
Pore velocity, u_0	2.83×10^{-6} m/s	7.47×10^{-6} m/s
Dispersion coefficient, D_L	6.24×10^{-8} m ² /s	7.14×10^{-7} m ² /s
Inlet concentration, C_0	0.1 kg/m ³	0.05 kg/m ³
Soil bulk density, ρ_b	1350 kg/m ³	1350 kg/m ³

Table 1: Properties of soil columns and experimental conditions

For the parameter estimation, the software package ATHENA Visual Studio 10 (Stewart and Associates, USA) was used⁹. The PDEs are solved with forward finite differences and a Bayesian estimator is used to estimate the parameter values.

Initially, the results of equilibrium batch experiments were fitted with Eq.(1) to estimate the parameters ($K_{d,n}$) of sorption isotherms (Table 2, Fig.1). The high uncertainty of K_d

value is due to the small number of estimated parameters and inherent inconsistencies of Freundlich model. Then, these parameter values were fixed, and the results of kinetic (non-equilibrium) batch tests were fitted to the numerical solution of Eqs. (3) and (5) to estimate the rate constant, a , and fraction, f (Table 2, Fig.2). It is worth noting that we were unable to reproduce the datasets of batch experiments by using the one-site non-equilibrium model ($f = 0$).

Parameter	Glyphosate	2,4-D
K_d ($m^{3n} kg^{-n}$)	0.00788 ± 0.0064	0.0246 ± 0.0287
n	1.109 ± 0.343	1.48 ± 0.367
f	0.508 ± 0.026	0.903 ± 0.0245
a (s^{-1})	$1.65 \times 10^{-3} \pm 9.74 \times 10^{-4}$	$1.74 \times 10^{-4} \pm 1.79 \times 10^{-4}$

Table 2: Sorption parameters estimated from batch experiments

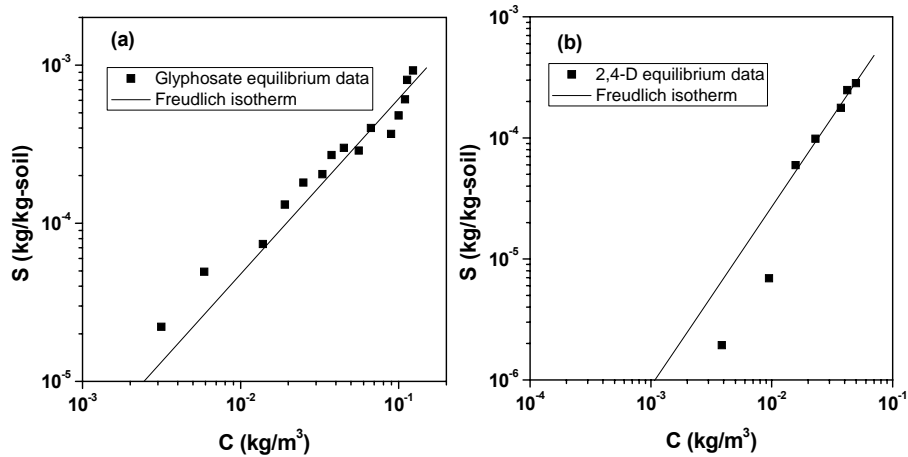


Figure 1: Equilibrium sorption data for (a) glyphosate and (b) 2,4-D

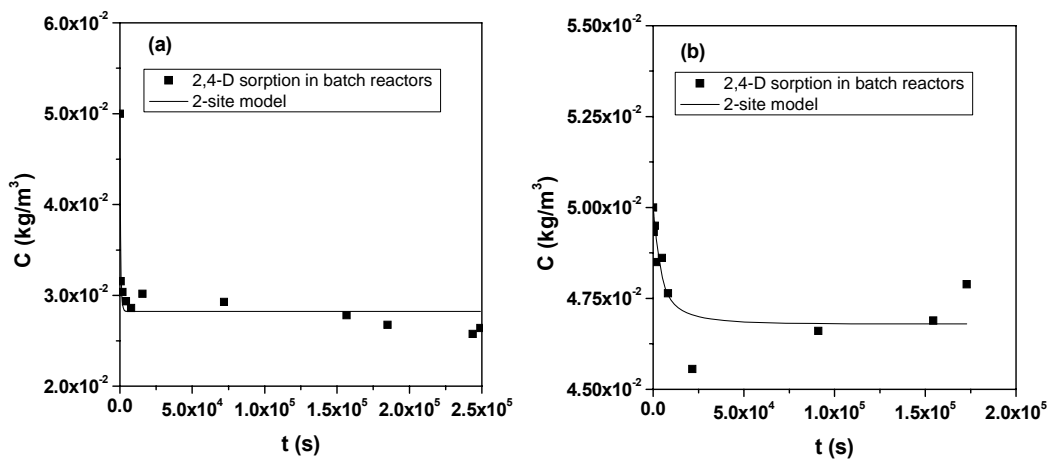


Figure 2: Kinetic sorption experiments in batch reactors for (a) glyphosate and (b) 2,4-D

Then, the pesticide concentration breakthrough curves of soil column experiments were fitted with the numerical solution of Eqs.(7) and (8) to estimate the sorption parameters for two cases: (1) by fixing the parameters of sorption isotherm (K_d, n) and estimating the rest parameters of the two-site model (f, a) (Table 3, Fig.3); (2) by estimating simultaneously the equilibrium and non-equilibrium parameters.

Parameter	Glyphosate	2,4-D
The equilibrium sorption parameters (K_d, f) are fixed		
f	$0.661 \pm 3.2 \times 10^{-4}$	$0.0186 \pm 4.5 \times 10^{-3}$
a (s^{-1})	$4.13 \times 10^{-7} \pm 2 \times 10^{-10}$	$1.22 \times 10^{-8} \pm 1.32 \times 10^{-8}$
All parameters are estimated		
K_d ($m^{3n} kg^{-n}$)	$0.013 \pm 5.3 \times 10^{-6}$	0.136 ± 0.363
n	$1.236 \pm 8 \times 10^{-4}$	3.09 ± 0.85
f	0.62	0.58
a (s^{-1})	$2.67 \times 10^{-7} \pm 4.6 \times 10^{-8}$	$1.3 \times 10^{-7} \pm 7.3 \times 10^{-7}$

Table 3: Sorption kinetic parameters estimated from soil column experiments

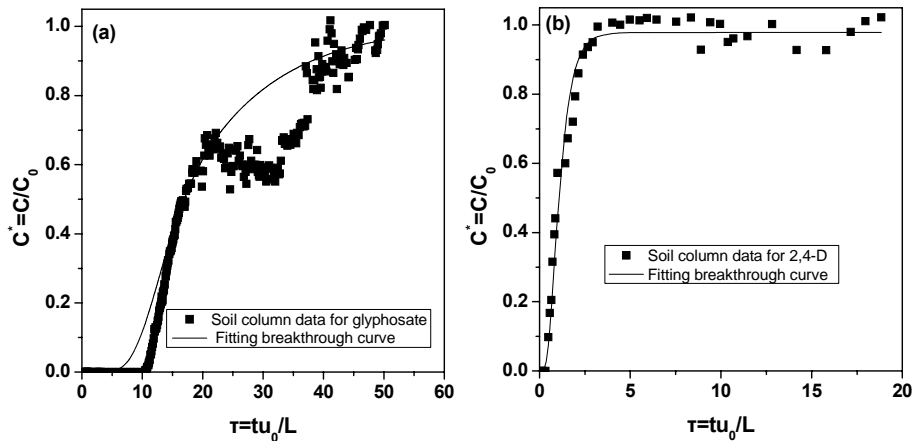


Figure 3: Experimental (soil column) and numerically predicted (2-site model) concentration breakthrough curve for (a) glyphosate and (b) 2,4-D

Obviously, in both cases (glyphosate and 2,4-D), the sorption rate constant a obtained from soil column tests is almost 4 orders of magnitude smaller than that obtained from batch tests (Tables, 2, 3). In the stirred batch reactor, the soil particles and liquid phase were well-mixed and it is reasonable to assume that the pesticide concentration in both the aqueous solution and solid surface is uniformly distributed throughout the suspension. On the other hand, the slow continuous flow of liquid phase through the complex pore space of the soil column is characterized by a non-uniform flow field at the pore scale with result that local gradients of pesticide concentration arise¹⁰. The solute transport between the mobile and

immobile regions is governed by molecular diffusion⁷. However, the pore-scale diffusion between mobile and immobile regions introduces a mass-transfer resistance that may affect the kinetics of solute sorption on the grain surface.

In order to incorporate both mechanisms of sorption and mass-transfer into a general model of solute transport in porous media, the non-linear two-site sorption model was combined with the two region model¹¹. Two new variables, C_m, C_{im} denote the pesticide concentration in the aqueous phase of mobile and immobile region, respectively, whereas the variables S_{m2}, S_{im2} denote the corresponding concentrations in the kinetic (type 2) sites of the solid phase. We assume that solute transport between the mobile and immobile region is described by a 1st order relation with rate constant, k_c, f_m, f_{im} are the ratios of equilibrium (type 1) to total sites in mobile and immobile regions, φ_m, φ_{im} are the porosities of the two regions ($\varphi_m + \varphi_{im} = \varphi$), whereas the sorption rate constants are a_m and a_{im} , respectively. Mass balances in each region result in the following set of dimensionless equations

$$\frac{\partial C_m^*}{\partial \tau} = \frac{\left(\frac{\varphi}{\varphi_m}\right) \left[\left(\frac{D_L}{Lu_0}\right) \frac{\partial^2 C_m^*}{\partial z^2} - \frac{\partial C_m^*}{\partial z} \right] - \left(\frac{k_c L}{u_0 \varphi_m}\right) (C_m^* - C_{im}^*) - \frac{a_m \rho_b L}{\varphi_m u_0 C_0} \left[(1-f_m) K_d C_0^n C_m^{*n} - S_{m2} \right]}{1 + (\rho_b / \varphi_m) f_m K_d n C_0^{n-1} C_m^{*n-1}} \quad (9)$$

$$\frac{\partial C_{im}^*}{\partial \tau} = \frac{\frac{k_c L}{u_0 \varphi_{im}} (C_m^* - C_{im}^*) - \frac{a_{im} \rho_b L}{\varphi_{im} u_0 C_0} \left[(1-f_{im}) K_d C_0^n C_{im}^{*n} - S_{im2} \right]}{1 + (\rho_b / \varphi_{im}) f_{im} K_d n C_0^{n-1} C_{im}^{*n-1}} \quad (10)$$

$$\frac{\partial S_{m2}}{\partial \tau} = \left(\frac{a_m L}{u_0}\right) \left[(1-f_m) K_d C_0^n C_m^{*n} - S_{m2} \right] \quad (11)$$

$$\frac{\partial S_{im2}}{\partial \tau} = \left(\frac{a_{im} L}{u_0}\right) \left[(1-f_{im}) K_d C_0^n C_{im}^{*n} - S_{im2} \right] \quad (12)$$

The inverse modeling of soil column breakthrough curves with Eqs.(9)-(12) allows us to estimate the non-equilibrium sorption and mass-transfer parameters (Table 4, Fig.4).

Parameter	Glyphosate	2,4-D
a_m (s ⁻¹)	$3.73 \times 10^{-7} \pm 2.3 \times 10^{-10}$	$3.45 \times 10^{-9} \pm 1.04 \times 10^{-8}$
a_{im} (s ⁻¹)	$3.22 \times 10^{-8} \pm 4.43 \times 10^{-11}$	2.0×10^{-10}
f_m	$0.714 \pm 1.15 \times 10^{-3}$	0.0
f_{im}	$0.155 \pm 1.11 \times 10^{-4}$	$0.0247 \pm 5.84 \times 10^{-3}$
k_c (m ² s ⁻¹)	$4.51 \times 10^{-7} \pm 1.3 \times 10^{-10}$	$7.9 \times 10^{-6} \pm 9.8 \times 10^{-6}$
φ_m	0.3	0.362 ± 0.110

Table 4: Parameters estimated from soil column experiments by coupling the 2-region with 2-site model

Although the prediction of experiments is not improved (Figs.3,4) the two-region & two-site model enables us to decouple the flow field (φ_m) from mass-transfer (k_c) limitations and take into account the sorption kinetics for mobile (a_m, f_m) and immobile (a_{im}, f_{im}) regions.

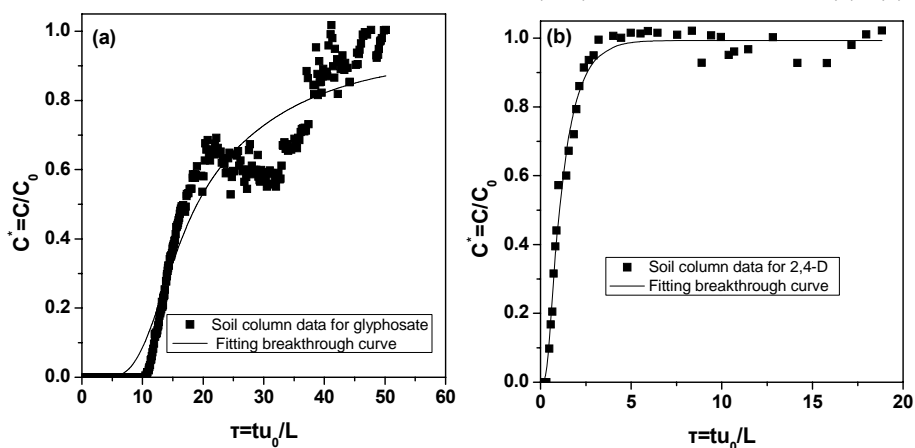


Figure 4: Experimental (soil column) and numerically predicted (2-region model & 2-site model) concentration breakthrough curve for (a) glyphosate and (b) 2,4-D

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