Predictive Models for Soil Contaminants

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A Source Book for Research and Development

By

Donald Stanton Gamble

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Special recognition of four people is made for a variety of important reasons:

Cooper H. Langford
G. R. Barrie Webster
Cluni Chakrabarti
My wife Betty

INTRODUCTION TO THE MODELS

I Background

The reason for the book is the chemical contamination of soil and water. The worldwide scale of the issue has to be recognized. All of the food for 7 billion people comes from soil and water. The industries that these same people need in order to live spill or leak many types of chemicals into that soil and water. The wide variety of industries especially includes agriculture. In the real world there are no perfect answers, only practical tradeoffs. No contamination, no pay checks. The failure to understand that causes confusion leading to conflicts. The only sensible option is new technology with which to manage the best tradeoffs. The new technology has to be derived from basic science.

The technology for this is multidisciplinary. Several kinds of chemistry have to be integrated with hydrology engineering. That package should support toxicology in soil and water. An important fact not yet accounted for in soil and water toxicology is that it is time dependent. That is caused by the time dependent chemical and physical processes.

The objective of this book is to illustrate proof of a concept. The concept is that the physical chemistry of chemicals in soil and water can be quantitatively described and instantly predicted. Such predictions are intended to be integrated with hydrology engineering, as discussed elsewhere. To achieve this, analytical chemistry methods have been developed that determine the (Moles/g) of empty and filled sorption sites. Spreadsheet kinetics models translate them into (Moles/L) as required. With empty and filled sorption sites included among the reactants and products, chemical stoichiometry and material balance calculations can rigorously support kinetics and mechanism calculations. Spreadsheets are useful because they are already coded for mathematical functions and graphics.

The instantly predictive kinetics models are available as email attachments from the author in either Microsoft Excel.xlsx or Corel Quattro Pro 8 formats.

II Analytical Chemistry of Solution Solid Interfaces

At the molecular level, all of the world's oceans, lakes, rivers, and aquifers have solution solid interfaces. Their physical chemistry is fundamentally different from that of dry surfaces as described in standard textbooks. Different concepts and analytical chemistry methods have to be used. The graphic AInterface@ shows structured layers of water in the interface. The structured water layers control sorption of hydrophobic molecules like atrazine into the interface. That limits the (Moles/g) of an organic chemical that can be sorbed. This defines the total number of labile sorption sites, that is, the sorption capacity $\boldsymbol{\theta}_C$.

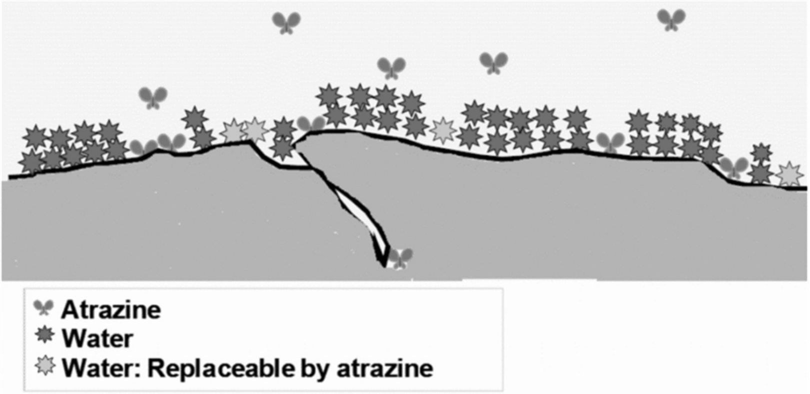


Fig. I-1 A solution solid interface

The experimental methods for dry surface (**m^2/g**) in standard textbooks are not relevant for solution solid interfaces. Freundlich isotherms used for dry surfaces are also not relevant here. They could not have been used for the kinetics models reported in the book. Instead, the models required experimental (Moles/g) for empty and filled sorption sites. There are two related reasons for that. The first is that material balances have to be determined by a combination of analytical chemistry measurements of reaction products, and material balance calculations like those in the graphic 'Material Balances'.

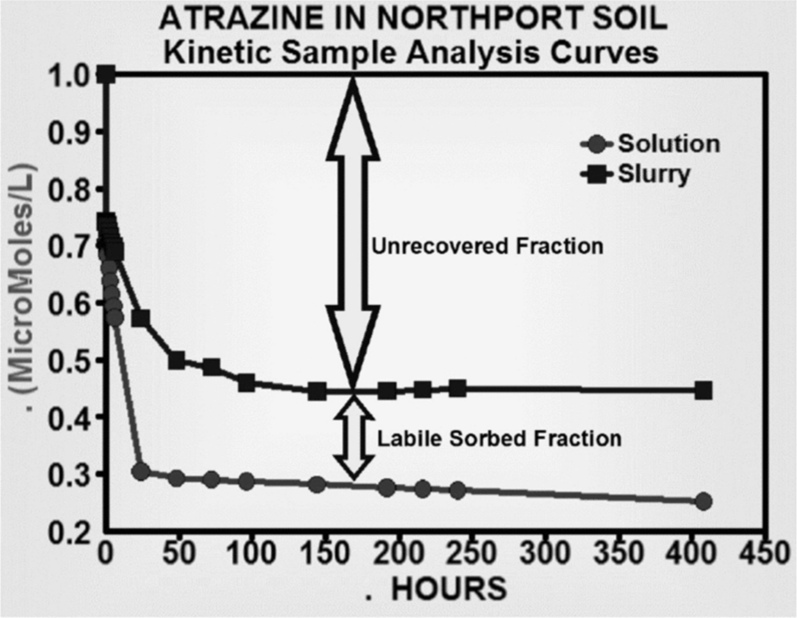
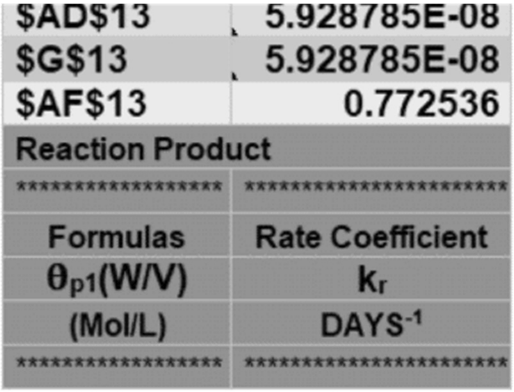


Fig. I-2 Material balance calculations using chemical analyses

The purpose of the material balance calculations is the identification of the separate fractions that can include dissolved, labile sorbed, physically trapped, and chemically reacted fractions. The material balance calculations indicated by the arrows together with the chemical analysis of reaction products give the information about reactants and products that is shown in Table 1. The correct kinetics used for the spreadsheet models used the type of information in this table. Correct chemical stoichiometry requires experimental numbers for all of the reactants and products. Three points about Table 1 should be noted. First, the reactants and products include empty and filled sorption sites. Secondly, sorption has two reactants. Finally, the chemical reactions observed to date have one reactant split between dissolved and labile sorbed fractions. That is because the sorption and desorption are not kinetically rate determining. They were faster than the chemical reactions. The articles found in the chapters report the experimental methods and explain the kinetics that were used for creating the models. They also show the kinetics equations described in Laidler's standard reference book *Chemical Kinetics*. His equation for second order kinetics has been rearranged for use in the model spreadsheets.

III Calculation of Kinetic Rate Coefficients

The calculation of kinetic rate coefficients is illustrated with the example of Sheet B of Model #8. Two experimental curves like those in the graphic 'Material Balances' were separately fitted to polynomials by the method of least squares. The curves were matched point by point for the same time data by interpolation of the fitted curves. The subtractions for material balance calculations were then done with the matched pairs of data points. The resulting experimental data for dissolved, labile sorbed, and chemically reacted fractions were entered into Sheet B. No intraparticle diffusion was found in this experiment.



AD13	5.928785E-08
G13	5.928785E-08
AF13	0.772536
Reaction Product	
******************	***********************
Formulas	Rate Coefficient
θ_{p1}(W/V)	k_r
(Mol/L)	DAYS^{-1}
******************	***********************

Fig. I-3 Chemical reaction cells: Sheet B columns AE & AF

The calculations account for the fact that a soil is the ultimate example of physically and chemically irregular mixtures that are also dynamic. Because of that, the calculations produced kinetic rate coefficients that decrease with reaction time. That effect was first reported by Cooper Langford. This is confirmed by the articles found in the chapters. An important consequence is that process half lives for chemicals in soils can't be calculated in the usual way. For each data point, the kinetic rate coefficients were calculated in 4 steps:

(a) Cell AF 1 reads the experimental value in cell AD 13
(b) Cell AF 2 monitored the calculated value in cell G 13
(c) Cell AF 3: the kinetics formula in cell AE 13 reads the trial value of k in Cell AF 13 which was copied from Cell AF 3.

(d) The trial value of the kinetic rate coefficient **k** in Cell AF 3 was adjusted until the numbers in Cells AF 1 and AF 2 matched. **Table 1** shows the stoichiometry that was required for the calculations with which the models were set up. Without that stoichiometry, correct model calculations are not possible. The graphic ‘Kinetics & mechanisms’ gives a visual impression of the processes and environmental implications of the predictive models.

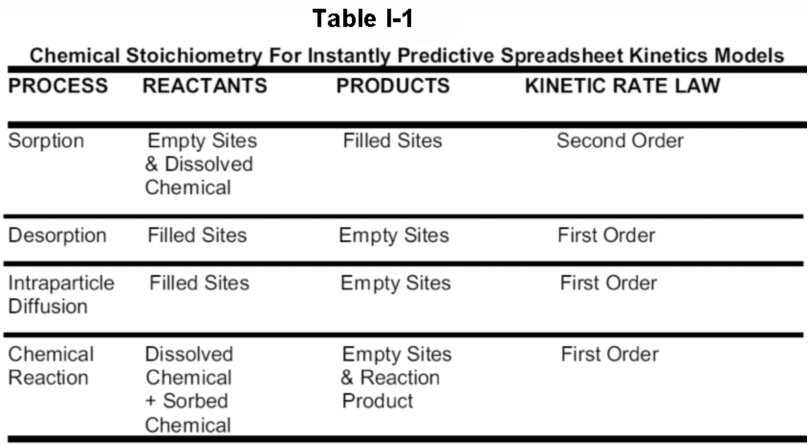


Table I-1

Chemical Stoichiometry For Instantly Predictive Spreadsheet Kinetics Models

PROCESS	REACTANTS	PRODUCTS	KINETIC RATE LAW
Sorption	Empty Sites & Dissolved Chemical	Filled Sites	Second Order
Desorption	Filled Sites	Empty Sites	First Order
Intraparticle Diffusion	Filled Sites	Empty Sites	First Order
Chemical Reaction	Dissolved Chemical + Sorbed Chemical	Empty Sites & Reaction Product	First Order

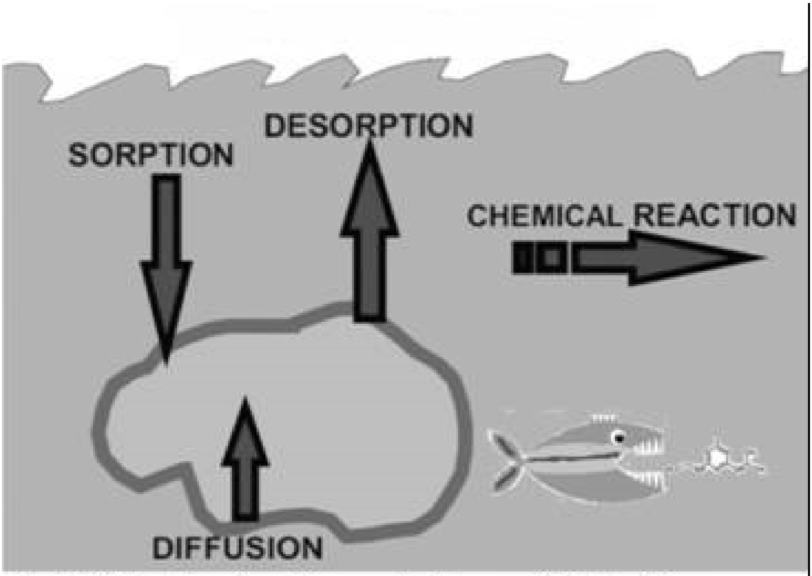
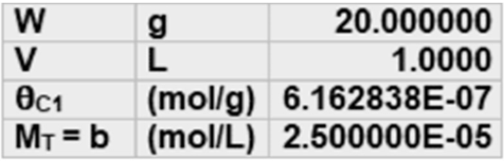


Fig. I-4 Mechanism in a solution solid interface

IV Using the Models

Each model spreadsheet has a set of yellow cells like this one on page A.**W** is g of soil slurried in 1.0000 L. $\boldsymbol{\theta_{C1}}$ is the (Moles/g) of total sorption sites on the soil. That is, it is the labile sorption capacity. $\mathbf{M_T}$ is the initial concentration, (Moles/L), of the dissolved chemical.



W	g	20.000000
V	L	1.0000
θ_{C1}	(mol/g)	6.162838E-07
$M_T = b$	(mol/L)	2.500000E-05

Fig. I-5 Data entry cells on a spreadsheet page A

Before changes are made these are the experimental numbers. Instant predictions are made by typing and entering different numbers for **W** the weight of soil or $\mathbf{M_T}$, the initial concentration. Solution volume **V** or $\boldsymbol{\theta_{C1}}$ can also be changed but that is not as useful. In each chapter boxes like this one are used to show experimental conditions, and the conditions used for the instant predictions are shown as examples.

The spreadsheet models are available from the author as email attachments.

CHAPTER ONE

MODEL #14. ATRAZINE IN ORGANIC SOIL: COREL QUATTRO PRO 8 FORMAT

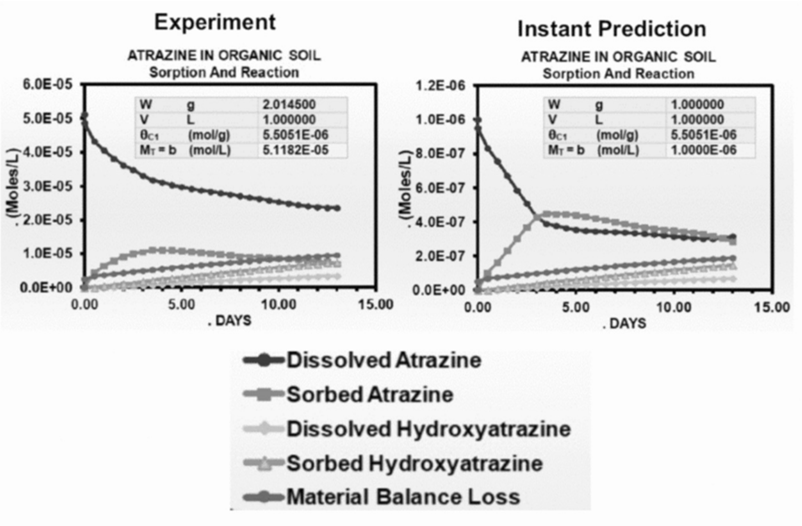


Fig. 1-1 Mechanism.

The experiment was done with 2.0146 g/L of soil and an initial concentration of 5.1182 X 10^{-5} (Moles/L). The prediction was made for 1.0000 g/L of soil and 1.0000 X 10^{-6} (Moles/L) initial concentration. In Fig. 1-1 the curves for dissolved and sorbed atrazine have changed shape because each is controlled by two processes, sorption and desorption. Each of the other curves is controlled by one process. The model demonstrates the feasibility of accounting for the sorption kinetics of a reaction product. This example has hydroxyatrazine. The material balance loss was unaccounted for because effluent analysis did not find it. Intraparticle diffusion was not expected as it might be for mineral soils. A possibility is covalent bonding to the organic soil. That is, chemisorption.

Fig. 1-2 illustrates the importance of monitoring the filling of the labile sorption sites. There are implications for leaching and soil remediation. The saturation of sorption sites can change the kinetics.

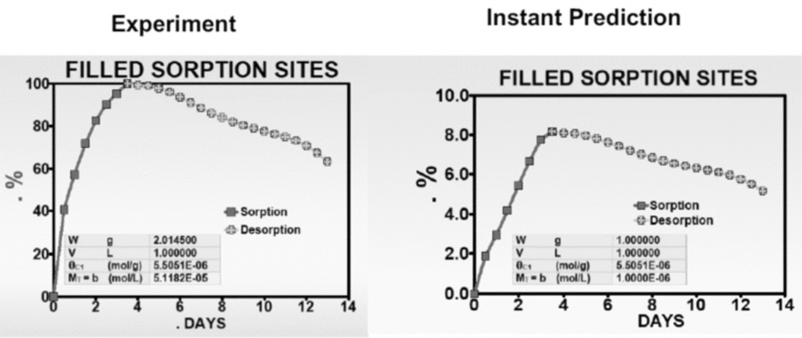


Fig. 1-2 Filled sorption sites.

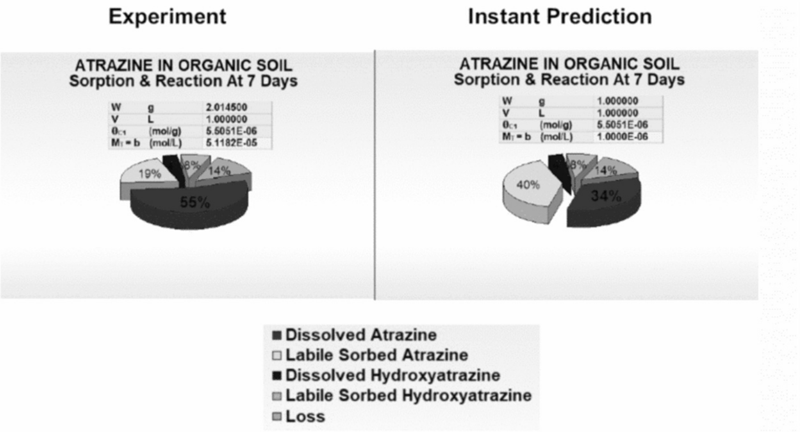


Fig. 1-3 Model#14. Fractions at 7 days..

Fig. 1-3 is a spot check for the distribution of total mass among the fractions. It is controlled by the kinetic rate coefficients and initial solution concentration. Spot checks should be used for soil remediation.

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ATRAZINE IN ORGANIC SOIL: CHEMICAL SPECIATION DURING HETEROGENEOUSCATALYSIS

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Two Brønsted acid catalysts are known to cause the hydrolysis of atrazine. They are H^+ and un-ionized carboxyl groups, both of which can exist in organic soils. When hydroxyatrazine is the only reaction product, there are four chemical species. These are the reactant and product in both free and sorbed states. A typical heterogeneous kinetics experiment would monitor only one or two of these. An HPLC technique has now been demonstrated however, which monitors five chemical species during the course of heterogeneous catalysis experiments. These are solution-phase reactant and product, reversibly sorbed reactant and product, and material balance loss. A 2-week experiment can produce equilibrium and rate constants for sorption and the reaction rate constant. These are relevant to the persistence and movement of atrazine in soils. The constants are consistent with those previously found for a humic acid.

The prediction and management of pesticide behaviour in soils require several types of physical and chemical information. These include the kinetics and equilibria of sorption, the kinetics of chemical reactions, and chemical speciation. The sorption parameters are related to pesticide movement in soils, and reaction rate constants are related directly to their persistence. For soils with high organic matter content, the types, amounts, and chemical reactivity of organic chemical functional groups will also have to be known. The quantitative functional group information is necessary for the use of exact chemical stoichiometry. Atrazine [2-chloro-4-(ethylamino)-

6-(isopropylamino)- s-triazine] is a widely used selective herbicide for the control of annual grasses and broad-leaved weeds. When it is applied to a soil containing high levels of organic matter, the important phenomena might include reversible sorption of atrazine, catalyzed hydrolysis of the atrazine, reversible desorption of hydroxyatrazine reaction product, and a material balance loss. If the chemical reaction in a heterogeneous catalysis system yields only one reaction product, then a complete description of the system would require four chemical analyses. The amounts of reactant and product would have to be measured in both the free and sorbed states. The monitoring of all four variables throughout a kinetics experiment has usually not been practical. Frequently only the product in the free state is measured. In such cases, important information is lost. In our earlier work we demonstrated an indirect calculation technique by which it was possible to obtain some of the required information (Gamble and Khan, 1988). However, to get better insight into the foregoing processes, direct experimental measurements are preferable. According to Mill (1980), a widely held opinion is that laboratory tests are the key to effective assessment of environmental hazards. He states that well-designed laboratory tests will provide the necessary kinetics and equilibrium constants at a fraction of the cost of field tests. Chemical stoichiometry must be taken into account to establish quantitative relationships. Some authors (Freeman and Cheung, 1981; Karickhoff, 1984; Perdue and Wolfe, 1983) have recognized the importance of soil organic matter fractions (such as humic acid, acidic functional groups) to sorption and hydrolysis. This implies that they should be measured and accounted for in the interpretive calculations. This applies to hydrolysis, believed to be very important in chemical decomposition of pesticides in soils (Macalady and Wolfe, 1984; Perdue and Wolfe, 1982). In addition, Karickhoff and Morris (1985) have stated monitoring both physical phases is useful. At the level of general strategy, Wolfe (1980) has advised that the emphasis of environmental investigations should be shifted from observation to prediction. The existing research tactics and experimental methods have not always met these needs. The present objectives have been chosen with this in mind. In view of the foregoing, this research was initiated with the following objectives:

1. Development of an experimental method by which it will be possible to monitor the chemical species including free and sorbed forms of both reactants and products throughout the course of a kinetics experiment, to monitor any material balance loss during a kinetic experiment, and to determine the kinetics of sorption and catalyzed hydrolysis. The purpose is to provide the basis for diagnostic or predictive laboratory tests.

2. Testing the correctness of the developed experimental method against independent information.

Theory

I. Analytical Chemical Method

Assuming that the suspended soil particles of the sample are uniformly distributed throughout the volume of the reaction solution, the weight of soil particles in an aliquot injected into the HPLC is calculated from Eq. 1. W_s and W_A are the weights (g) of the soil sample and of the injected aliquots of soil particles respectively.

$$W_A = (V_A/V_s)W_s \qquad (1)$$

V_s and V_A are the corresponding volumes (L). Post injection filtration traps the soil particles on a 0.5-µm stainless steel inline filter where they are washed by the mobile phase. Microfiltration with 0.45-µm pore size is universally used for the arbitrary operational definition of dissolved and undissolved materials. The 0.5-µm filters are the commercially available line filters closest to that pore size. The volume V_m of the mobile phase available for eluting a labile sorbed compound is determined by the flow rate U (mL/min) of the mobile phase and the retention time t_R (min) of that compound. It is calculated from Eq. 2.

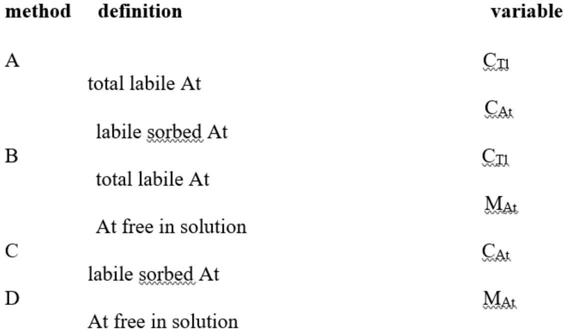
$$v_m = (Ut_R/W_A) \times 10^{-3}\ (\mathrm{L/g}) \qquad (2)$$

If the elution times t_E were too large relative to t_R, then tailing or shape distortions would be expected in the chromatographic peak. The retention time might itself be affected. If, however, $t_E \ll t_R$, then the eluted portion of the compound is expected to make increases in the peak height and peak area, proportional to the amount eluted. The peak shape will not be distorted, and the retention time will not be changed. Preinjection filtration is done with commercially available 0.45-µm filters. Injection of the filtrate should give a direct measurement of that portion of the compound that is free in solution. A simple subtraction should then determine the concentration of the reversibly sorbed portion of the compound. Under field conditions, some of the compound might become nonlabile by sorption onto sites for which the sorption and desorption rates are very slow. This would decrease both its bioavailability and its transport by flowing soil water. Any such nonlabile sorption is expected to be manifested in the method as a material balance loss. This should make it possible to monitor changes in the non labile sorption throughout the course of a heterogeneous kinetics experiment. Two possible complications must however be considered. First, any reaction byproducts that exist should be determined. Also the question of solvent effects on sorption and desorption should be considered. While water is the only environmentally important solvent, the HPLC mobile phases being used are generally mixed aqueous organic solvents. The determination of corrections for any experimental artifacts of this sort may be possible.

II. Sorption and Desorption of Atrazine by Organic Soil

Wu and Gschwend (1986) have proposed that the kinetics of sorption of hydrophobic organic compounds into soil particles may be described by a second-order differential equation with an effective diffusivity parameter.

Table I. Experimental Variables for the Calculation of the First-Order Hydrolysis Rate Constant k_{rz}



method	definition	variable
A	total labile At	C_{T1}
	labile sorbed At	C_{At}
B	total labile At	C_{T1}
	At free in solution	M_{At}
C	labile sorbed At	C_{At}
D	At free in solution	M_{At}

During the last three decades, however, a number of other authors have experimentally demonstrated first-order kinetics behavior for the sorption and desorption of organic compounds into and out of soil particles (Khan, 1973; Fava and Eyring, 1956; Karickhoff, 1980; Karickhoff and Morris, 1985; Perdue and Wolfe, 1982) into and out of soil particles. The experimental data available to date are too insensitive to the choice of mathematical form for the Wu - Gschwend model to be proven uniquely correct. On the basis of the 30-year accumulation of experimental demonstrations with organic compounds, first-order kinetics is assumed to be the most useful description for the present atrazine work. Equations 3 and 4 give the rate of loss from solution by sorption and the rate of gain in solution by desorption.

$$r_1 = -k_{s1} M_{At} \qquad k_{s1} \equiv k_{B1} C_0 \tag{3}$$

$$r_2 = k_{s2} C_{At} \tag{4}$$

M_{At} is the molarity of atrazine free in solution. C_{At} and C_0 are the concentrations of labile sorbed atrazine and of unoccupied sorption sites for atrazine and hydroxatrazine (moles/liter of total slurry). Both k_{al} and k_{a2} are first-order constants, while k_{B1} is inherently second order. Usually C_0 is constant to a close approximation (Gamble and Khan, 1988). The ratio r_2/r_l can be used to test for sorption equilibrium and for calculating the sorption equilibrium constant:

$$\frac{r_2}{r_1} = \frac{k_{s2}}{k_{B1}} \frac{C_{At}}{C_0 M_{At}} \tag{5}$$

Let

$$Q_1 \equiv \frac{C_{At}}{C_0 M_{At}} = \frac{\theta_{At}}{\theta_0 M_{At}} \tag{6}$$

θ_{At} and θ_o are the amounts of labile sorbed atrazine and of unoccupied sorption sites (moles/gram of organic soil). Note that units cancel in Eq. 6.

$$\frac{r_1}{r_2} Q_1 = \frac{k_{B1}}{k_{s2}} \tag{7}$$

Sorption equilibrium established at $t = \infty$ gives equations 8-11. Before

$$\lim_{t\to\infty}\left(\frac{r_1}{r_2}\right) = -1 \tag{8}$$

$$\lim_{t\to\infty} Q_1 = \bar{K}_1 \tag{9}$$

$$\bar{K}_1 = \frac{C_{\mathrm{At}}}{C_0 M_{\mathrm{At}}} = \frac{\theta_{\mathrm{At}}}{\theta_0 M_{\mathrm{At}}} \tag{10}$$

$$\bar{K}_1 = \frac{k_{\mathrm{B1}}}{k_{\mathrm{s2}}} \tag{11}$$

$$Q_1 < \bar{K}_1 \tag{12}$$

equilibrium is established, the following conditions exist: M_{At} is bigger than its equilibrium value; θ_{At} is smaller than its equilibrium value; and

$$Q_1 < \bar{K}_1$$

Q_l should therefore increase toward K_l as an asymptotic limit, as sorption equilibrium is approached. An experimental plot of Q_1 vs t should therefore identify that portion of a heterogeneous kinetics experiment for which sorption equilibrium exists. The net rate of change of atrazine in solution is Eq. 13, which is obtained as the sum of Eqs. 3 and 4.

$$\frac{dM_{\mathrm{At}}}{dt} = -k_{\mathrm{s1}}M_{\mathrm{At}} + k_{\mathrm{s2}}C_{\mathrm{At}} \tag{13}$$

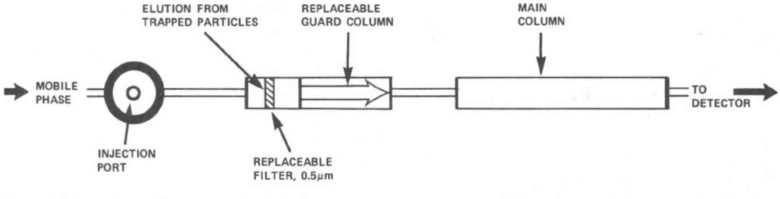


Figure 1. Conventional high-pressure liquid chromatograph, showing the location of the trapped particles being eluted (40–80 μg of particles introduced per injection).

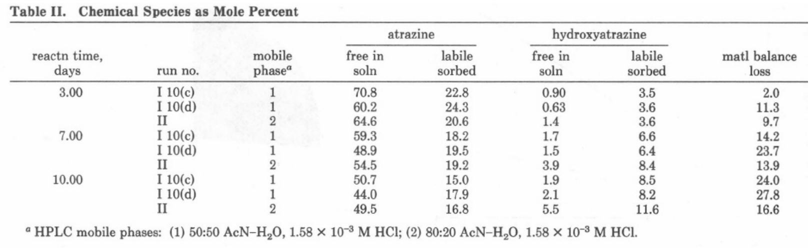


Table II. Chemical Species as Mole Percent

			atrazine		hydroxyatrazine		
reactn time, days	run no.	mobile phase[a]	free in soln	labile sorbed	free in soln	labile sorbed	matl balance loss
3.00	I 10(c)	1	70.8	22.8	0.90	3.5	2.0
	I 10(d)	1	60.2	24.3	0.63	3.6	11.3
	II	2	64.6	20.6	1.4	3.6	9.7
7.00	I 10(c)	1	59.3	18.2	1.7	6.6	14.2
	I 10(d)	1	48.9	19.5	1.5	6.4	23.7
	II	2	54.5	19.2	3.9	8.4	13.9
10.00	I 10(c)	1	50.7	15.0	1.9	8.5	24.0
	I 10(d)	1	44.0	17.9	2.1	8.2	27.8
	II	2	49.5	16.8	5.5	11.6	16.6

[a] HPLC mobile phases: (1) 50:50 AcN–H_2O, 1.58×10^{-3} M HCl; (2) 80:20 AcN–H_2O, 1.58×10^{-3} M HCl.

Before equilibrium has been established

$$\frac{dM_{At}}{dt} \neq 0 \qquad (14)$$

The integral rate law is Eq. 15. M_1 and M_2 are the integration limits for M_{At}.

$$\ln\left(\frac{M_2}{M_1}\right) - k_{s2}\int_{t_1}^{t_2} f_1(t)\,dt = -k_{s1}(t_2 - t_1) \qquad (15)$$

$$f_1(t) \equiv C_{At}/M_{At}$$

Equation 15 may be solved with numerical integration and an iterative calculation, to give the constants k_{s1}, k_{b1}, and k_{s2}.

III. Sorption and Desorption of Hydroxyatrazine by Organic Soil

The arguments are nearly parallel to those for atrazine. For sorption equilibrium they give Eqs. 16-18.

$$\bar{K}_2 = \frac{C_{\mathrm{AtOH}}}{C_0 M_{\mathrm{AtOH}}} = \frac{\theta_{\mathrm{AtOH}}}{\theta_0 M_{\mathrm{AtOH}}} \qquad (16)$$

$$\bar{K}_2 = \frac{k_{\mathrm{B3}}}{k_{\mathrm{s4}}} \qquad (17)$$

$$k_{\mathrm{s3}} = k_{\mathrm{B3}} C_0 \qquad (18)$$

Equation 19 is now the test function for equilibrium. The meanings of the symbols correspond to those for atrazine.

$$Q_2 \equiv \frac{C_{\mathrm{AtOH}}}{C_0 M_{\mathrm{AtOH}}} = \frac{\theta_{\mathrm{AtOH}}}{\theta_0 M_{\mathrm{AtOH}}} \qquad (19)$$

Because hydroxyatrazine must desorb toward equilibrium, Q_2 should decrease toward K_2 as an asymptotic limit as equilibrium is approached, as indicated by Eq. 20.

$$Q_2 > \bar{K}_2 \qquad (20)$$

Before sorption equilibrium has been established, Eqs. 21 and 22 are the differential and integral rate laws. The constants are again evaluated by using numerical integrations and iterative calculations.

$$\frac{\mathrm{d}M_{\mathrm{AtOH}}}{\mathrm{d}t} = -k_{\mathrm{s3}} M_{\mathrm{AtOH}} + k_{\mathrm{s4}} C_{\mathrm{AtOH}} \qquad (21)$$

$$\ln\left(\frac{M_2}{M_1}\right) + k_{\mathrm{s3}}(t_2 - t_1) = k_{\mathrm{s4}} \int_{t_1}^{t_2} f_2(t)\,\mathrm{d}t \qquad (22)$$

$$f_2(t) \equiv C_{\mathrm{AtOH}} / M_{\mathrm{AtOH}}$$

IV. Hydrolysis Reaction

The reaction is governed by Brønsted acid catalysis (Perdue and Wolfe, 1983). The two catalysts that have been identified to date are H^+ and un-ionized carboxyl groups (Gamble and Khan, 1985, 1988; Gamble et al., 1983; Haniff et al., 1985). Organic soil has been postulated to contain a mixture of humic acid and unhumified particles of plant material. Undissolved humic acid is a weak acid cation exchanger, with carboxyl groups bound to the polymer and hydrogen ions confined to the particles by the Donnan potential (Gamble, 1989). Both of the Brønsted acid catalysts are therefore expected to be present and active. A kinetics experiment should therefore measure their combined effects. With the conversion of units from θ_{At} to C_{At} the previously presented differential rate law (Gamble and Khan, 1988) for the reaction on the sorption sites is Eq. 23. The subscript r indicates that this is a chemical reaction rate.

$$\left(\frac{dC_{At}}{dt}\right)_r = -k_{r2}C_{At} \tag{23}$$

It must be carefully distinguished from sorption-desorption rates and from total rates of change. Assuming that atrazine is removed from the whole system by only one process, then the equality in Eq. 24 is valid.

$$\frac{dC_{T1}}{dt} = \left(\frac{dC_{At}}{dt}\right)_r \tag{24}$$

$$\frac{dC_{T1}}{dt} = -k_{r2}C_{At} \tag{25}$$

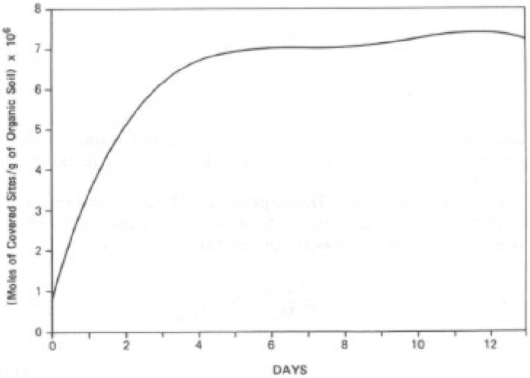


Figure 4. Total coverage of sorption sites, by reversibly sorbed atrazine and reversibly sorbed hydroxyatrazine.

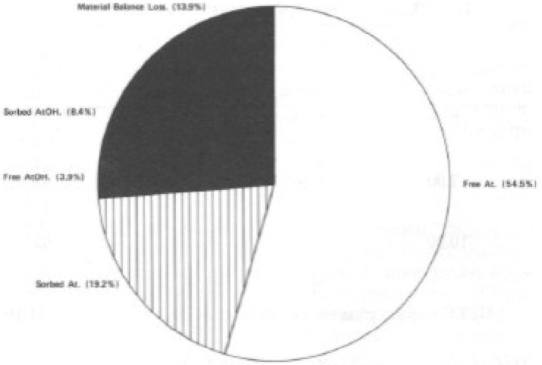


Figure 3. Chemical species at 7.0 days reaction time, mole percent of initial atrazine. Key: At, atrazine; AtOH, hydroxyatrazine; free, portions in the solution phase; sorbed, reversibly sorbed portions.

Table III. Constants for the Spreadsheet Calculation[a]

item	value
year	88
init month	4
init day	26
init hour	8
init min	22.000
std At, M	2.5177×10^{-5}
std AtOH, M	2.9660×10^{-6}
soln, mL	25.3164
soil dry wt, g	0.051 000
days at $t = 0$	32 259.3486
init At, M	$5.118\,200 \times 10^{-5}$

[a] Key: At = atrazine; AtOH = hydroxyatrazine.

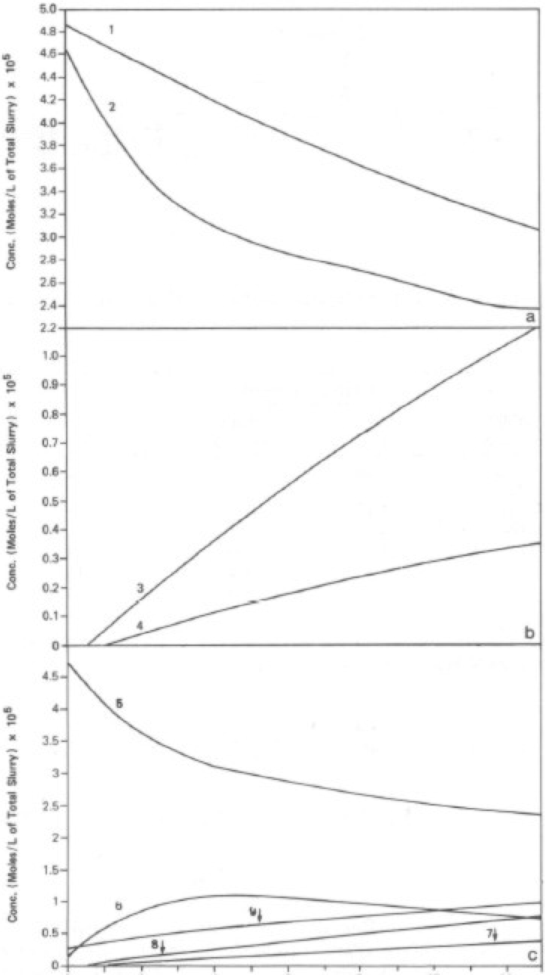


Figure 2. (a) Effect of microfiltration before and after sample injection, on atrazine: 1, whole slurry injected, with subsequent in-line microfiltration, 0.5-μm stainless steel filter; 2, microfiltration before injection, 0.45-μm Nylon 66 filter. (b) Effect of microfiltration before and after sample injection, on hydroxyatrazine: 3, whole slurry injected, with subsequent in-line microfiltration, 0.5-μm stainless steel filter; 4, microfiltration before injection, 0.45-μm Nylon 66 filter. (c) Chemical species during a kinetics run: 5, atrazine in solution; 6, reversibly sorbed atrazine; 7, hydroxyatrazine in solution; 8, reversibly sorbed hydroxyatrazine; 9, material balance loss.