Maynard, M. S.; Ku, C. C.; Jacob, T. A. Fate of Avermectin B_{1a} on Citrus Fruits. 1. Distribution and Magnitude of the Avermectin B_{1a} and ^{14}C Residue on Citrus Fruits from a Field Study. *J. Agric. Food Chem.* **1989a**, *37*, 178–183.

Maynard, M. S.; Iwata, Y.; Wislocki, P. G.; Ku, C. C.; Jacob, T. A. Fate of Avermectin B_{1a} on Citrus Fruits. 2. Distribution and Magnitude of the Avermectin B_{1a} and ^{14}C Residue on Fruits from a picked Fruit Study. *J. Agric. Food Chem.* **1989b**, *37*, 184–189.

Price, J. F. Field Evaluations of New Pesticides for Control of Leafminers, Mites and Aphids on Flower Crops. *Proc. Fla. State Hortic. Soc.* **1983**, *96*, 287–291.

Reed, D. K.; Tromley, N. J.; Reed, G. L. Activity of Avermectin B_1 against Codling Moth (Lepidoptera: olethreutidae). *J. Econ. Entomol.* **1985**, *78*, 1067–1071.

Schuster, D. J.; Everett, P. H. Response of *Liriomyza trifollii* (Diptera: agromyzidae) to Insecticides on Tomato. *J. Econ. Entomol.* **1983**, *76*, 1170–1174.

Wright, J. E. Biological Activity of Avermectin B_1 against the Boll Weevil (Coleoptera: curculionidae). *J. Econ. Entomol.* **1984**, *77*, 1029–1032.

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Atrazine in Organic Soil: Chemical Speciation during Heterogeneous Catalysis†

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Two Brönsted 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 behavior 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 have recognized (Freeman and Cheung, 1981; Karickhoff, 1984; Perdue and Wolfe, 1983) 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

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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

$$W_A = (V_A/V_s)W_s \tag{1}$$

and of the injected aliquots of soil particles respectively. V_s and V_A are the corresponding volumes (L). Postinjection 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 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.

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

If the elution time 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 nonlabile 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. 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. 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_{s1} and k_{s2} 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_1 can be used to test for sorption equilibrium and for calculating the sorption equilibrium constant:

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

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

$$\frac{r_2}{r_1} = \frac{k_{s2}}{k_{B1}}\frac{C_{At}}{C_0M_{At}} \tag{5}$$

Let

$$Q_1 \equiv \frac{C_{At}}{C_0M_{At}} = \frac{\theta_{At}}{\theta_0M_{At}} \tag{6}$$

θ_{At} and θ_0 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 eq 8–11. Before equilibrium is established, the following conditions exist: M_{At} is bigger than its equilibrium value; θ_{At} is smaller than its equilibrium value; and

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

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

$$\bar{K}_1 = \frac{C_{At}}{C_0M_{At}} = \frac{\theta_{At}}{\theta_0M_{At}} \tag{10}$$

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

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

Q_1 should therefore increase toward $\bar{K}_1$ 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 eq 3 and 4.

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

Table I. Experimental Variables for the Calculation of the First-Order Hydrolysis Rate Constant k_{r2}

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

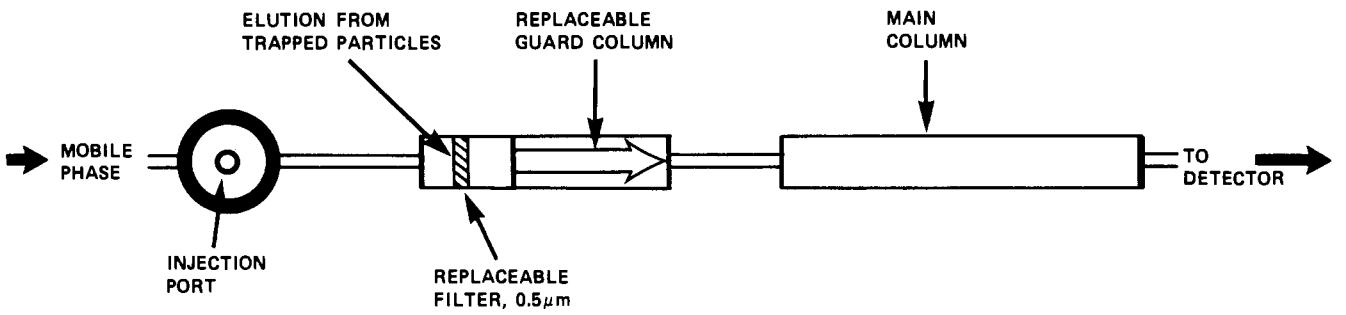

Figure 1. Conventional high-pressure liquid chromatograph, showing the location of the trapped particles being eluted (40–80 μg of particles introduced per injection).

Table II. Chemical Species as Mole Percent

reactn time, days	run no.	mobile phase[a]	atrazine: free in soln	atrazine: labile sorbed	hydroxyatrazine: free in soln	hydroxyatrazine: 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

$$\frac{dM_{At}}{dt} \neq 0 \tag{14}$$

The integral rate law is eq 15. M_1 and M_2 are the integration

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

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

limits for 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 eq 16–18.

$$\bar{K}_2 = \frac{C_{AtOH}}{C_0 M_{AtOH}} = \frac{\theta_{AtOH}}{\theta_0 M_{AtOH}} \tag{16}$$

$$\bar{K}_2 = \frac{k_{B3}}{k_{s4}} \tag{17}$$

$$k_{s3} = k_{B3} C_0 \tag{18}$$

Equation 19 is now the test function for equilibrium. The meanings of the symbols correspond to those for atrazine. Because hydroxyatrazine must desorb toward equilibrium, Q_2 should decrease toward $\bar{K}_2$ as an asymptotic limit as equilibrium is approached, as indicated by eq 20.

$$Q_2 \equiv \frac{C_{AtOH}}{C_0 M_{AtOH}} = \frac{\theta_{AtOH}}{\theta_0 M_{AtOH}} \tag{19}$$

$$Q_2 > \bar{K}_2 \tag{20}$$

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

$$\frac{dM_{AtOH}}{dt} = -k_{s3} M_{AtOH} + k_{s4} C_{AtOH} \tag{21}$$

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

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

IV. Hydrolysis Reaction. The reaction is governed by Brönsted 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 Brönsted 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. 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.

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

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

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

C_{T1} is the total labile atrazine, defined by eq 26. k_{r2} is the first-order rate constant previously described (Gamble and Khan,

$$C_{T1} = M_{At} + C_{At} \tag{26}$$

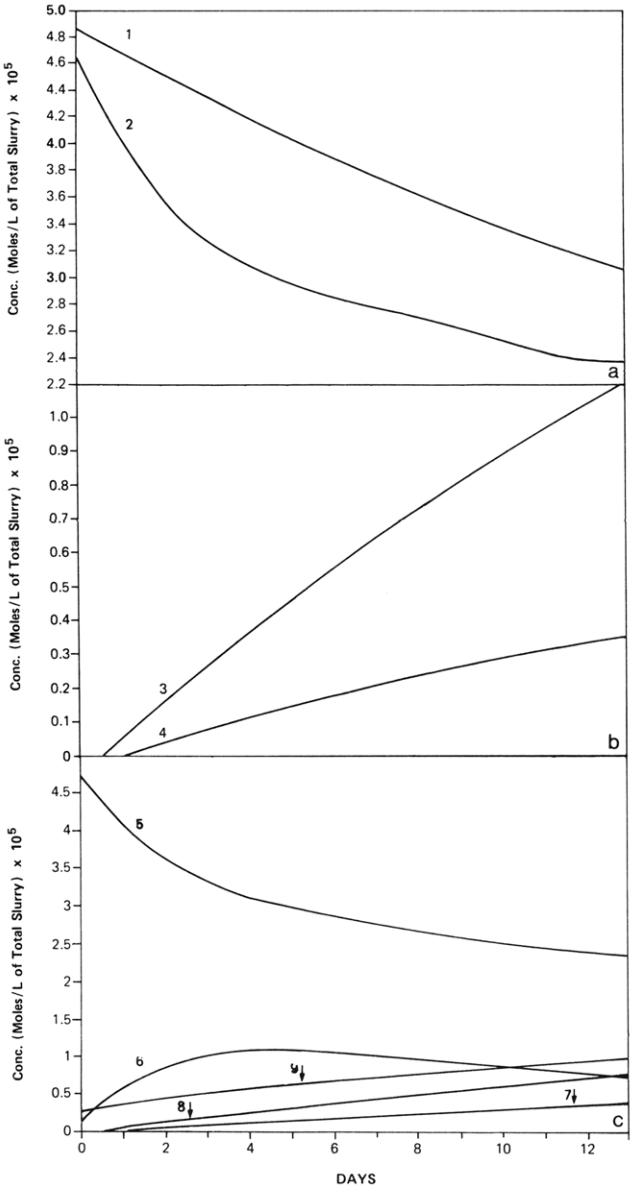

Figure 2. (a) Effect of microfiltration before and after sample injection, on atrazine: 1, whole slurry injected, with subsequent in-line microfiltration, 0.5-μm stainless steel filter; 2, microfiltration before injection, 0.45-μm Nylon 66 filter. (b) Effect of microfiltration before and after sample 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.

1988) for reaction on the catalytic sites. It is the parameter that should reflect the mixture of the two types of catalysts.

The analytical chemical data provide a choice of four calculation methods for the calculation of the reaction rate constant k_{r2}. Each method is based on a different set of variables and correspondingly uses a different integral rate law derived from eq 25. The sets of variables are listed in Table I. Method B was chosen because the two variables are measured directly. Since subtractions are avoided in this way, this calculation method makes the best use of the experimental data. Equation 27 is the integral rate law, which has been obtained from eq 25 and 10.

$$\int_{C_1}^{C_2}(1/M_{At})\,dC_{T1} = -k_{r1}(t_2 - t_1) \tag{27}$$

$$k_{r2} = \frac{V_s}{W_s}\frac{k_{r1}}{\bar{K}_1\theta_0}$$

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.

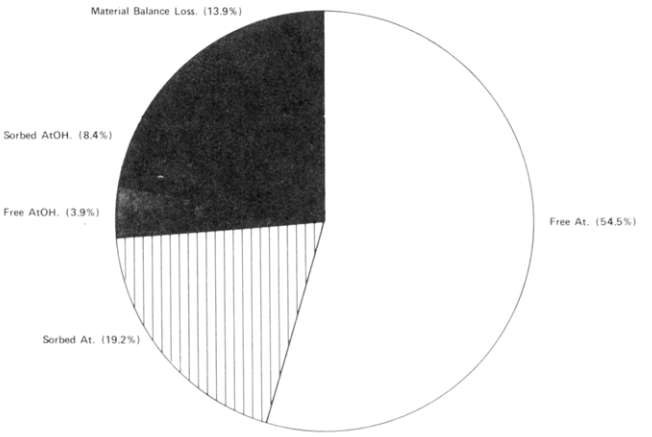

Figure 3. Chemical species at 7.0 days reaction time, mole percent of initial atrazine. Key: At, atrazine; AtOH, hydroxyatrazine; free, portions in the solution phase; sorbed, reversibly sorbed portions.

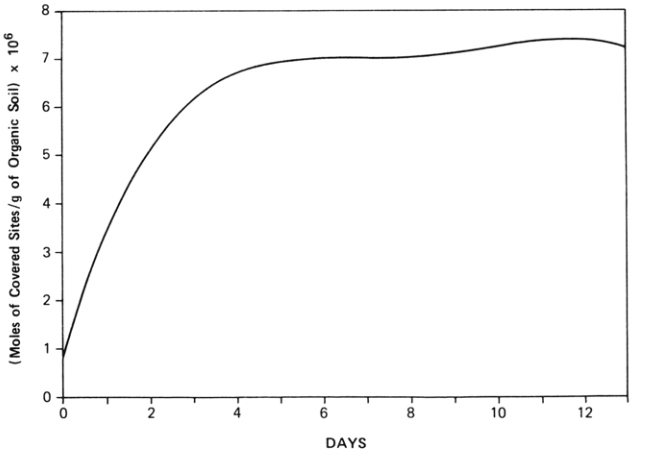

Figure 4. Total coverage of sorption sites, by reversibly sorbed atrazine and reversibly sorbed hydroxyatrazine.

The conversion of labile sorbed atrazine into total labile hydroxyatrazine may be characterized by the empirical rate constant k_{p3}, according to eq 28. C_{T2} is the total labile hydroxyatrazine (moles/liter of total slurry). The integral rate law is eq 29. If the conversion of labile sorbed atrazine into total labile

$$dC_{T2}/dt = k_{p3}C_{At} \tag{28}$$

$$\int_{C_1}^{C_2}(1/C_{At})\,dC_{T2} = k_{p3}(t_2 - t_1) \tag{29}$$

hydroxyatrazine were the only process, then eq 30 would be valid. If, however, $(V_s/W_s)(k_{p3}/\bar{K}_2\theta_0) < k_{r2}$, then this would imply that some additional physical or chemical process also exists.

$$k_{r2} = \frac{V_s}{W_s}\frac{k_{p3}}{\bar{K}_2\theta_0} \tag{30}$$

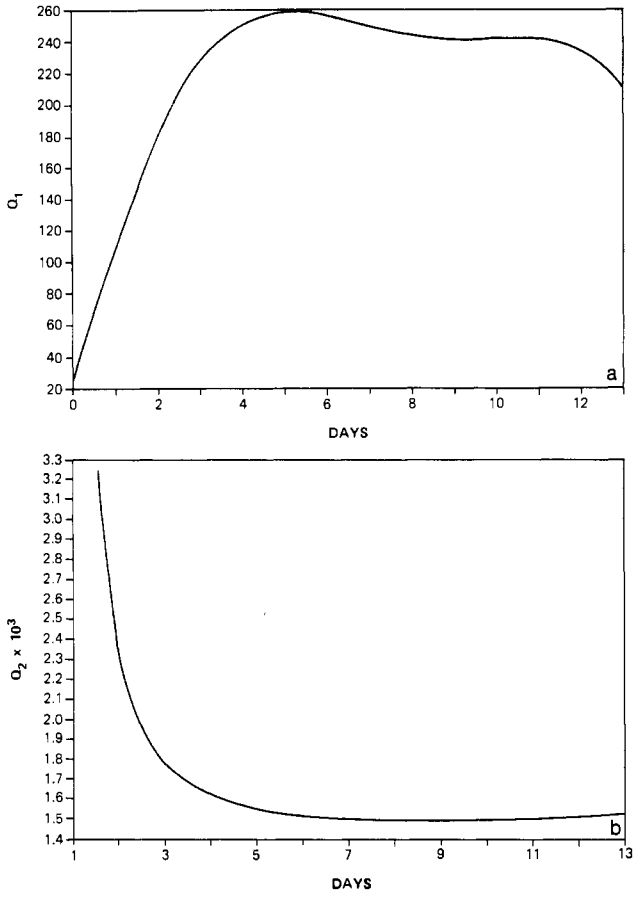

Figure 5. Tests for sorption equilibrium at the plateaus after 5.0 days: (a) atrazine, $Q_1 = \bar{K}_1$ after 5.0 days; (b) hydroxyatrazine, $Q_2 = K_2$ after 5.0 days. $\bar{K}_1$ and $\bar{K}_2$ are the law of mass action equilibrium functions.

EXPERIMENTAL SECTION

Equipment. The reaction vessel was a Pyrex cylinder 7.3 cm high by 3.0 cm in diameter, having a screw cap with sample parts. During use it had a Teflon-coated stirring bar and was placed in a fitted double-walled Pyrex container. Connection to a circulating bath maintained the sample temperature at 25.0 °C. The high-pressure liquid chromatograph was essentially the previously described conventional system (Gamble and Khan, 1988). Figure 1 shows this conventional system in order to emphasize the importance of the inline 0.5-μm microfilter and the cartridge-type guard column. These are contained in the same Supelco disposable unit. Disposable 1-mL syringes were used with MSI Cameo Nylon 66 0.45-μm disposable microfilters, but without needles. For direct injections of standards, reaction solution filtrates, and unfiltered whole slurries, 100-μL Hamilton 710 syringes with fixed needles were used.

Reagents. The organic soil was a Typic Mesisol peat collected on the Agriculture Canada Substation, Ste-Clothilde, Quebec. It contained 37.70% organic C, 4.80% H, and 0.7072 (mmol/g) of carboxyl groups. The wet density was 1.14 (g/mL). The preparation and detailed chemical analyses have been previously reported (Gamble, 1989).

Atrazine and hydroxyatrazine were crystalline solids prepared and analyzed as previously described (Gamble and Khan, 1988; Gamble et al., 1983). Water redistilled under N_2 was used for the preparation of all standard stock solutions, standards, and samples. Chromatography-grade acetonitrile and methanol were used for HPLC work.

Standard Stock Solutions. Standard stock solutions were 1.5×10^{-4} M HCl, 1.0×10^{-4} M atrazine, 1.0×10^{-4} M hydroxyatrazine, and 1.5×10^{-4} M atrazine.

Analytical Standards. HPLC analyses employed mixed standards that ranged from 3.0×10^{-5} M atrazine and 0.0 M hydroxyatrazine to 0.0 M atrazine and 3.0×10^{-5} M hydroxyatrazine.

Procedure. A 50-mg portion of organic soil was suspended with stirring in approximately 15 mL of redistilled H_2O for about 2 days. This wetted all the surfaces and sorbed H_2O into soil particles. The hydrolysis reaction was started by the addition of atrazine standard stock solution, addition of HCl to give a concentration of 1.0×10^{-4} M, and adjustment of total volume to 25.0 mL. Stirring maintained a uniform suspension of organic soil particles throughout the whole solution, at 25.0 °C.

Two types of HPLC analyses were done alternately at measured times. Each sample injection was bracketed by injections of standards. The first type of analysis used a preinjection filtration. A small aliquot (less than 0.1 mL) was removed and filtered with a disposable syringe fitted with a disposable

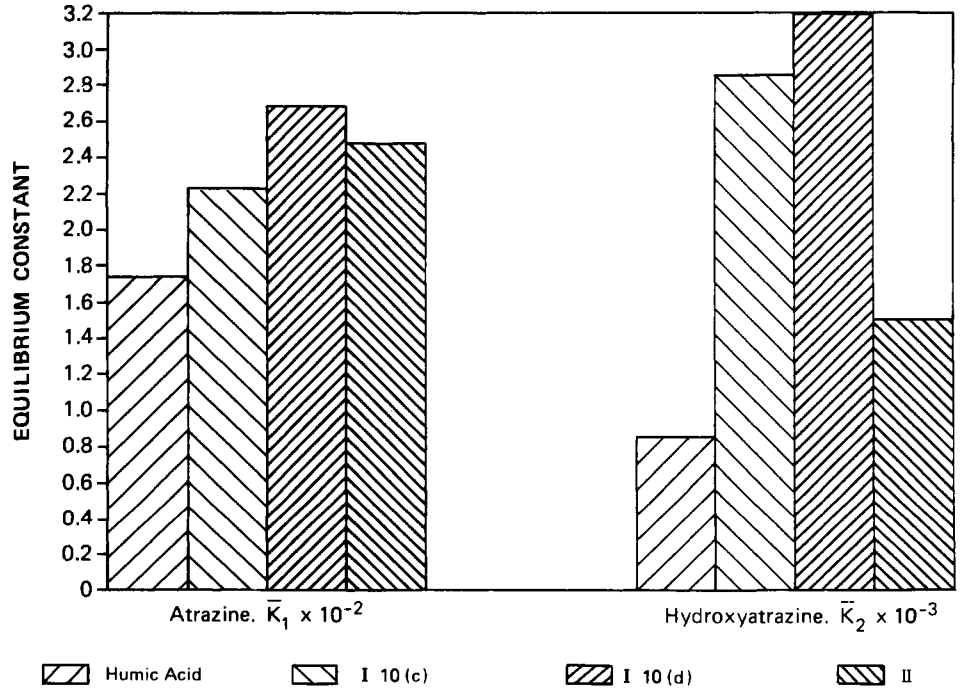

Figure 6. Sorption equilibrium constants at 25.0 °C for humic acid (Gamble and Khan, 1988) and the organic soil. Organic soil values are shown for the replicate experiments Ic, Id, and II. Values adopted for subsequent calculations: $\bar{K}_1 = 2.36 \times 10^2$, relative standard deviation 9.2%; $K_2 = 1.50 \times 10^3$, relative standard deviation 1%.

Table IV. Rate Constants for Sorption and Desorption by Organic Soil at 25.0 °C

process	constant	std error	$t_{1/2}$, days	reactn time, days	site coverage by At, mole fraction
At sorption	$k_{s1} = 5.017 \times 10^{-2}$ days^{-1}	8.51×10^{-3}	13.8	$0.0 \le t \le 5.0$	$0.0 \le x_{At} \le 7.62 \times 10^{-3}$
	$k_{B1} = 37.08$ (mol/L of slurry)$^{-1}$ days^{-1}	6.29			
At desorption	$k_{s2} = 0.1507$ days^{-1}	2.56×10^{-2}	4.60	$0.0 \le t \le 5.0$	$0.0 \le x_{At} \le 7.62 \times 10^{-3}$
AtOH sorption	$k_{s3} = 2.018$ days^{-1}	1.64×10^{-2}	0.343	$1.5 \le t \le 5.0$	$5.58 \times 10^{-3} \le x_{At} \le 7.62 \times 10^{-3}$
	$k_{B3} = 1.491 \times 10^{3}$ (mol/L of slurry)$^{-1}$ days^{-1}	12.1			
AtOH desorption	$k_{s4} = 0.9928$ days^{-1}	8.08×10^{-3}	0.698	$1.5 \le t \le 5.0$	$5.58 \times 10^{-3} \le x_{At} \le 7.62 \times 10^{-3}$

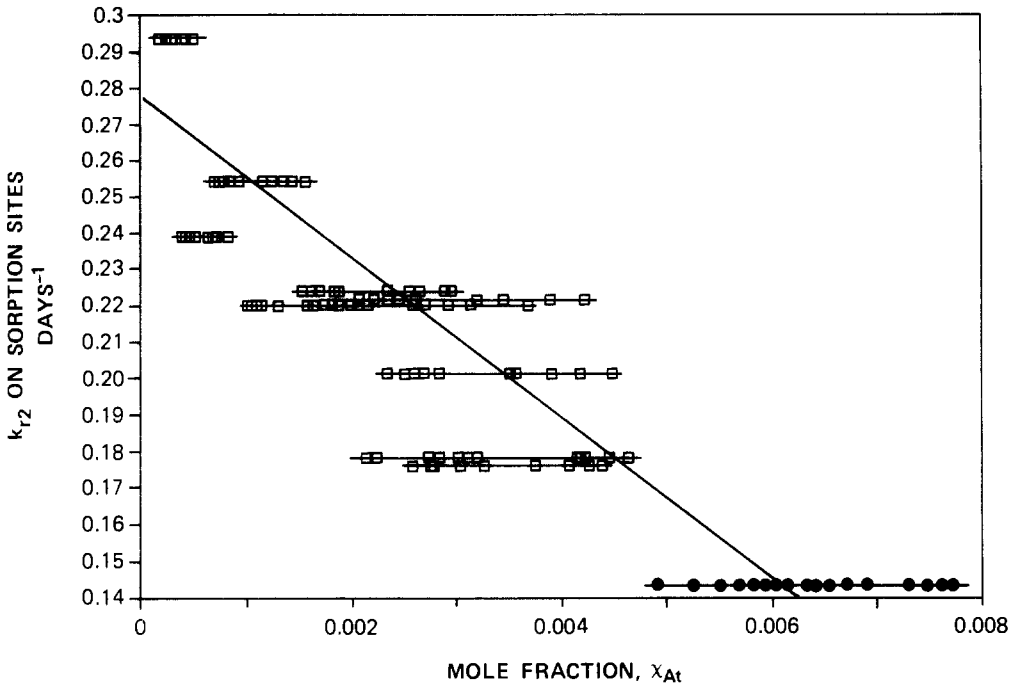

Figure 7. First-order reaction rate constant for atrazine hydrolysis on carboxyl catalytic sorption sites: □, Alberta Chernogem humic acid, 2.828×10^{-3} mol/g of carboxyl groups (Gamble, 1989); ●, Quebec typic Mesisol Peat, 0.7072×10^{-3} mol/g of carboxyl groups (Gamble, 1989). $K_{r2} = 0.1430$ days^{-1}, standard error 0.000 53 days^{-1}, $4.92 \times 10^{-3} \le X_{At} \le 7.62 \times 10^{-3}$.

0.45-μm microfilter. When about 50 μL of filtrate had been collected in the filter unit below the membrane, a Hamilton syringe was filled sufficiently to fill a 20-μL injection loop. The second type used a postinjection filtration. A 30-μL aliquot was taken directly into the Hamilton syringe, and the 20-μL loop was filled with the whole slurry. About 40 μg of suspended particles was trapped on the inline microfilter, where they were washed by the mobile phase. Each injection gave both atrazine and hydroxyatrazine peaks. These were read by the UV detector at 230 nm.

With flow rates of 1.0 mL/min and retention times of 6–18 min, the relative amount of extractant was about 200–450 L/g of organic soil. This is about 4–5 orders of magnitude greater than the conventional volumes of extractant per gram (Baily and White, 1964; Chiba, 1969; Purkayastha and Cochrane, 1973; Khan, 1973; Khan et al., 1975; Smith, 1976, 1978, 1981; Cotterill, 1980; Smith and Milward, 1983). The mobile phases listed in Table II are similar to the customary extractants (Baily and White, 1964; Chiba, 1969; Pukayastha and Cochrane, 1973; Khan, 1973, 1975; Smith, 1976, 1978, 1981; Cotterill, 1980; Smith and Milward, 1983). An electronic spreadsheet was used for converting the raw data into concentration vs time kinetics curves.

RESULTS AND DISCUSSION

I. Slurry and Microfiltrate Analysis Curves. Parts a and b of Figures 2 show the differences between HPLC analyses of a slurry with inline microfiltration and with preinjection microfiltration. Injections of the whole slurry followed by inline microfiltration consistently gave higher curves than those obtained by preinjection microfiltration. The curves were produced by polynomial least-squares fits of the measurements. Four questions about the experimental method must be considered during the examination of the experimental results: (1) recoveries during the inline extractions; (2) freedom of the chromatographic peaks from distortion; (3) condition of the main column; (4) detection of equilibrium and nonequilibrium conditions for sorption.

Purkayastha and Cochrane (1973) used several solvents including methanol and acetonitrile–H_2O for the extraction of *s*-triazines from soils. With solvent amounts ranging from 3.3 to 10.0 mL/g, they obtained recoveries of 87–119%. Using methanol–H_2O solvents, Cotterill (1980) obtained similar results for various herbicides. Comparable extraction experiments by Smith (1981) have also given high yields. The addition of H_2O,either before or during extraction, may increase the recoveries (Smith and Milward, 1983; Chiba, 1969). The present method uses solvent to sample ratios that are greater by 4 or 5 orders of magnitude. In addition, water is present both before and during extraction. As a direct experimental check, the mobile phase was changed for one experiment. No effect on recovery could be found.

No tailing, asymmetry, or other peak shape effects were seen, and no changes in retention times were observed.

The disposable line filter and guard column generally protected the main column. The replacement of these after 1 or 2 weeks readily solved any pressure increase problems. In addition, it should be noted that the method produced types and amounts of information in 3 weeks

Table V. Material Balance Loss: Relationships to Reversibly Sorbed Atrazine and Hydroxyatrazine

X sorbed compd (mol)/ L total slurry	C_0	C_1	R^b
At	1.686×10^{-5}	−0.985	−0.992 97
	$\sigma = 0.028 \times 10^{-5}$	$\sigma = 0.030$	
AtOH	0.3466×10^{-5}		
	$\sigma = 0.0033 \times 10^{-5}$	$\sigma = 0.8341$	0.999 20
		0.0070	

[a] $y = C_0 + C_1X$ (moles/liter of total slurry); catalytic carboxyl sorption sites, 1.353 (millimoles/liter of total slurry); reaction time, $5.0 \leq t \leq 13.0$ days. [b] Correlation coefficient.

of work that could only have been obtained, if at all, by several months of work with a large number of samples (Gamble and Khan, 1988).

II. Monitoring of Chemical Species. After about 5 days of reaction time, the difference between the two atrazine curves changed little. However, the difference between the hydroxyatrazine curves increased throughout the experiment. Both atrazine curves should have intercepts equal to the initial concentration in (moles/liter of slurry), while the two hydroxyatrazine curves should have zero intercepts. Discrepancies in the intercepts are no greater than the standard deviations. Table VI (Appendix) contains the numerical data for the curves in Figure 2a,b.

A microcomputer spreadsheet was used for the calculation of chemical species. Table III is a list of constants used in the spreadsheet. Figure 2c shows kinetics curves for chemical species throughout the course of the experiment, and Figure 3 is a spot check of the chemical species at 7.0 days of reaction time. The numerical data for these figures are recorded in Table VII (Appendix) for future use. Solution-phase atrazine decreased continuously, while labile sorbed atrazine has a maximum at approximately 4.5 days. Beyond this maximum, the difference between free and labile sorbed atrazine changed little. The corresponding curves for hydroxyatrazine increase continuously, with the difference between them also increasing. The material balance loss curve also shows a continuous increase.

The cause of the material balance loss is not yet known. Gas chromatography analysis by previously reported methods (Behki and Khan, 1986) failed to find any dealkylated reaction products of either atrazine or hydroxyatrazine. The experimental constant k_{p3} found for hydroxyatrazine does not fit eq 29. There is instead the following inequality: $(V_s/W_s)(k_{p3}/\bar{K}_2\theta_0) < k_{r2}$. From this, it follows that eq 31, previously reported (Gamble and

$$k_{p1} = -(W_s/V_s)\bar{K}_2k_{r2}\theta_0 \tag{31}$$

Khan, 1988) for humic acid, does not apply in this case. Hamaker et al. (1966) and Smith (1981) reported that under field conditions the recoverable portion of an organic chemical sorbed into a soil decreases with time. This is exactly the behavior of the material balance loss that has been monitored here. A number of authors have noted that equilibration times of 3–10 h were common (Burns et al., 1973; Harris and Warren, 1964; Knight and Tomlinson, 1967) for herbicide sorption by soils. However, Damanakis et al. (1970) reported much longer times for some peat soils. That type of slow sorption might be the cause of the material balance loss observed here. During the last two decades, many authors have reported that an initial stage of fast sorption is followed by a second stage that is much slower and irreversible (Talbert and Fletchall, 1965; Mill, 1980; Parris, 1980; Karickhoff, 1980, 1984; Freeman and Cheung, 1981; Di Toro and Horzempa, 1982; Macalady and Wolfe, 1984; Karickhoff and Morris, 1985). The initial 5-day sorption followed by the material balance loss resembles that behavior. Hamaker et al. (1966) suggested that the organic chem-

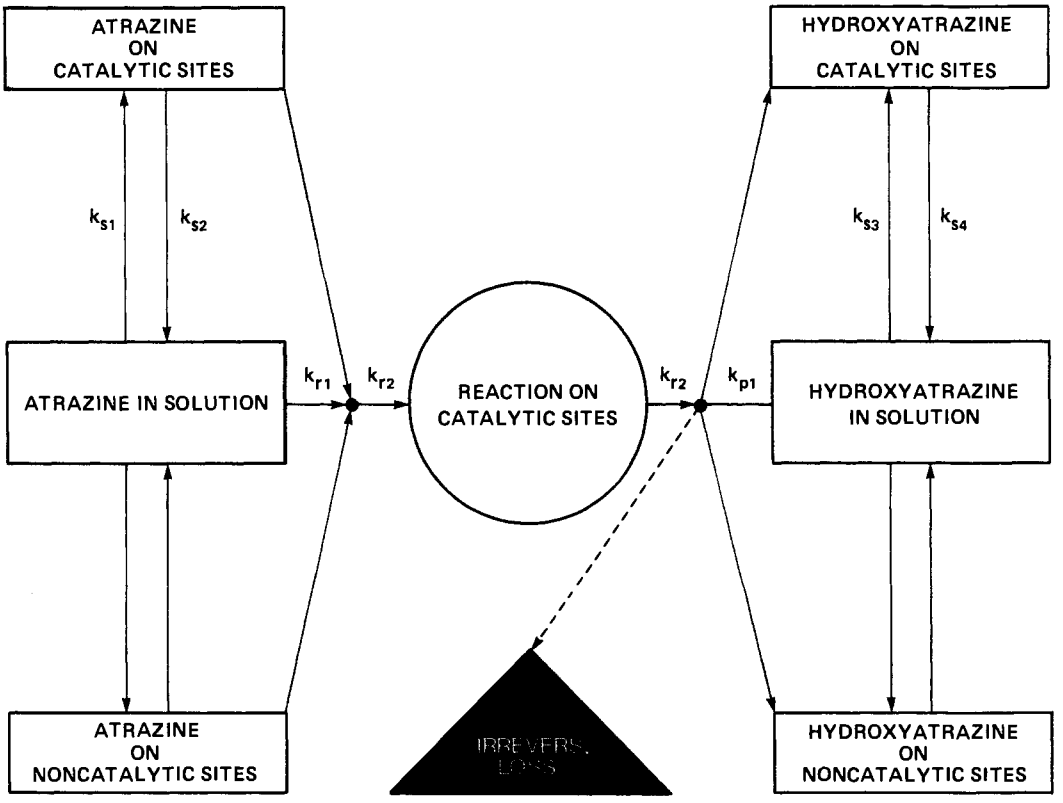

Figure 8. Atrazine–organic soil system. Sorption and reaction, with material balance loss. Kinetic rate constants are indicated for those sorption, desorption, and reaction processes observed in the present case.

Table VI. Atrazine–Organic Soil System at 25.0 °C: Effect of Phase Separations on Kinetics Measurements

point no.	At (whole slurry), M × 10^5	At filtrate (0.45 mm), M × 10^5	AtOH (whole slurry), M × 10^6	AtOH (filtrate) (0.45 mm), M × 10^6	reactn time, days
1	4.865	4.705	0.000	0.0000	0.000
2	4.778	4.343	0.000	0.0000	0.500
3	4.693	4.059	0.489	0.0000	1.000
4	4.609	3.813	1.016	0.1816	1.500
5	4.526	3.610	1.535	0.3684	2.000
6	4.444	3.444	2.046	0.5513	2.500
7	4.364	3.308	2.550	0.7303	3.000
8	4.286	3.198	3.046	0.9053	3.500
9	4.209	3.108	3.534	1.0765	4.000
10	4.133	3.034	4.014	1.2438	4.500
11	4.058	2.973	4.487	1.4071	5.000
12	3.985	2.921	4.952	1.5666	5.500
13	3.914	2.875	5.409	1.7221	6.000
14	3.844	2.833	5.858	1.8738	6.500
15	3.775	2.792	6.300	2.0215	7.000
16	3.707	2.751	6.734	2.1653	7.500
17	3.641	2.710	7.160	2.3052	8.000
18	3.577	2.667	7.578	2.4413	8.500
19	3.514	2.623	7.989	2.5734	9.000
20	3.452	2.577	8.392	2.7016	9.500
21	3.391	2.532	8.787	2.8259	10.000
22	3.332	2.487	9.175	2.9463	10.500
23	3.275	2.445	9.554	3.0627	11.000
24	3.219	2.408	9.926	3.1753	11.500
25	3.164	2.379	10.290	3.2840	12.000
26	3.110	2.361	10.647	3.3888	12.500
27	3.058	2.358	10.996	3.4896	13.000

Table VII. Atrazine–Organic Soil System at 25.0 °C: Chemical Species during the Kinetics Run

	atrazine		hydroxyatrazine		material balance loss		
point no.	free in soln, M × 10^5	labile sorbed, mol/L of slurrry × 10^5	free in soln, M × 10^6	labile sorbed, mol/L of slurry × 10^6	mol/L of slurry × 10^6	mol/g of soil × 10^6	reactn time, days
1	4.705	0.161	0.0000	0.0000	2.5290	1.255	0.000
2	4.343	0.425	0.0000	0.0000	3.3990	1.687	0.500
3	4.059	0.634	0.0000	0.4890	3.7660	1.869	1.000
4	3.813	0.796	0.1816	0.8342	4.0802	2.025	1.500
5	3.610	0.916	0.3684	1.1665	4.3891	2.179	2.000
6	3.444	1.001	0.5513	1.1494	4.6918	2.329	2.500
7	3.308	1.056	0.7303	1.8195	4.9882	2.476	3.000
8	3.198	1.109	0.9053	2.1403	5.2784	2.620	3.500
9	3.108	1.101	1.0765	2.4572	5.5623	2.761	4.000
10	3.034	1.099	1.2438	2.7703	5.8399	2.899	4.500
11	2.973	1.085	1.4071	3.0796	6.1113	3.034	5.000
12	2.921	1.065	1.5666	3.3850	6.3764	3.165	5.500
13	2.875	1.039	1.7221	3.6866	6.6353	3.294	6.000
14	2.833	1.011	1.8738	3.9843	6.8879	3.419	6.500
15	2.792	0.983	2.0215	4.2782	7.1343	3.542	7.000
16	2.751	0.956	2.1653	4.5684	7.3743	3.661	7.500
17	2.710	0.932	2.3052	4.8546	7.6082	3.777	8.000
18	2.667	0.910	2.4413	5.1370	7.8347	3.889	8.500
19	2.623	0.891	2.5734	5.4155	8.0571	4.000	9.000
20	2.577	0.875	2.7016	5.6903	8.2721	4.106	9.500
21	2.532	0.860	2.8259	5.9612	8.4809	4.210	10.000
22	2.487	0.846	2.9463	6.2282	8.6835	4.310	10.500
23	2.445	0.830	3.0627	6.4916	8.8797	4.408	11.000
24	2.408	0.811	3.1753	6.7509	9.0698	4.502	11.500
25	2.379	0.785	3.2840	7.0060	9.2540	4.594	12.000
26	2.361	0.749	3.3888	7.2582	9.4310	4.682	12.500
27	2.358	0.701	3.4896	7.5064	9.6020	4.766	13.000

ical compounds slowly diffuse into the interiors of soil particles. Other authors have agreed with this (Chiba, 1969; Adams, 1973; Khan, 1973), and it might explain the material balance loss. This suggests that a future investigation could seek to correlate the material balance loss with radiotracer measurements of bound residues. Measurements of particle distributions would contribute insight to such a project.

Total labile sorption has been plotted in Figure 4, in order to determine whether there are any systematic trends. After the first 5 days of increase, there is a smaller continuing increase. Although this latter increase after 5 days is consistent with both theory and results reported previously for humic acid (Gamble and Khan, 1988), it is hardly greater than the experimental error.

III. Sorption Equilibria and Kinetics. The test functions Q_1 and Q_2 plotted in Figure 5 show the behaviors predicted by eq 9, 12, 19, and 20. Sorption–desorption equilibrium has evidently been reached after 5.0 days, so that Q_1 and Q_2 become $\bar{K}_1$ and $\bar{K}_2$. Beyond 5.0 days,

Table VIII. Labile Sorption: Establishment of Equilibrium[a]

	atrazine		hydroxyatrazine		labile total:	
no.	$Q_1 \times 10^{-2}$	$X_1 \times 10^3$	$Q_2 \times 10^{-3}$	$X_2 \times 10^3$	$X_T \times 10^3$	days
1	0.240	1.129		0.000	1.129	0.000
2	0.687	2.983		0.000	2.983	0.500
3	1.102	4.452		0.343	4.795	1.000
4	1.474	5.585	3.244	0.586	6.170	1.500
5	1.793	6.427	2.239	0.819	7.246	2.000
6	2.056	7.023	1.919	1.049	8.073	2.500
7	2.261	7.415	1.764	1.277	8.692	3.000
8	2.411	7.638	1.675	1.502	9.141	3.500
9	2.510	7.727	1.617	1.725	9.452	4.000
10	2.566	7.711	1.579	1.945	9.656	4.500
11	2.588	7.618	1.551	2.162	9.780	5.000
12	2.584	7.472	1.532	2.376	9.848	5.500
13	2.562	7.292	1.518	2.588	9.880	6.000
14	2.531	7.710	1.507	2.797	9.894	6.500
15	2.496	6.900	1.500	3.003	9.903	7.000
16	2.464	6.711	1.496	3.207	9.918	7.500
17	2.437	6.538	1.493	3.408	9.946	8.000
18	2.419	6.386	1.492	3.606	9.992	8.500
19	2.409	6.353	1.492	3.801	10.050	9.000
20	2.406	6.138	1.494	3.994	10.130	9.500
21	2.409	6.036	1.496	4.184	10.220	10.000
22	2.412	5.936	1.499	4.372	10.310	10.500
23	2.408	5.825	1.503	4.557	10.380	11.000
24	2.387	5.689	1.508	4.739	10.430	11.500
25	2.340	5.508	1.513	4.918	10.430	12.000
26	2.251	5.260	1.519	5.095	10.350	12.500
27	2.107	4.918	1.525	5.269	10.190	13.000

[a] Organic soil carboxyl content is 0.7072×10^{-3} mol/g.

Table IX. Labile Sorption of Atrazine and Hydroxyatrazine at 25.0 °C (Organic Soil Carboxyl Groups in Free Acid Form)

	atrazine		hydroxyatrazine	
sample	$\bar{K}_1$	rel SD, %	$\bar{K}_2$	rel SD, %
Chernozem humic acid[a]	1.74×10^2	1.84	0.85×10^3	26.6
organic soil, run I 10(c)	2.23×10^2	11.3	2.85×10^3	8.99
organic soil, run I 10(d)	2.68×10^2	7.24	3.18×10^3	20.0
organic soil, run II	2.48×10^3	2.8	1.50×10^3	0.61

[a] Gamble and Khan, 1988.

the curves are not assumed to have any structural details that are meaningful outside the experimental errors. The numerical data are listed in Table VIII (Appendix).

The numerical values obtained for $\bar{K}_1$ and $\bar{K}_2$ have been averaged to give the values presented in Figure 6 and Table IX (Appendix). They are shown with similar results from two preliminary experiments. As a check on the correctness of the experimental method, they have also been compared with the values found previously (Gamble and Khan, 1988) for Alberta Chernozem humic acid. All three of the organic soil experiments have given excellent agreement with each other and with the humic acid, for the atrazine $\bar{K}_1$. Experiment 10 also shows good agreement with the humic acid experiment, for the hydroxyatrazine $\bar{K}_2$. The two preliminary experiments do not agree quite as well, but their values are suspect because of some irregularities in their data. Hydroxyatrazine is more strongly sorbed by about 1 order of magnitude.

According to the rate constants in Table IV, hydroxyatrazine is more labile than atrazine in addition to being more strongly sorbed. Hydroxyatrazine is sorbed both faster and more strongly than atrazine is. This is consistent with Ashton's report (Ashton, 1961; Baily and White, 1964) that the lateral movement of hydroxyatrazine in soils is faster than that of atrazine. The two compounds differ in at least one other way. Atrazine has a sorption rate constant only about one-third as great as its desorption rate constant. Hydroxyatrazine, however, has a sorption rate constant about twice as large as its desorption constant.

Table X. Atrazine–Organic Soil System at 25.0 °C: Pseudo-First-Order Reaction Rate Constants for Hydrolysis on the Catalytic Carboxyl Sorption Sites[a]

point no.	X_{At}	reactn time, days
11	7.618×10^{-3}	5.000
12	7.472×10^{-3}	5.500
13	7.292×10^{-3}	6.000
14	7.710×10^{-3}	6.500
15	6.900×10^{-3}	7.000
16	6.711×10^{-3}	7.500
17	6.538×10^{-3}	8.000
18	6.386×10^{-3}	8.500
19	6.353×10^{-3}	9.000
20	6.138×10^{-3}	9.500
21	6.036×10^{-3}	10.000
22	5.936×10^{-3}	10.500
23	5.825×10^{-3}	11.000
24	5.689×10^{-3}	11.500
25	5.508×10^{-3}	12.000
26	5.260×10^{-3}	12.500
27	4.918×10^{-3}	13.000

[a] Conditions: rate constant, $k_{r2} = 0.1430$ days^{-1}; standard error = 0.000 53 days^{-1}; unoccupied sites, 0.6717×10^{-3} mol/g; carboxyl content, 0.7072×10^{-3} mol/g (37).

Table XI. First-Order Rate Constants for Atrazine Conversion in Organic Soil Slurries at 25.0 °C[a]

process	constant, days^{-1}	std error	$t_{1/2}$, days
hydrolysis on catalytic carboxyl sites	$k_{r2} = 0.1430$	5.26×10^{-4}	4.85
conversion of reversibly sorbed reactant into total recoverable product	$K_{p3} = 0.09025$	2.76×10^{-4}	7.68

[a] Conditions: reaction time (days), $5.000 \le t \le 13.000$; site coverage by atrazine (mole fraction), $7.618 \times 10^{-3} \ge X_1 \ge 4.918 \times 10^{-3}$.

IV. Atrazine Hydrolysis Kinetics. Because the experimental method uniquely provides numerical values for free and sorbed species of both the reactant and the product, as illustrated by Figures 2 and 3, there is now a choice of four sets of experimental variables with which the first-order rate constant for atrazine conversion on the catalytic sites may be calculated. Listed in Table I, each calculation method uses an integral rate law form related to the chosen variables. Method B has been used here with the corresponding equation (26), because the two variables are direct experimental measurements. The avoidance of subtractions makes the best use of the experimental data by minimizing the effects of experimental errors.

The first-order rate constant for hydrolysis on the catalytic sorption sites, k_{r2}, is plotted in Figure 7, with Chernozem humic acid values (Gamble and Khan, 1988). Each kinetics experiment is insensitive to the k_{r2} change during its course. A set of kinetics experiments therefore produces a chord plot. The collection of nonidentical carboxyl groups contained in the organic soil is expected to give a spectrum of kinetic rate constants. Albery et al. (1985) have proposed a gaussian distribution of ln k_{r2} values.

X_{At}, the mole fraction of sites occupied by atrazine, is the one independent variable that shows close agreement between the organic soil value and the previous humic acid values (Gamble and Khan, 1988). A plot of k_{r2} against

moles/gram of sites occupied by atrazine does not put the organic soil value on the same curve with the humic acid values. A plot against grams of organic soil/liter of slurry would simply produce confusion. The samples, their carboxyl group contents, the experimental methods, and the calculation techniques were all different. The close agreement, therefore, provides another independent check on the correctness of the present method.

The dependence of k_{r2} on the mole fraction of sites occupied by atrazine has two implications: One is that Brönsted acid catalysis operates as suggested by Perdue and Wolfe (1983). The other is that the two samples with different carboxyl contents have at least comparable K_A vs α spectra. If the relationship in Figure 7 is sufficiently general, then it would be useful for the comparison of samples, extrapolations of laboratory measurements to field conditions, and general predictions. An important point is that logarithmic plots tend to obscure discrepancies, and the close agreement here has been obtained without their use. Karickhoff (1984) has pointed out that sorption may make a substantial change in the apparent reactivity of an organic compound. In the present work this is manifest in the difference between k_{r2} and k_{r1}. The numerical data for k_{r2} in organic soil are listed in Tables X and XI (Appendix).

V. Characteristics of the Material Balance Loss. Total labile hydroxyatrazine was found to give a good linear least-squares fit against total labile atrazine. The slope, however, was 0.6425 (mole of hydroxyatrazine/mole of atrazine) instead of 1.0. This means that only 64.3 mol % of the atrazine that disappears is represented by recovered hydroxyatrazine. Table V shows that the material balance loss is highly correlated with both the labile sorbed atrazine and the labile sorbed hydroxyatrazine. While the material balance loss and labile sorbed hydroxyatrazine increase together, the material balance loss increases as the labile sorbed atrazine decreases. This implies that the material balance loss is not directly caused by atrazine concentrations or concentration gradients.

VI. General Conclusions. Figure 8 is a postulated general model for the heterogeneous catalysis of atrazine hydrolysis in aqueous slurries of organic soil. In the most general possible case, noncatalytic sorption sites might exist as indicated. The present case has not shown any evidence of them, however. To the extent that hydroxyatrazine remains sorbed onto the catalytic sites on which it was formed, catalyst poisoning would exist. According to Table VIII (Appendix), the mole fraction of sites covered by hydroxyatrazine ranged from 0.0 to 5.27×10^{-3} during the experiment. Wang et al. suggested (in preparation) that atrazine and hydroxyatrazine might not compete directly for the same humic sorption sites.

For the heterogeneous catalysis of hydrolysis, Zepp and Wolfe (1987) made the two assumptions that mass transfer between physical phases is fast in comparison with the rates of chemical reaction and equilibrium is maintained. The experimental method developed here provides direct experimental checks on these two questions, so that no assumptions are necessary. In fact, the experimental results show that atrazine has a sorption rate constant not much more than one-third that of the hydrolysis on the sorption sites. This has an important consequence. The sorption equilibrium is not established for 5 days, during which the hydrolysis reaction removes atrazine from the sorption sites more quickly than it does from the external solution. For the sorption and desorption of 2,4-D and picloram by humic acid, Khan (1973) observed rate constants, energies of activation, and heats of activation indicating physical sorption. The present results for atrazine and hydroxyatrazine are likewise consistent with physical sorption.

A unique feature of the experimental method is that it can track the distinction between labile sorbed compounds and material balance loss throughout a whole chemical kinetics experiment. The required chemical analyses are simple and fast and do not deplete the sample by using large aliquots. Burns et al. (1973a,b) have commented that, for experiments in which adsorption is measured by difference between concentrations of initial and equilibrium solutions, determining whether or not decomposition of adsorbate takes place is essential. The present experimental method is uniquely effective in doing that. Wu and Gschwend (1986) have recently expressed the opinion that more research is needed on the effects of soil properties on the kinetics of sorption. The method should be useful for that purpose.

Because the experimental method is novel, independent checks on the correctness of the results are important. Not only are there satisfactory answers for the four experimental questions but also $\bar{K}_1$, $\bar{K}_2$, and k_{r2} results agree very well with those previously reported for a humic acid. This experimental method has a number of other potential uses. Preliminary trials indicate that it might be profitable for clays, clays having hydrous metal oxide coatings, whole soils, microbiological cultures, and tissue cultures. The requirement is that samples should have small particles that can be maintained in suspension by stirring. Because cation-exchange columns are available for HPLC use, it should also be possible to extend the method to metal ion interactions with some or all of the above types of samples.

SYMBOLS

C_0	unoccupied sorption sites (moles/liter of total slurry)
C_{At}	labile sorbed atrazine (moles/liter of total slurry)
C_{AtOH}	labile sorbed hydroxyatrazine (moles/liter of total slurry)
C_{T1}	total labile atrazine (free + sorbed) (moles/liter of total slurry)
C_{T2}	total labile hydroxyatrazine (free + sorbed) (moles/liter of total slurry)
C_1 and C_2	integration limits for C_{T1} or C_{T2}
$\bar{K}_1$	atrazine sorption equilibrium function
$\bar{K}_2$	hydroxyatrazine sorption equilibrium function
k_{B1}	atrazine sorption second-order rate constant (molarity × days)$^{-1}$
k_{B3}	hydroxyatrazine sorption second-order rate constant (molarity × days)$^{-1}$
k_{p3}	hydroxyatrazine apparent rate constant for appearance in solution (days)$^{-1}$
k_{r1}	atrazine apparent rate constant for disappearance from solution (days)$^{-1}$
k_{r2}	atrazine first-order rate constant for reaction on the catalytic sorption sites (days)$^{-1}$
k_{s1}	atrazine first-order rate constant for sorption from solution (days)$^{-1}$
k_{s2}	atrazine first-order rate constant for desorption into solution (days)$^{-1}$
k_{s3}	hydroxyatrazine first-order rate constant for sorption from solution (days)$^{-1}$
k_{s4}	hydroxyatrazine first-order rate constant for desorption into solution
M_{At}	molarity of atrazine in solution
M_{AtOH}	molarity of hydroxyatrazine in solution

M_1 and M_2	integration limits for M_{At} or M_{AtOH}
Q_1	test function for atrazine sorption equilibrium
Q_2	test function for hydroxyatrazine sorption equilibrium
r_1	atrazine rate of loss from solution by sorption (molarity/day)
r_2	atrazine rate of gain in solution by desorption (molarity/day)
t	reaction time (days)
t_1 and t_2	integration limits for t
t_E	elution time for compounds sorbed onto the HPLC column (minutes)
t_R	retention time for HPLC peaks (minutes)
θ_0	number of unoccupied sorption sites (moles/gram of organic soil)
θ_{At}	number of sorption sites occupied by atrazine (moles/gram of organic soil)
θ_{AtOH}	number of sorption sites occupied by hydroxyatrazine (moles/gram of organic soil)
U	flow velocity of the HPLC mobile phase (milliliters/minute)
V_A	volume of sample slurry aliquot taken for analysis (liters)
V_s	volume of sample slurry (liters)
v_m	volume of HPLC mobile phase available for washing trapped sample particles (liters/gram)
W_A	mass of sample slurry particles injected (grams)
W_S	mass of sample slurry particles (grams)

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Ali Ismaily carried out valuable kinetics experiments using the novel HPLC procedure. Rod McDowell contributed some important gas chromatography analyses for byproducts.

APPENDIX

Data on atrazine–organic soil systems are given in Tables VI–XI.

Registry No. Atrazine, 1912-24-9; hydroxyatrazine, 2163-68-0.

LITERATURE CITED

Adams, R. S. Factors Influencing Soil Adsorption and Bioactivity Of Pesticides. *Residue Rev.* **1973**, *47*, 1–54.

Albery, W. J.; Bartlett, P. N.; Wilde, C. P.; Darwent, J. R. A General Model For Dispersed Kinetics In Heterogeneous Systems. *J. Am. Chem. Soc.* **1985**, *107*, 1854–1859.

Ashton, F. M. Movement Of Herbicides In Soil With Simulated Furrow Irrigation. *Weeds* **1961**, *9*, 612–619.

Bailey, G. W.; White, J. L. Review Of Adsorption And Desorption Of Organic Pesticides By Soil Colloids With Implications Concerning Pesticide Bioactivity. *J. Agric. Food Chem.* **1964**, *12*, 324–332.

Behki, R. M.; Khan, S. U. Degradation Of Atrazine By Pseudomonas: N-Dealkylation And Dehalogenation Of Atrazine And Its Metabolites. *J. Agric. Food Chem.* **1986**, *34*, 746–749.

Burns, I. G.; Hayes, M. H. B.; Stacey, M. Some Physico-Chemical Interactions Of Paraquat With Soil Organic Materials And Model Compounds. I. Effects Of Temperature, Time, And Adsorbate On Paraquat Adsorption. *Weed Res.* **1973a**, *13*, 67–78.

Burns, I. G.; Hayes, M. H. B.; Stacey, M. Some Physico-Chemical Interactions Of Paraquat With Soil Organic Materials And Model Compounds. II. Adsorption And Desorption Equilibria In Aqueous Suspensions. *Weed Res.* **1973b**, *13*, 79–90.

Chiba, M. Factors Affecting The Extraction Of Organochlorine Insecticides From Soil. *Residue Rev.* **1969**, *30*, 63–113.

Cotterill, E. G. The Efficiency Of Methanol For The Extraction Of Some Herbicide Residues From Soil. *Pestic. Sci.* **1980**, *11*, 23–28.

Damanakis, M.; Drennan, D. S. H.; Fryer, J. D.; Holly, K. The Adsorption And Mobility Of Paraquat On Different Soils And Soil Constituents. *Weed Res.* **1970**, *10*, 264–277.

Di Toro, D. M.; Horzempa, L. M. Reversible And Resistant Components Of PCB Adsorption-Desorption: Isotherms. *Environ. Sci. Technol.* **1982**, *16*, 594–602.

Fava, A.; Eyring, H. Equilibrium And Kinetics Of Detergent Adsorption-A Generalized Equilibrium Theory. *J. Phys. Chem.* **1956**, *60*, 890–898.

Freeman, D. H.; Cheung, L. S. A Gel Partition Model For Organic Desorption From A Pond Sediment. *Science* **1981**, *214*, 790–792.

Gamble, D. S. Titrations Of Organic Soils With Standard Base: Solubility Of Ionizable Functional Group At 25 °C. *Can. J. Soil Sci.* **1989**, *69*, 313–325.

Gamble, D. S.; Khan, S. U. Atrazine Hydrolysis In Soils: Catalysis By The Acidic Functional Groups Of Fulvic Acid. *Can. J. Soil Sci.* **1985**, *65*, 435–443.

Gamble, D. S.; Khan, S. U. Atrazine Hydrolysis In Aqueous Suspensions Of Humic Acid At 25.0 °C. *Can. J. Chem.* **1988**, *66*, 2605–2617.

Gamble, D. S.; Khan, S. U.; Tee, O. S. Atrazine Hydrolysis. Part I; Proton Catalysis At 25 °C. *Pestic. Sci.* **1983**, *14*, 537–545.

Hamaker, J. W.; Goring, C. A. L.; Youngson, C. R. *Organic pesticides in the Environment*; Americal Chemical Society: Washington, DC, 1966; p 23.

Haniff, M. I.; Zenius, R. H.; Langford, C. H.; Gamble, D. S. The Solution Phase Complexing Of Atrazine By Fulvic Acid: Equilibria At 25 °C. *J. Environ. Sci. Health* **1985**, *B20*(2), 215–262.

Harris, C. I.; Warren, G. F. Adsorption And Desorption Of Herbicides By Soil. *Weeds* **1964**, *12*, 120–126.

Karickhoff, S. W. Sorption Kinetics of Hydropholic Pollutants in Natural Sediments. In *Contaminants and Sediments*; Baker, R. A., Ed.; Ann Arbor Science: Ann Arbor, MI, 1980; Vol. 2, pp 193–205.

Karickhoff, S. W. Organic Pollutants In Aquatic Systems. *J. Hydraulic Eng.* **1984**, *110*, 707–735.

Karickhoff, S. W.; Morris, K. R. Sorption Dynamics Of Hydrophonic Pollutants In Sediment Suspension. *Environ. Toxicol. Chem.* **1985**, *4*, 469–479.

Khan, S. U. Equilibrium and Kinetic Studies Of The Adsorption Of 2, 4 D and Picloram On Humic Acid. *Can. J. Soil Sci.* **1973**, *53*, 429–434.

Khan, S. U.; Greenhalgh, R.; Cochrane, W. P. Determination Of Linuron Residue In Soil. *Bull. Environ. Contam. Toxicol.* **1975**, *13*, 602–610.

Knight, B. A. G.; Tomlinson, T. E. The Interaction Of Paraquat (1:′-Dimethyl 4:4′-Dipyridylium Dichloride) With Mineral Soil. *J. Soil Sci.* **1967**, *18*, 233–243.

Macalady, D. L.; Wolfe, N. L. "Abiotic Hydrolysis of Sorbed Pesticides." *ACS Symp. Ser.* **1984**, *259*, 221–244.

Mill, T. Data Needed To Predict The Environmental Fate of Organic Chemicals. In *Dynamics, Exposure and Hazard Assessment of Toxic Chemicals*; Haque, R., Ed.; Ann Arbor Science: Ann Arbor, MI, 1980; Vol. 9, pp 297–322.

Parris, G. E. Covalent Binding of aromatic Amines to Humates. 1. Reactions with Carbonyls and Quinones. *Environ. Sci. Technol.* **1980**, *14*, 1099–1106.

Perdue, E. M.; Wolfe, N. L. Modification of pollutant hydrolysis kinetics in the presence of humic substances. *Environ. Sci. Technol.* **1982**, *16*, 847–852.

Perdue, E. M.; Wolfe, N. L. Predictions of Buffer Catalysis in Field and Laboratory Studies of Pollutant Hydrolysis Reactions. *Environ. Sci. Technol.* **1983**, *17*, 635–642.

Purkayastha, R.; Cochrane, W. P. Comparation of Electron Capture and Electrolytic Conductivity Detectors for the Residue Analysis of s-Triazine Herbicides. *J. Agric. Food Chem.* **1973**, *21*, 93–98.

Smith, A. E. Comparison of Solvent Systems for Extracting Herbicide Residues from Weathered Field Soils. *Pestic. Sci.* **1978**, *9*, 7-11.

Smith, A. E. Comparison of Solvent Systems for the Extraction of Atrazine, Benzoylprop, Flamprop, and Frifluralin from Weathered Field Soils. *J. Agric. Food Chem.* **1981**, *29*, 111-115.

Smith, A. E. Use of Acetonitrile for the Extraction of Herbicide Residues from Soils. *J. Chromatogr.* **1976**, *129*, 309-314.

Smith, A. E.; Milward, L. J. Comparison of Solvent Systems for the Extraction of Dielofop Acid, Picloram, Simazine, and Triallate from Weathered Field Soils. *J. Agric. Food Chem.* **1983**, *31*, 633-637.

Talbert, R. E.; Fletchall, O. H. The Adsorption of some s-Triazines in Soils. *Weeds* **1965**, *13*, 46-52.

Wang, X.-d.; Langford, C. H.; Gamble, D. S.; Zienius, R. H. The Interaction of Atrazine with Laurentian Fulvic Acid: Binding and Hydrolysis. In preparation, 1988.

Wolfe, N. L. Determining the Role of Hydrolysis in the Fate of Organics in Natural Waters. In *Dynamics, Exposure and Hazard Assessment of Toxic Chemicals*; Haque, R., Ed.; Ann Arbor Science: Ann Arbor, MI, 1980; pp 163-177.

Wu, S.-C.; Gschwend, P. M. Sorption Kinetics of Hydrophobic Organic Compounds to Natural Sediments and Soils. *Environ. Sci. Technol.* **1986**, *20*, 717-725.

Zepp, R. G.; Wolfe, N. L. Abiotic Transformations of Organic Chemicals at the Particle-Water Interface. In *Aquatic Surface Chemistry*; Stumm, W., Ed.; Wiley: New York, 1987; Chapter 16, pp 423-455.

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Effect of High Dietary Nitrate on the Disposition of Sulfamethazine [4-Amino-*N*-(4,6-dimethyl-2-pyrimidinyl)benzenesulfonamide] in Swine†

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Swine (58-74-kg initial weight) were fed a corn-soybean meal basal diet that contained 110 ppm sulfamethazine [4-amino-*N*-(4,6-dimethyl-2-pyrimidinyl)benzenesulfonamide; sulmet] and 0, 10, 100, 500, or 1000 ppm nitrate. The concentrations of nitrite in the oral cavity and the concentrations of desaminosulfamethazine [*N*-(4,6-dimethyl-2-pyrimidinyl)benzenesulfonamide, DA-sulmet] in the blood were increased by feeding the highest levels of nitrate; however, 10 or 100 ppm of nitrate in the diet had little or no effect on nitrite and DA-sulmet concentrations in the oral cavity. Supplementing the diet with all levels of nitrate had little or no effect on the concentrations of sulmet and N^4-Ac-sulmet in swine blood.

Sulfamethazine [4-amino-*N*-(4,6-dimethyl-2-pyrimidinyl)benzenesulfonamide, sulmet; Figure 1] is used extensively by the swine industry to prevent and control bacterial infections and to increase animal growth rate and improve feed efficiency. Concern about tissue residues was the impetus for studies on the disposition of sulmet and related sulfonamide drugs in swine. When [^{14}C]sulmet was administered orally to swine, most of the radioactivity was excreted in the urine as sulmet and N^4-acetylsulfamethazine (N^4-Ac-sulmet; Figure 1) (Paulson et al., 1981). A unique metabolite, desaminosulfamethazine [*N*-(4,6-dimethyl-2-pyrimidinyl)benzenesulfonamide, DA-sulmet; Figure 1] was also present in the blood and other tissues from swine dosed with [^{14}C]sulmet (Paulson and Struble, 1980; Paulson et al., 1981). Subsequent studies with rats demonstrated that high dietary nitrite greatly enhanced the conversion of sulmet to DA-sulmet (Paulson, 1986) and the deamination of other sulfonamide drugs (Woolley and Sigel, 1982; Nelson et al., 1987). Later it was unequivocally shown that sulmet in the presence of nitrite and acid conditions in the stomach of the rat was converted to a diazonium cation (DZ-sulmet; Figure 1) and that this reactive intermediate was a precursor to DA-sulmet (Paulson et al., 1987).

Observations that DZ-sulmet was weakly mutagenic when evaluated by the Ames test (Paulson et al., 1987) and that the half-life of DA-sulmet in swine tissues was several times longer than the half-life of sulmet (Mitchell and Paulson, 1986) were the stimulus for additional investigations to determine the effect of dietary nitrite on the disposition of sulmet in swine (Paulson and Feil, 1987). Comparative studies in which swine were given a single oral dose of [^{14}C]sulmet in combination with nitrite (165 mg of [^{14}C]sulmet and 2.25 g of $NaNO_2$ in 1.5 kg of feed) or with [^{14}C]-DZ-sulmet alone (165 mg of sulmet equiv in 1.5 kg of feed) provided evidence that sulmet in the presence of nitrite and the acid conditions in the gastrointestinal tract of swine was converted to DZ-sulmet and that DZ-sulmet was a precursor to DA-sulmet (Figure 1) (Paulson and Feil, 1987). Nitrite supplementation decreased the concentration of sulmet and increased the concentration of DA-sulmet in the swine blood.

The levels of nitrite used in the experiments described above were in excess of the levels expected in conventional corn-soybean meal swine diets. However, high concentrations of nitrate are sometimes present in feed and H_2O consumed by swine (Wright and Davison, 1964), and there is much evidence that nitrate is reduced to nitrite by microbes in the oral cavity and, under certain condi-

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