Influence of Soil Aggregate Size on Atrazine Sorption Kinetics

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Soil aggregate size may be an important physical property regulating herbicide behavior; however, little information exists to evaluate this effect. The influence of aggregate size on atrazine [6-chloro-*N*-ethyl-*N*′-(1-methylethyl)-1,3,5-triazine-2,4-diamine] sorption coefficients (K_d) and sorption kinetics is investigated by batch equilibration using a suite of whole (0–5 mm) and crushed (<0.4 mm) aggregates isolated from two Iowa soils. Atrazine K_d values for both whole and crushed aggregates equilibrated for 72 h ranged between 3.02 and 4.09. Although significant differences occurred when size classes within soil type were compared, the magnitude of the aggregate effects on atrazine K_d values appears to be minor. Time-course experiments for atrazine sorption by whole aggregates analyzed using a modified first-order regression equation indicated that sorption was initially rapid (within 24 h), followed by a period of slower sorption. Aggregate size influenced the rate constants somewhat, but the effects also were minor.

Keywords: *Aggregate; atrazine; sorption; kinetics*

INTRODUCTION

The persistence and movement of atrazine [6-chloro-*N*-ethyl-*N*′-(1-methylethyl)-1,3,5-triazine-2,4-diamine] in soils are controlled partially by sorption reactions. The effects of numerous soil properties including texture (Weber, 1970), pH (Bailey and White, 1970), mineralogy (Laird et al., 1992), and organic matter content (Hayes, 1970) on atrazine sorption have received considerable attention. However, information on the effects of soil aggregate size on the sorption and movement of pesticides is scarce. Ghadiri and Rose (1991), investigating pesticide enrichment in eroded sediments from an Australian soil with a history of pesticide application, reported that higher pesticide concentrations occurred in outer aggregate regions relative to inner regions. They rationalized that the pesticides were sorbed onto aggregate surfaces and that diffusional processes were insufficient to bring about a uniform distribution of sorbed pesticide within the aggregate. A few pesticide movement studies (Davidson and Chang, 1972; Hance, 1976; Dekkers and Barbera, 1977; Achik et al., 1991) have been conducted using a limited suite of soil aggregate sizes and a few select pesticides. Pore size associated with soil aggregates influenced pore water residence time, which would control pesticide penetration into large and small pores spaces. Large and small size aggregates would therefore have different rates of equilibration with pesticides (Brusseau and Rao, 1989).

Some model simulations postulate that diffusion effects due to aggregate size will influence the exchange of pesticides into and out of aggregates (Brusseau and Rao, 1989). However, the influence of aggregate size on atrazine sorption is not understood at the present time. The objective of this study was to determine the rate and amount of atrazine sorption by large and small soil aggregates. Sorption of atrazine to a suite of whole and crushed aggregates obtained from two Iowa soils was also investigated. Crushed aggregates removed the effects of intra-aggregate porosity on sorptive processes.

Table 1. Select Physicochemical Properties of Clarion and Edina Soil Aggregates [from Collado and Karlen (1992)]

soil	aggregate size (mm)	texture (%) sand	silt	clay	OC (g kg^{-1})
Clarion	0.0–0.5	41.6	37.8	20.6	25.8
	0.5–1.0	43.1	36.6	20.3	26.6
	1.0–2.0	40.0	38.4	21.6	26.4
	2.0–3.0	40.1	38.2	21.7	27.6
	3.0–4.0	39.4	38.7	21.9	27.6
	4.0–5.0	40.2	38.3	21.5	29.7
Edina	0.0–0.5	2.2	74.6	23.2	24.7
	0.5–1.0	3.5	72.6	23.8	23.1
	1.0–2.0	4.3	72.7	23.0	24.0
	2.0–3.0	3.2	73.2	23.5	23.5
	3.0–4.0	2.7	73.7	23.6	23.9
	4.0–5.0	2.7	73.5	23.8	25.8

MATERIALS AND METHODS

Isolation of Soil Aggregates. Six sizes (0–0.5, 0.5–1, 1–2, 2–3, 3–4, and 4–5 mm) of soil aggregates were obtained by dry-sieving from the Ap horizons (0–15 cm) of Wisconsinan-age glacial till (Clarion loam; fine-loamy, mixed, mesic Typic Hapludolls) and loess (Edina silt loam; fine, montmorillonitic, Typic Argialbolls) soils. Soil locations, cropping history, and aggregate extraction have been described by Collado and Karlen (1992). The aggregate sizes within each soil type had similar textures and OC contents (Table 1), which allowed atrazine sorption comparison between aggregate sizes within soils. The sorption of atrazine to aggregate from each size class crushed to pass a 0.4-mm sieve also was determined.

Atrazine Sorption by Whole and Crushed Aggregates. Batch equilibration measurements of atrazine sorption were performed by placing 4 g of air-dried whole (all isolated sizes) and crushed aggregates into 25-mL glass centrifuge tubes and adding 20 mL of 2 μg mL^{-1} atrazine (99.0% purity, Chem Service, West Chester, PA) dissolved in 0.01 M $CaCl_2$. Replicate tubes along with controls (atrazine without soil) were

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agitated at room temperature (21–23 °C) using a rocking shaker (Eberbach shaker, Eberbach Corp., Ann Arbor, MI) at 60 cycles m^{-1} (6-cm stroke length). Observation of the aggregates after shaking revealed that some aggregate destruction did inevitably occur during the equilibration processes. Additional aggregate destruction during removal from tubes complicated our ability to determine the amount of aggregate breakdown during equilibration. Although aggregate breakdown was unavoidable, we believe that the magnitude of aggregate destruction was minimized by agitating the tubes at the shaker's lowest speed. Equilibration was reached in 72 h, and no atrazine degradation products were observed in preliminary experiments. After equilibration, the tubes were centrifuged, and 3 mL of supernatant was filtered using a 0.2-μm nylon filter disk in a glass HPLC autosampler vial. Atrazine in the initial and equilibrium solution was quantified by an HPLC system which consisted of a Waters Nova-Pak 4-μm C_{18} column (Waters Chromatography, Marlborough, MA) using a mobile phase of acetonitrile (AcN) and Millipore Milli-Q H_2O at a gradient of AcN/H_2O of 65/35 at 1 mL min^{-1} with UV detection at 220 nm. External standards that ranged in concentration from 0 to 2.5 μg mL^{-1} were used to quantify atrazine in solution. The minimum detectable atrazine concentration in the equilibrium solution was determined to be 5 ng per injection (using 30-μL injection volume). Ten repeated autoinjections of the same sample had a mean atrazine concentration that varied by <2%. Recovery of atrazine in controls ranged from 95 to 105% (compared with controls at time 0 h), and no atrazine degradation products were observed in any, samples throughout the equilibration periods. The difference between initial atrazine concentration (mg L^{-1}) and in the equilibrium solution was attributed to sorption by soil aggregates. The sorption equilibrium partition coefficient K_d (L kg^{-1}) was calculated as

$$K_d = \text{mg of atrazine kg}^{-1} \text{ of soil/mg of atrazine L}^{-1} \text{ of equil solution} \quad (1)$$

Atrazine Sorption Kinetics. The batch equilibration technique described above was used to determine atrazine sorption kinetics of 0–0.5-, 1–2-, and 3–4-mm whole soil aggregates from both soil types. Duplicate samples were shaken for 1, 3, 6, 24, 48, and 72 h, and the quantity of atrazine sorbed was determined as previously described. Sorption kinetics were described by nonlinear least squares procedures (SAS Institute, 1985) using the regression equation

$$S_T = S_i(1 - e^{-k_1 t}) + k_2 t \quad (2)$$

where S_T is total atrazine sorbed to soil (mg kg^{-1}), S_i is the initial atrazine sorbed (mg kg^{-1}), k_1 is a first-order rate constant (h^{-1}), and k_2 (mg h^{-1}) is a zero-order rate constant describing the increase in atrazine sorption above S_i.

RESULTS AND DISCUSSION

Atrazine Sorption by Whole and Crushed Aggregates. Atrazine K_d values for whole and crushed aggregates of both soils ranged between 3.02 and 4.09 (Table 2). The narrow range of atrazine K_d values within each soil type reflects the similar physicochemical properties of the aggregates size classes (Table 1). The smallest aggregate size (0–0.5 mm) for both soil types and the 1.0–2.0- and 2.0–3.0-mm aggregates for the Edina soil had different atrazine K_d values (one-way ANOVA, $P < 0.05$) than other aggregates within soil types. Although these differences were statistically significant, the difference due to size on atrazine K_d values was less than 25%. Also, aggregate effects appear to be minor since the overall mean atrazine K_d values by soil type for whole vs crushed aggregates for the Clarion (3.42 vs 3.36) and Edina (3.88 vs 3.83) soils were similar.

Table 2. Comparison of Mean Atrazine K_d Values for Whole and Crushed Soil Aggregates Determined Using the Batch Equilibration Method

soil	aggregate size (mm)	K_d values for soil aggregates[a] whole	crushed[b]
Clarion	0.0–0.5	3.02 (0.11)	nd[c]
	0.5–1.0	3.48 (0.05)	3.34 (0.04)
	1.0–2.0	3.51 (0.09)	3.09 (0.21)
	2.0–3.0	3.61 (0.04)	3.31 (0.10)
	3.0–4.0	3.44 (0.01)	3.63 (0.01)
	4.0–5.0	3.47 (0.01)	3.43 (0.04)
	lsd (0.05)	0.22	0.38
	mean[d]	3.42 (0.21)	3.36 (0.21)
Edina	0.0–0.5	3.54 (0.11)	nd
	0.5–1.0	4.07 (0.15)	3.81 (0.08)
	1.0–2.0	3.78 (0.02)	3.72 (0.14)
	2.0–3.0	3.70 (0.01)	3.68 (0.01)
	3.0–4.0	4.09 (0.06)	4.02 (0.24)
	4.0–5.0	4.09 (0.07)	3.91 (0.09)
	lsd (0.05)	0.28	0.48
	mean[d]	3.88 (0.24)	3.83 (0.19)

[a] Comparison of atrazine K_d for whole and crushed soil aggregates by soil type using a one-way ANOVA. Standard deviations are given in parentheses. [b] Whole soil aggregates crushed to pass a 0.4-mm sieve. [c] nd, not determined. [d] Mean atrazine K_d by soil type and aggregation.

The aggregates were crushed to the common size of <0.4 mm to remove the influence of intra-aggregate porosity on sorptive processes. No differences were found in atrazine K_d for the crushed Edina soil aggregates. However, atrazine K_d values differed slightly in crushed Clarion aggregates. Although these differences were statistically significant, atrazine K_d differences between crushed aggregates were less than 20% and probably can be ignored. When the atrazine K_d values for each individual whole vs crushed aggregate size class between soil types were compared, no significant differences (Student's t-test, $P < 0.05$) occurred. These data suggest that the influence of intra-aggregate porosity on atrazine sorption is minimal. The lack of aggregate effects on atrazine sorption may be due to the equilibration time (72 h) used for the K_d estimates. In future work, additional time may be necessary to allow the herbicide to diffuse into the micropores associated with the aggregates. However, interpretation of sorption data gathered from long-term incubation studies is complicated by the loss of herbicide in the equilibrium solution due to biotic and abiotic processes not associated with sorption.

Atrazine Sorption Kinetics. The adsorption of atrazine was examined using eq 2, which is a modified form of first-order kinetics. Equation 2 represents adsorption as a first-order process with an asymptotic limit S_i and a rate constant k_1. The simultaneous adsorption and desorption reactions are therefore considered as the net forward reaction toward adsorption. The first-order approach to sorption has been used previously to describe the sorption process in soil (Aharoni and Sparks, 1991). The additional zero-order rate constant, k_2, describes sorption above the asymptotic limit (S_i). In this study, eq 2 was used as a simple, empirical model of more complex processes, not as a strict evaluation of the kinetic rate laws governing sorption. More complex models exist, but independent estimations of adsorption and desorption rates or multiple sorption sites are difficult to obtain and were not considered necessary to this study. The modified-first-

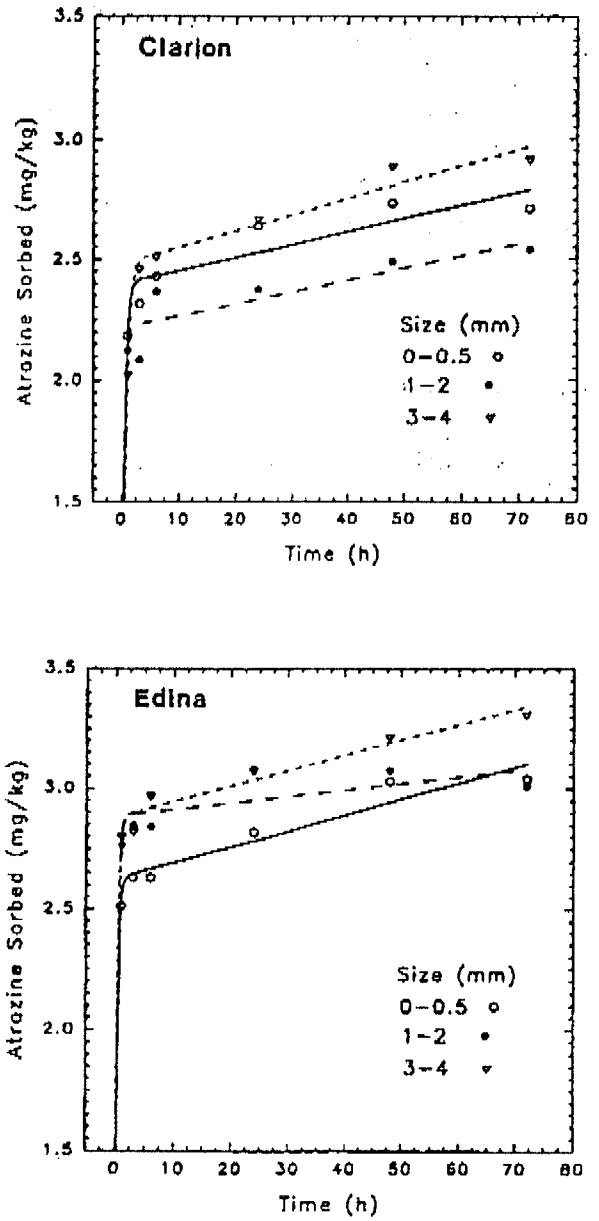

Figure 1. Kinetics of sorption of atrazine to three sizes of aggregates from the Clarion (top) and Edina (bottom) soils. Symbols represent means and the lines represent predicted quantities of sorbed atrazine (S_T).

order model (eq 2) fit the experimental data reasonably well ($P < 0.01$), as shown in Figure 1. Regression analyses (results not shown) found that a strict first-order model (k_2 removed or set to zero) resulted in greater residual sums of squares, smaller F values, and systematic lack of fit, in comparison to eq 2.

Time-course experiments (Figure 1) show that sorption is initially rapid, followed by a period during which the adsorbed fraction increases at a slower rate. Regression parameters are shown in Table 3. The initial rapid phase of adsorption was completed within 24 h. Rate constants (k_1) describing initial adsorption to the Clarion aggregates decreased as aggregate size increased. This trend would be expected if diffusional effects were greater in larger aggregates. Rate constants describing initial adsorption to the Edina aggregates were similar across size classes. However, differences in the rate constants have little overall effect on the process over the 72-h time course. The parameter S_i represents the initial amount of atrazine sorbed

Table 3. Kinetic Parameters Describing Atrazine Sorption to Soil Aggregates during Batch Equilibrium Experiments

		parameters[a]		
soil	size (mm)	S_i (mg kg^{-1})	k_1 (h^{-1})	k_2 (mg kg^{-1} h^{-1})
Clarion	0–0.5	2.22 (0.06)	3.11 (1.09)	0.0048 (0.0016)
	1–2	2.40 (0.05)	2.37 (0.36)	0.0054 (0.0012)
	3–4	2.49 (0.04)	1.65 (0.14)	0.0067 (0.0010)
Edina	0–0.5	2.89 (0.04)	3.15 (0.56)	0.0027 (0.0001)
	1–2	2.63 (0.04)	3.05 (0.60)	0.0066 (0.0011)
	3–4	2.88 (0.04)	3.48 (1.08)	0.0063 (0.0041)

[a] Values in parentheses are standard errors of the parameter estimates.

during the first-order process. Values of S_i show the same trends as the K_d values in Table 2. The 0–0.5-mm Clarion aggregates had S_i values similar to those of the other sized aggregates. The S_i values for the Edina aggregates were similar, as were the K_d values for these size classes shown in Table 2.

The rate constants controlling sorption during the latter phases of the time-course experiment (k_2) were similar in all aggregate size classes. All values of k_2 were different from zero ($P < 0.05$). This parameter may describe the continuing slow movement of atrazine into the less accessible internal microsites within the aggregates. McCall and Agin (1985) reported that adsorption of picloram increased slowly over long periods of time and showed evidence that these increases could be described by a two-site sorption model. The slowly increasing adsorption phenomenon described by McCall and Agin (1985) may be the same mechanism that accounts for the slow increase in adsorption in our experiments.

Aggregate size within the range used in these experiments had little effect on atrazine sorption kinetics. The aggregates used in these studies had a substantial number of relatively large surface cavities and fractures (as observed with a microscope). Although no direct measurement of pore space was made, we believe that the large number of surface depressions and fractures provides a large amount of internal pores, which would have the effect of lowering diffusional resistance relative to that of the aggregate matrix. Our data indicate that atrazine rapidly diffused through the macroaggregate structures, as evidenced by the similar rate constant (k_1) for different-sized aggregates and the similarity of adsorption coefficients between whole and crushed aggregates. The slow increase in sorption observed after 24 h of equilibration may be an effect of aggregate structure but at the microaggregate scale. Although these aggregates are from two soils formed under different conditions, they are similar in many ways. It is conceivable that aggregates from other soils may behave differently due to variations in soil pH, texture, and OC content.

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