

# Clomazone Sorption in Soil: Incubation Time, Temperature, and Soil Moisture Effects

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Sorption–desorption of the herbicide clomazone in a silty clay loam soil was evaluated for time, temperature, and moisture dependence. In unsaturated soil, clomazone sorption peaked at different times depending on incubation temperature. Soil moisture had little effect on clomazone sorption. The apparent  $K_d$  increased (2.4-fold at 5 °C and 4.1-fold at 35 °C) throughout the 84-day incubation period. Clomazone extractable with water in 15 min decreased with incubation time, while that recovered between 15 min and 24 h was essentially constant. Desorption kinetics were well characterized with a simple radial diffusion model by adjusting a single parameter (concentration of the labile pool). Batch equilibrium sorption isotherms (saturated soil) were temperature independent (5–35 °C). The data indicate that the time-dependent sorption of clomazone in unsaturated soil is controlled by a temperature-dependent process. Clomazone losses from solution explained much of the increase in apparent  $K_d$  over time.

**Keywords:** *Clomazone; sorption; biodegradation; volatilization*

## INTRODUCTION

The fate of a pesticide in soil is often controlled by its sorption properties (Jury et al., 1991; Sims et al., 1991). Most regulatory environmental fate and transport models predict chemical fate in soils utilizing sorption constants obtained from batch sorption isotherms. The experimental procedures used for these isotherm determinations eliminate structural and diffusional barriers to sorption and thus do not account for the effects of physical constraints encountered under field conditions. Sorption in unsaturated soil is a dynamic process dependent on time and environmental conditions (Scribner et al., 1992) and is thus not completely described by sorption coefficients ( $K_f$  or  $K_d$ ) derived from batch isotherms. The initial rate of sorption of a chemical in unsaturated soil is often slower and less extensive than that measured in batch sorption experiments, but with time the apparent  $K_d$  (the ratio of sorbed to solution concentrations) tends to increase and may eventually exceed the sorption constant from isotherm data (McCall and Agin, 1985; Scribner et al., 1992). Consequently, the longer a pesticide is in contact with the soil, the more resistant the remaining pesticide will become to processes such as microbial degradation or leaching.

The herbicide clomazone [2-[(2-chlorophenyl)methyl]-4,4-dimethyl-3-isoxazolidinone] is water soluble (1100 mg/L at 25 °C) and volatile ( $vp = 1.92 \times 10^{-2}$  Pa at 25 °C) (Weed Science Society of America, 1989) and has a  $K_{ow}$  (octanol/water partition coefficient) of 350 (FMC Corp., 1986). Batch sorption isotherms for clomazone revealed a correlation between  $K_d$  and the organic carbon content of 19 soils and sediments (Loux et al., 1989b). A  $K_{oc}$  value of 150 mL/g for clomazone was derived from this

correlation. Loux et al. (1989b) suggested the primary mechanism of clomazone sorption is hydrophobic interaction with organic matter. Because of greater sorption and longer persistence of clomazone in a Drummer silty clay loam soil (5.8% organic matter) than in a Cisne silt loam soil (1.3% organic matter), Loux et al. (1989a) proposed that bioavailability and degradation of clomazone in soil are functions of clomazone sorption.

In a study of clomazone fate in a Flanagan silty clay loam soil (Mervosh et al., 1995), dissipation rates over an 84-day period were slower than predicted by first-order degradation kinetics, and mineralization was not well correlated with microbial respiration. The objectives of the present study, using samples of the clomazone-treated soil from the aforementioned study, were to determine the effects of incubation conditions (time, temperature, and soil moisture) on clomazone sorption in unsaturated soil. In addition, the possible interdependence of sorption, biodegradation, volatilization, and bound residue formation was examined.

## MATERIALS AND METHODS

**Soil.** The soil was a silty clay loam (fine, montmorillonitic, mesic, Aquic Argiudoll), Flanagan series, containing 31% clay, 53% silt, and 16% sand size fractions and 2.6% organic carbon content and having a pH in water of 5.9 (A&L Laboratories, Fort Wayne, IN). Moist soil samples were collected in October 1992 and March 1993 from the top 10 cm (A horizon) of a tilled field near Champaign, IL. No clomazone had been applied to the field for at least 3 years prior to sampling. Soil was sieved through a 2-mm screen, mixed, and stored moist at 5 °C in thin-walled polyethylene bags.

**Chemicals.** Technical grade clomazone [2-[(2-chlorophenyl)methyl]-4,4-dimethyl-3-isoxazolidinone] (92.3% purity) was supplemented with uniformly aromatic ring-labeled [ $^{14}$ C]-clomazone ( $1.04 \times 10^9$  Bq/mmol and 98.6% chemical purity) for use in clomazone equilibrium sorption studies. Soil used for desorption studies was treated with formulated clomazone (emulsifiable concentrate, 46.7% clomazone in xylene range aromatic solvents) supplemented with [ $^{14}$ C]clomazone as described below.

**Clomazone Analysis.** Analysis of [ $^{14}$ C]clomazone was performed using a Waters (Milford, MA) liquid chromatograph

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equipped with a UV detector and a Radiomatic Flo-One Beta (Packard Instrument Co., Meriden, CT) radioactivity flow detector. Operating parameters were as follows: injection volume, 0.2 mL; mobile phase flow rate, 1.5 mL/min; reversed phase  $C_{18}$  column (Beckman Ultrasphere ODS,  $4.6 \times 250$  mm,  $5\text{-}\mu\text{m}$  particle size); detector wavelength, 220 nm; Ultima-Flo M (Packard Instrument Co.) scintillation fluid flow rate, 4.2 mL/min. The mobile phase gradient (% water/% acetonitrile) was as follows (gradient change was linear during unspecified time intervals): 0–5 min, 70/30; 6–20 min, 60/40; 22–24 min, 0/100; 28–30 min, 100/0; 32–35 min, 70/30. Retention time for clomazone was approximately 17 min. Changes in gradient composition from 22 to 35 min were to clean the column and prepare it for the following chromatographic run.

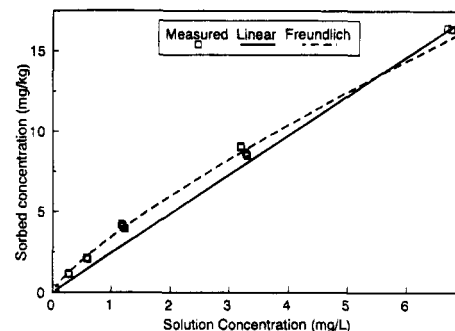
**Batch Equilibrium Sorption Isotherms.** In a preliminary study, clomazone sorption equilibrium was attained within 2 h at 25 °C in a batch system containing a 1:5 ratio of soil to 0.01 M  $\text{CaCl}_2$  and an initial solution concentration of 5  $\mu\text{g}$  of clomazone/mL.

Clomazone sorption isotherms were determined from measurements conducted in triplicate. Aliquots of technical grade and [ $^{14}\text{C}$ ]clomazone stock solutions (in 0.01 M  $\text{CaCl}_2$ ) were diluted with 0.01 M  $\text{CaCl}_2$  to prepare 25-mL treatment solutions containing 73.1 Bq/mL and 0.1, 0.5, 1, 2, 5, or 10  $\mu\text{g}$  of clomazone/mL. Treatment solutions were added to 5 g of air-dry soil (19 mg of  $\text{H}_2\text{O/g}$  of soil) in PTFE (Teflon) 50-mL centrifuge tubes. Sealed tubes were shaken for 8 h at 5, 25, or 35 °C and then centrifuged at 2000g for 5 min. Each of two 1-mL aliquots of the supernatant was removed and mixed in 15 mL of scintillation cocktail. The equilibrium concentration of clomazone in solution was determined by liquid scintillation spectrometry (LSS); the equilibrium concentration of sorbed clomazone was calculated from the difference between initial and final solution concentrations. All subsequent studies were performed using unsaturated soil.

**Desorption Studies.** Two types of desorption measurements were taken. The first type of measurement was desorption kinetics (over a 0–24-h desorption period), which was studied under commonly used benchmark soil conditions (300 kPa and 25 °C). The second type of measurement was batch desorption (24-h desorption period) examined in soils treated with clomazone and incubated for up to 84 days over a range of temperatures and water tensions. Samples of Flanagan silty clay loam soil (25 g dry weight basis) that were incubated for up to 84 days after application of 0.5 mg of [ $^{14}\text{C}$ ]clomazone containing approximately 4670 Bq to the soil surface were used for both types of desorption measurement. The 0.5 mg of clomazone (in a 0.2-mL aliquot) was uniformly applied to the soil surface ( $44.2\text{ cm}^2$ ) in approximately 25 drops. On a bulk soil basis, the solution concentration used was 10-fold less than the solubility limit and corresponded to approximately 1 kg of clomazone/ha $^{-1}$  on an area basis.

Following [ $^{14}\text{C}$ ]clomazone application, desorption kinetics were determined in triplicate using unsaturated soil samples for incubation periods of (incubation at 25 °C and 300 kPa of water tension, water content of 210 g of  $\text{H}_2\text{O/kg}$  of dry soil) 0, 3, 7, 14, 28, 56, or 84 days. At the time of sampling, each replicate was thoroughly mixed and 1 g of soil was weighed into each of six 8-mL glass scintillation vials. Immediately after 5 mL of 0.01 M  $\text{CaCl}_2$  was added to each vial, the vials were sealed with aluminum-lined caps and shaken for 0.25, 0.5, 1, 4, 12, or 24 h. Upon removal of a vial from the shaker, a 1.5-mL aliquot of the soil slurry was transferred to a siliconized (found to prevent clomazone sorption to the tube walls) microcentrifuge tube. The tubes were centrifuged for 20 s at 11750g in an Eppendorf 5415 C centrifuge. One milliliter of the supernatant was mixed with 15 mL of scintillation cocktail and analyzed by LSS. HPLC analysis of extracts revealed that at least 92% of the radioactivity recovered in this manner was unaltered clomazone.

Batch desorption measurements were obtained using triplicate soil samples that were incubated for 0, 3, 7, 14, 28, 56, or 84 days under the following conditions: 5, 15, 25, or 35 °C and 300 kPa of soil water tension; 25 °C and 100, 300, 700, or 1500 kPa of soil water tension. The procedures were as described above for desorption kinetics (1 g of soil and 5 mL



**Figure 1.** Equilibrium sorption isotherm at 25 °C for clomazone in a Flanagan silty clay loam. Parameters for the Freundlich equation were generated using nonlinear least-squares regression.

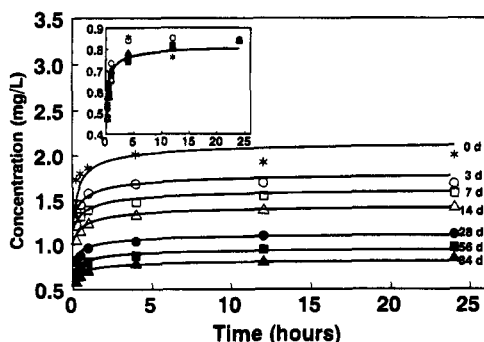
of 0.01 M  $\text{CaCl}_2$  in each glass scintillation vial), except that the extent of desorption was measured at only one time, after samples had been shaken for 24 h. Total extracted radioactivity was determined by combining 20 g of soil, 100 mL of ethyl acetate, and 20 mL of 0.01 M  $\text{CaCl}_2$  in a 250-mL polyethylene bottle and shaking for 12 h. Following a 5-min centrifugation at 2000g, the ethyl acetate phase was subjected to rotary evaporation and resuspension in a water/acetonitrile (70:30) solution. The resuspended material was filtered through a  $0.45\text{-}\mu\text{m}$  PTFE filter (Alltech Associates, Inc., Deerfield, IL), and the total extractable clomazone was determined by LSS. Extraction efficiency from this soil was determined to be 84.9% (Mervosh et al., 1995).

**Data Analyses.** Sorption isotherms were generated by plotting clomazone sorbed [ $C_s$ ] (mg/kg) vs clomazone in solution [ $C_w$ ] (mg/L) at equilibrium. The Freundlich adsorption equation,  $C_s = K_f C_w^{1/n}$ , indicates the relationship between these two parameters (Hamaker and Thompson, 1972). Both  $1/n$  and  $K_f$  are positive empirical constants, where  $1/n$  is constrained to lie between 0 and 1. These constants were determined using a modified version of CXTFIT (Parker and van Genuchten, 1984). Desorption data were analyzed by the general linear models procedure of SAS Release 6.08 (SAS Institute Inc., Cary, NC). Fisher's protected least significant difference (lsd) values at an alpha level of 0.05 were generated. Figures include lsd(0.05) values derived from the incubation time by shaking time interaction (kinetics study) or from the temperature (or soil moisture) by incubation time interaction.

## RESULTS AND DISCUSSION

**Equilibrium Sorption Isotherms.** In a saturated batch system, clomazone sorption at equilibrium did not increase as temperature increased from 5 to 35 °C. Thus, only the sorption isotherm at 25 °C is presented in Figure 1, which is based on 36 measurements (2 subsamples were obtained from each of the 3 replicates for each of the 6 initial soil solution concentrations). As initial clomazone concentration increased from 0.1 to 10 mg/L, the equilibrium  $C_s/C_w$  ratio decreased from 5.23 to 2.34 L/kg, indicating nonlinear sorption. As noted, the data correspond extremely well to the Freundlich isotherm,  $K_f = 3.29$ ,  $1/n = 0.80$ , and an  $r^2$  for the regression of 0.997. The deviation of  $1/n$  from a value of 1 suggests that clomazone sorption in this soil may be a saturable process and not solely due to hydrophobic sorption to soil organic matter (Hassett et al., 1981). The least-squares fit of the linear partition coefficient  $K_d$ , also shown in Figure 1, was 2.44. On the basis of a 2.6% organic carbon fraction, this gives an estimate of 94 L/kg for the  $K_{oc}$  of clomazone.

Loux et al. (1989b) reported isotherms for clomazone sorption on 19 soils and sediments with  $1/n$  values ranging from 0.91 to 0.99. For their data, a positive correlation ( $r^2 = 0.62$ ) existed between  $K_d$  values and



**Figure 2.** Radial diffusion model fit to observed desorption kinetics, employing constant  $R$ ,  $K$ , and  $D$  for all incubation periods and optimizing  $C_i$  for each incubation period [lsd (0.05) = 0.1 mg/L]. The inset illustrates the similarity in desorption kinetics regardless of incubation time, with all observations scaled by the solution concentration after 24 h of desorption and 84 days of incubation.

soil organic carbon contents. The authors proposed that hydrophobic bonding to organic matter was the primary, but not only, mechanism of clomazone sorption in soils. The mean  $K_{oc}$  value for clomazone was 150 L/kg with a standard deviation of 54 L/kg (Loux et al., 1989b), which is in close agreement with the values predicted (144–169 L/kg) by the semiempirical relationships between  $K_{oc}$  and  $K_{ow}$  developed by Karickhoff (1981) and Hassett et al. (1981), respectively. Our observed value of 94 L/kg for the Flanagan soil is within the range of observed values from the 19 soils studied by Loux et al. (1989b).

**Desorption Kinetics.** With increasing incubation time in soil, the fraction of applied clomazone extracted with water decreased (Figure 2). Clomazone desorption was initially rapid and then slowed considerably after samples had shaken for 4 h. Samples shaken for 24 h appeared to be nearly at equilibrium in terms of clomazone partitioning between sorbed and solution phases. At this time, the quantities of clomazone in solution for soil incubated at 35 °C for 0 and 84 days after clomazone application were 66.3 and 19.0% of applied, respectively (Figure 2).

Due to the rapid initial desorption of clomazone, our clomazone desorption data exhibited a poor fit to a first-order kinetic model. However, as can be observed in Figure 2, the concentration of clomazone desorbed between shaking times of 15 min and 4 h remained nearly constant regardless of soil residence time, varying between 9.5 and 11.5%. This suggests a characteristic desorption process that does not depend directly on the soil incubation time.

A simple radial diffusion model was employed in an attempt to characterize the desorption process. Assuming spherically shaped soil aggregates of uniform clomazone concentration, the batch desorption study is analogous to the problem of heat flow from a sphere into a well-stirred fluid. The following equation, given by Carslaw and Jaeger (1959), provides the solution for this problem, giving the average temperature of the fluid as a function of time:

$$C(t) = \frac{C_i}{K + 1} - \frac{6KC_i \sum_{n=1}^{\infty} \exp[-D\alpha_n^2 t] \frac{1}{(K R \alpha_n)^2 + 9(K + 1)}}{1} \quad (1)$$

In eq 1, the  $\alpha_n$  (1/L),  $n = 1, 2, 3, \dots$  are the roots of

$$\tan(R\alpha) = 3R\alpha/[3 + K(R\alpha)^2] \quad (2)$$

where  $C(t)$  represents the observed concentration of the clomazone in solution.

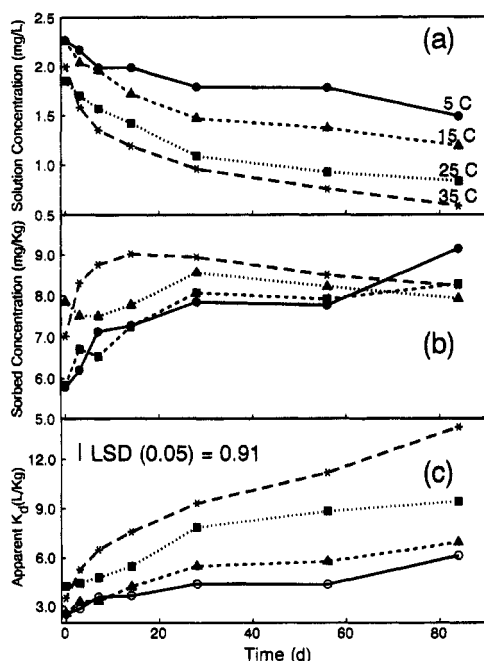
With respect to the desorption study, this model has four parameters, the effective aggregate radius,  $R$  (L), an intra-aggregate diffusion coefficient,  $D$  (L<sup>2</sup>/T), a capacitance partition coefficient between the soil and liquid,  $K$  (dimensionless), and the initial concentration of the aggregate,  $C_i$  (mg/L). A nonlinear least-squares fit of this model to the desorption data for each incubation time was performed. A high degree of correlation was observed between  $R$  and  $D$ ; hence,  $R$  was arbitrarily assigned unit value in the regressions, reducing the model to three parameters. Furthermore, it was observed that the parameters  $K$  and  $D$  were relatively constant for all seven incubation periods. Assuming  $R$ ,  $K$ , and  $D$  are independent of incubation time and assigning a fixed value for each, the individual desorption kinetics for each incubation time were characterized by least-squares optimization of  $C_i$ .

In addition to the observed solution clomazone concentration as a function of time and incubation period, the corresponding model fit is given in Figure 2. In this figure, only  $C_i$  is allowed to vary between incubation periods. The fixed values of  $R$ ,  $K$ , and  $D$  used to generate this figure were 1, 0.061, and 0.0037, respectively. The best fit values of  $C_i$  varied from 2.26, 1.89, 1.70, 1.51, 1.18, 1.01, to 0.87 mg/L for incubation periods of 0, 3, 7, 14, 28, 56, and 84 days, respectively. The ability to reasonably describe the desorption process with this simple radial diffusion model with constant  $R$ ,  $K$ , and  $D$  for all incubation times suggests that desorption is controlled by a physical diffusion process. In addition, Figure 2 suggests the presence of a water-extractable, "saturated" sorbed pool, since the desorption curves coalesce to a single curve when scaled by the batch desorption data. The clomazone mass in this sorbed pool appears to be independent of incubation time.

As incubation time increased from 0 to 84 days, the amount of clomazone in solution for samples shaken for 15 min decreased from 86.3 to 68.6% of the amount in solution for samples shaken for 24 h. This observation fits the trend of decreasing best fit values of  $C_i$  observed above. Decreased rate or extent of desorption with increasing chemical residence time in soils has been observed for picloram (McCall and Agin, 1985), fluroxypyr (Lehmann et al., 1990), carbofuran (Shelton and Parkin, 1991), and simazine (Scribner et al., 1992). Aging of clomazone residues appears to result in a declining pool of labile (possibly solution phase) material and an essentially constant pool of more slowly desorbable material.

**Effects of Incubation Temperature and Time on Sorption.** For all incubation temperatures, with increasing incubation time in unsaturated soil, the concentration of clomazone present in solution after 24 h of desorption decreased (Figure 3a). The magnitude of this decrease was greater as the incubation temperature increased. For soil incubated at 35 °C, water-extractable clomazone decreased by more than 3-fold (66.3 to 19.0% of applied) as incubation time proceeded from 0 to 84 days, whereas the total amount of clomazone recovered in ethyl acetate extracts decreased by less than a factor of 2 (101.4 to 60.2% of applied) over the same period (Figure 3b).

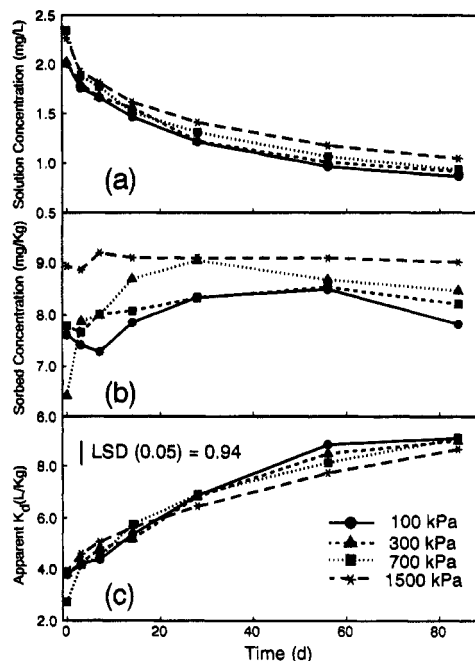
The concentration of clomazone sorbed to the soil reached a maximum in 14 days for the 35 °C incubation,



**Figure 3.** Clomazone solution concentration (a), sorbed concentration (b), and apparent  $K_d$  (c) as a function of incubation temperature and time in unsaturated Flanagan silty clay loam. Data were obtained from a 24-h desorption study.

in 28 days for 25 °C, and in 84 days for both the 15 and 5 °C incubations (Figure 3b). At 5 and 15 °C, sorption progressed slowly throughout the incubation period. Even though equilibrium sorption was temperature independent, the apparent desorption  $K_d$  ( $C_s/C_w$ ) for clomazone in unsaturated soil increased with both increasing incubation time and incubation temperature (Figure 3c). The Stokes–Einstein formula for a chemical diffusion coefficient in soil solution suggests a linear increase in the diffusion coefficient with temperature (Sposito, 1989). Thus, taken together, the temperature independence of  $K_d$  in the equilibrium batch isotherms and the temperature dependence of apparent  $K_d$  in the unsaturated soil could be evidence of a rate-limiting physical diffusion phenomenon, assuming other temperature-dependent processes, such as biodegradation, did not affect sorption equilibrium. However, since the amount of material sorbed (Figure 3b) was essentially independent of temperature above 5 °C, it would appear that something in addition to physical diffusion constraints is controlling the apparent  $K_d$ . At the temperatures employed in this study, distribution of clomazone between sorbed and solution phases was continuing to change 84 days after clomazone application to the soil. Increases in apparent  $K_d$  of 2.4-fold at 5 °C and 4.1-fold at 35 °C occurred over the 84-day incubation period (Figure 3c). Reported increases in apparent  $K_d$  over time have been on the order of 4-fold for picloram in a silty clay loam soil during a 300-day incubation (McCall and Agin, 1985) and 15-fold for simazine residues aged for up to 20 years in a field (Scribner et al., 1992).

The increasing proportion of sorbed clomazone with incubation time may be associated with clomazone degradation rates that were slower than predicted by a first-order kinetics model (Mervosh et al., 1995). In particular, decreasing degradation rates in soil incubated at 35 °C may have been due to the large decrease in labile clomazone (Figure 3). Several other studies have reported that chemicals in a sorbed state were unavailable to microbial degraders (Ogram et al., 1985;



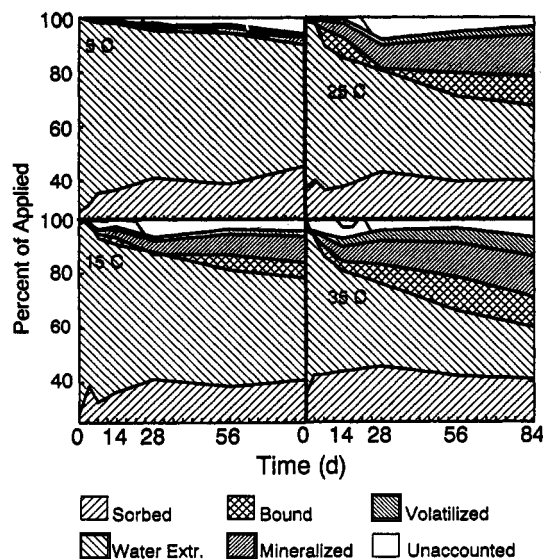
**Figure 4.** Clomazone solution concentration (a), sorbed concentration (b), and apparent  $K_d$  (b) as a function of soil water tension and incubation time in unsaturated Flanagan silty clay loam. Data were obtained from a 24-h desorption study.

Shelton and Parkin, 1991; Greer and Shelton, 1992; Scribner et al., 1992; Sims et al., 1991, 1992). Degradation of phenol, aniline, and nitriloacetic acid fit a two-compartment model, suggesting the presence of an unavailable pool (Scow et al., 1986). Degradation of several other chemicals also appears to be limited by sorption on the basis of fit to other models (Alexander and Scow, 1989).

#### Effects of Soil Moisture and Time on Sorption.

At all soil water tensions, the percentage of applied  $^{14}\text{C}$  in solution decreased (Figure 4a), whereas the amount of material sorbed initially increased and then gradually declined (Figure 4b). The apparent  $K_d$  for clomazone increased (Figure 4c) over the 84-day incubation for all moisture treatments. The effect of soil moisture during incubation on clomazone desorption was nonsignificant (Figure 4c), although the apparent  $K_d$  appears to increase with increasing water content. Shelton and Parkin (1991) reported a more pronounced effect of moisture on the desorption of the insecticide carbofuran over a 30-day period. The minimal effect of soil moisture on clomazone desorption may be the result of the water solubility and volatility properties of clomazone. Jury et al. (1991), employing a Millington–Quirk model for tortuosity and assuming linear equilibrium partitioning between solid, liquid, and gaseous phases, illustrate that the effective liquid–vapor diffusion coefficient may be independent of water content (the water content dependence of the effective diffusion coefficient was shown to be a function of the chemical properties of the organic compound as well as soil physical and chemical properties). The relatively minor impact of soil water content on sorption suggests that, over the range of water contents studied, the effective liquid–vapor diffusion coefficient is relatively constant. The effect of soil moisture on clomazone degradation was also minimal (Mervosh et al., 1995) in this soil.

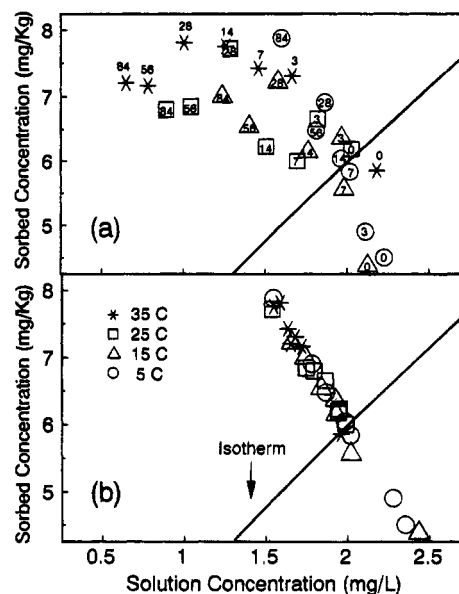
In these studies, clomazone was applied to the soil surface and was not physically mixed with the soil.



**Figure 5.** Temperature effects on clomazone mass distribution and fate (detected by radiocarbon) as a function of incubation time.

Thus, sorption of the herbicide was dependent on the rate and extent of clomazone diffusion throughout the soil matrix: diffusion both between and within soil particles. Diffusion-controlled sorption processes within/on soil particles are generally described in terms of one or both of the current prevailing theories: the intraorganic matter diffusion (IOMD) theory and the intraparticle diffusion (IPD) theory. The IOMD theory, espoused by Chiou (1989) and Brusseau and Rao (1989), assumes that soil organic matter is the primary sorbent, that sorption sites are three-dimensional, and that rate-limited sorption is due to the slow diffusion or partitioning of hydrophobic solutes into organic matter. The IPD theory attributes the slow approach to sorption equilibrium to rate-limited diffusion, and eventual entrapment, of solutes in intraparticulate micropores. Evidence in support of the IPD theory was provided by Steinberg et al. (1987), who observed the nearly complete release of aged fumigant residues upon grinding the soil. Enhanced release of bound residues by grinding has been reported primarily for relatively small molecules of high volatility.

The mechanisms responsible for the increases in apparent  $K_d$  with incubation time and temperature are unclear but may result from several processes, including interparticle diffusion, IOMD and IPD, and sorption-desorption hysteresis. The correlation of clomazone sorption with soil organic carbon content, the reasonable agreement between observed  $K_{oc}$  and predicted  $K_{oc}$  from either solubility or  $K_{ow}$  (Loux et al., 1989b), and the temperature independence of batch sorption isotherms observed herein suggest that hydrophobic sorption (either partitioning or adsorption) may be the primary sorption mechanism for the herbicide. The Flanagan soil used in the present study has relatively large organic carbon and clay contents, which would have provided significant sinks for either clomazone sorption via partitioning into organic matter or entrapment in micropores. Of considerable importance in ascribing a cause to the observed shifts in apparent  $K_d$  is the mass balance of carbon in the experimental system. Figure 5 shows the percentage of applied clomazone associated with each pool measured in an identical experiment reported previously (Mervosh et al., 1995). It is clear from these data that the percentage of applied cloma-



**Figure 6.** Influence of loss processes (degradation, volatilization, and bound residue formation) on apparent position of clomazone sorption equilibrium. Numbers within data symbols in (a) are incubation dates. The apparent solution concentrations in (b) were corrected for loss processes.

zone in solution is not controlled entirely by sorption but is influenced by other processes as well. After 84 days of incubation at 35 °C, most of the added radio-carbon either is in the form of some product (carbon dioxide or bound residue) or has volatilized from the soil surface. These data taken with the relatively constant pool of sorbed material show that the driving force for the sharp increase in  $K_d$  over time was loss of material from solution rather than continued sorption. However, the data do not explain why sorption equilibrium is not being maintained. As seen in Figure 2, the mass of desorbable material remains essentially constant over the incubation period; only the labile (released in less than 15 min) fraction decreases. Thus, it is apparent that the labile material is the focal point of most of the processes studied herein.

As stated above, because the extent of sorption at equilibrium in a saturated (batch) system was independent of temperature, the temperature dependence of apparent  $K_d$  for clomazone in an unsaturated soil suggests that a temperature-dependent physical process controlled sorption kinetics in the unsaturated soil. It should also be noted from Figure 5 that degradation, volatilization, and bound residue formation also exhibited temperature dependence. Figure 6 is an attempt to account for the effects of degradation, volatilization, and bound residue formation (loss processes) on apparent sorption equilibrium. It should be noted that loss processes were minimal at 5 °C, while sorption clearly increased over the incubation period (Figure 5). Making the assumption that losses occurred from the solution phase, we used independent measurements of each of the processes to correct the solution data for losses (Figure 6b). Once corrected, data sets for each incubation temperature converged on a single line, showing a gradual shift in the equilibrium position over time (nearly identical to the 5 °C data set). Thus, sorption-desorption hysteresis alone cannot explain the increase in apparent  $K_d$  with incubation time.

In summary, unsaturated soil treated with clomazone was not at equilibrium in terms of apparent  $K_d$  within an 84-day incubation, even though the amount of

material sorbed had become essentially constant. Desorption experiments conducted throughout the study revealed a nearly constant pool of material requiring greater than 15 min of agitation for release with water. As clomazone residence time in soil increased, material released in less than 15 min, referred to herein as labile, continued to diminish. Increasing incubation temperatures produced a greater increase in the change in apparent  $K_d$  over time than did increasing soil moisture content.

The observed changes in the labile clomazone pool over time may account for the slower than predicted degradation rates at longer incubation times (Mervosh et al., 1995). Our results suggest that, with increasing clomazone residence time in soil, a greater percentage of the remaining clomazone will become unavailable for microbial degradation, plant uptake, volatilization, surface runoff, or leaching. This work suggests that a greater understanding of the role of the labile fraction in controlling clomazone fate in soil is needed and should be the subject of future experiments.

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