

Organic Compounds in the Environment

Aging Effects on the Sorption–Desorption Characteristics of Anthropogenic Organic Compounds in Soil

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ABSTRACT

Field studies have demonstrated that prolonged pesticide–soil contact times (aging) may lead to unexpected persistence of these compounds in the environment. Although this phenomenon is well documented in the field, there have been very few controlled laboratory studies that have tested the effects of long-term aging and the role of differing sorbates on contaminant sorption–desorption behavior and fate in soils. This study examines the sorption–desorption behavior of chlorobenzene, ethylene dibromide (1,2-dibromomethane), atrazine (2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine), and 2,4-D (2,4-dichlorophenoxyacetic acid) on one soil type after 1 d, 30 d, and 14 mo of aging. Sorption isotherms were evaluated after each aging period to observe changes in the uptake of each compound by soil. Desorption kinetic data were generated after each aging period to observe changes in release from soil, and desorption parameters were evaluated using a three-site desorption model that includes equilibrium, nonequilibrium, and nondesorption sites. The data indicate no statistically significant increase in sorption for ethylene dibromide or chlorobenzene from 1 to 30 d, although sorption of 2,4-D increased slightly, and sorption of atrazine decreased slightly. Statistically significant increases in linear sorption coefficients (K_d), from 1 d to 14 mo of aging, were apparent for ethylene dibromide and 2,4-D. The K_d values for chlorobenzene, measured after 1 d, 30 d, and 14 mo of aging, were statistically indistinguishable. Aging affected the distribution of chemicals within sorption sites. With aging, the desorbable fraction decreased and the nondesorbable fraction, which was apparent after only 1 d of pesticide–soil contact, increased for all chemicals studied.

ALTHOUGH LABORATORY STUDIES of organic contaminant sorption by soils often employ equilibration times of 1 d or less, some studies have indicated that sorption is a slow process and may take longer time periods (hundreds of days) to reach equilibrium (Ball and Roberts, 1991; Pignatello and Xing, 1996). Furthermore, several desorption studies have found that the desorption-resistant fraction of a chemical increases with increased soil–chemical contact time in an effect termed “aging” (Pignatello, 1990; Pavlostathis and Mathavan, 1992; Johnson et al., 2001). Data from field studies have indicated that certain compounds (e.g., ethylene dibromide and simazine [1-chloro-3,5-bisethylamino-2,4,6-triazine]) demonstrate unexpected persistence given their water solubility and ease of degradation by soil microorganisms (Steinberg et al., 1987; Scribner et al., 1992). These observations suggest that aging has an

effect on sorption–desorption behavior and biological availability of organic contaminants and pesticides in soils. Despite the pronounced effects attributed to aging on contaminant binding, persistence, and bioavailability (Alexander, 2000), there are very few long-term, laboratory-controlled studies that explicitly measure sorption–desorption parameters as a function of aging time. Consequently, little is known about the magnitude of aging effects and how these differences might vary among sorbates.

Several researchers have suggested that for pesticides and organic contaminants, rates of sorption–desorption in soils correlate with solute hydrophobicity as indicated by octanol–water partition coefficients (K_{ow}) (Karickhoff and Morris, 1985; Brusseau and Rao, 1989b). In contrast, Oliver (1985) found that the desorption behavior of aged nonpolar organics in sediments was largely independent of sorbate properties. The compounds studied by Oliver (1985) exhibited nearly a four-order-of-magnitude range in K_{ow} values, but only included relatively nonpolar chlorinated hydrocarbons. Xing and Pignatello (1996) evaluated sorption isotherms for dichlorobenzene and dichlorophenol over periods of 1 and 30 d and found that the sorption coefficient, K_F , increased 1.3 times for dichlorobenzene ($\log K_F = 3.38$) and 2.7 times for dichlorophenol ($\log K_F = 2.75$). This suggested that the less polar compound (dichlorobenzene) exhibited faster sorption kinetics than the polar compound (dichlorophenol). These results are in agreement with the results of Brusseau and Rao (1989a) in which inverse linear free energy relationships were observed between sorption rate coefficients ($\log k$) and sorption equilibrium coefficients ($\log K_d$) for both nonpolar and polar compounds. Among compounds with similar partition coefficients, the polar compounds exhibited considerably slower sorption–desorption kinetics. This was attributed to the increased reactivity of polar compounds with polar functional groups of soil organic matter (a chemical nonequilibrium process), and diffusion through soil organic matter (a physical nonequilibrium process). Accordingly, polar compounds were rate-limited due to both processes, whereas nonpolar compounds were rate-limited solely by diffusion.

The objective of this study was to evaluate the effects of aging on the sorption and desorption dynamics of a few representative polar and nonpolar compounds in soils using long-term laboratory-controlled aging regimes. Sorption isotherms and desorption kinetics for chlorobenzene, ethylene dibromide, and 2,4-D in soil were measured after 1 d, 30 d, and 14 mo, and for atrazine after 1 and 30 d.

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MATERIALS AND METHODS

A Capac (fine-loamy, mixed, active, mesic Aquic Glossudalf) A-horizon soil was collected from Michigan State University farms, East Lansing. The soil was air-dried, ground, and sieved (2 mm). Selected soil properties were determined by the Michigan State University Plant and Soil Nutrient Laboratory. The Capac soil used is a sandy clay loam (54.6, 24.0, and 21.4% sand, silt, and clay, respectively) with an organic carbon content of 3.3%. The soil contained in polypropylene bottles was γ -irradiated with 5×10^4 Gy at the University of Michigan Ford Nuclear Reactor Laboratory using a ^{60}Co irradiator and remained sealed until use.

Sorption Studies

The quantities of soil and solution used to develop sorption isotherms corresponded to the amount needed to sorb approximately 50% of the added solute while minimizing headspace volume. Either 20-mL glass ampules (for ethylene dibromide and chlorobenzene) or 20-mL Corex glass tubes (for 2,4-D and atrazine) were used for the experiments. The ampules were closed by flame sealing and the tubes were closed using Teflon-lined screw caps. The tubes and ampules were autoclaved before use. A mass of soil was weighed and transferred to the ampule or tube using an autoclaved metal spatula and plastic funnel. A 0.005 M CaCl_2 solution, which had been autoclaved for 25 min and amended with 200 mg L^{-1} NaN_3 , was added to the tubes using a sterilized pipette. All additions of soil and solution to the ampules and tubes were performed in a laminar-flow hood.

Acetone stock solutions of the following compounds (Sigma Chemical Co., St. Louis, MO) were prepared: ^{14}C -chlorobenzene (radiochemical purity [RP] > 97%), ^{14}C -ethylene dibromide (RP > 98%), ^{14}C -2,4-D (RP > 97%), and ^{14}C -atrazine (RP > 93%). Stock solutions for each compound consisted of a "low concentration" solution, in which the compound was all ^{14}C -labeled, and a "high concentration" solution, which contained the ^{14}C -labeled compound and nonlabeled compound. The stock solutions, which consisted solely of the compound of interest dissolved in acetone, were stored in amber vials with Mininert valves in a -4°C freezer when not in use. An aliquot of the appropriate stock solution was added to the ampule or Corex tube (containing the sterilized soil and 0.005 M CaCl_2) using a 10-, 25-, or 100- μL syringe (final acetone concentration of <0.1%). The ampules were immediately flame-sealed, and the Corex glass tubes were immediately sealed with screw caps. Aliquots used for the sorption isotherms were from both the low and high concentration stock solutions rendering the initial aqueous concentration ranging from 5 to 20 000 $\mu\text{g L}^{-1}$. Seven initial solute concentrations were used (in triplicate) for each compound.

After sealing, the ampules or tubes were mixed ("aged") for either 1 d, 30 d, or 14 mo (pH = 6.2–6.5). Immediately after closure, the ampules or tubes were shaken on a reciprocating shaker for either 24 (for the 1-d aging period) or 72 h (for the 30-d and 14-mo aging periods). Soil-free "blanks" were also prepared and held for the same time period as the soil-containing samples to check for losses due to volatilization, leakage, sorption to glass walls, etc. Initial solute concentrations for the first set of blanks were 20.3 $\mu\text{g L}^{-1}$ (chlorobenzene), 14.3 $\mu\text{g L}^{-1}$ (atrazine), 35.2 $\mu\text{g L}^{-1}$ (ethylene dibromide), and 31.5 $\mu\text{g L}^{-1}$ (2,4-D). After shaking, the ampules or tubes were either analyzed immediately (1 d of aging) or stored in the dark with periodic shaking (30 d and 14 mo of aging). Before analysis, ampules were centrifuged at $635 \times g$ for 8 min and a 1-mL aliquot of the aqueous phase was re-

moved and added to 8 mL of scintillation fluid. Tubes were handled in the same manner except that they were centrifuged at $6722 \times g$ for 8 min. The samples in scintillation fluid were shaken, stored in the dark overnight, and analyzed the following day by liquid scintillation counting to determine the aqueous-phase concentrations. The amount of solute sorbed was determined by the difference in the amount of ^{14}C -radioactivity added and that recovered in solution.

Desorption Rate Studies

Ampules or tubes were prepared as described above, with the same amounts of soil and solution used as for the sorption experiments. A single initial solute concentration was used for each chemical. The exact concentration differed depending on the compound of interest, but in all cases the initial desorption concentration was chosen from the midpoint of the sorption isotherm. The samples were aged for periods of 1 d, 30 d, or 14 mo as described for the sorption isotherm experiments. Then, a quadruplicate set of ampules were opened by cutting the stem (1.6–2.0 cm from the top of the ampule) using a 6.35-mm (0.25-in) glass drill bit. The solution phase was sampled (200 μL) using a 200- μL pipette. Triplicate tubes were sampled by removing the caps and taking a 1-mL sample of the solution phase. These samples were analyzed using liquid scintillation counting. Then, a larger aliquot of the solution phase was removed (approximately 75–80% of the total volume of solution) using a 10- or 25-mL gas-tight syringe. The same volume of autoclaved 0.005 M CaCl_2 containing 200 mg L^{-1} NaN_3 was then added back into the ampule or tube. The ampules were flame-sealed again and shaken, and the tubes were recapped and shaken on a reciprocating shaker. At various time intervals, the quadruplicate set of ampules was centrifuged at $635 \times g$ for 8 min, the stems broken at the neck, and a 1-mL aliquot of the aqueous phase sampled and analyzed by liquid scintillation counting. The tubes were treated in the same manner as the ampules, except that triplicate samples were analyzed after centrifugation at $6722 \times g$ for 8 min.

Chemical Analysis

Chemicals were analyzed by reverse-phase high-pressure liquid chromatography using ultraviolet absorption detection at 220, 254, 210, and 234 nm for chlorobenzene, atrazine, ethylene dibromide, and 2,4-D, respectively. The volume ratio of acetonitrile to water in the mobile phase (1 mL min^{-1}) was 65:35, 50:50, 80:20, and 30:70 to 80:20 gradient for chlorobenzene, atrazine, ethylene dibromide, and 2,4-D, respectively. No significant degradation of chemicals during the aging regimes was observed except for formation of hydroxyatrazine in the 14-mo samples, which were discarded. Recovery of chemical from soil-free "blanks" was greater than 95%, and usually in the 97 to 98% range, for all aging periods.

Chemical analysis was performed on all soil-free "blanks" and stock solutions to monitor possible changes to the chemicals with time. This analysis was also performed on a representative number of randomly selected experimental (soil-containing) sorption isotherm and desorption kinetic samples.

Sorption Equilibrium Models

Linear regression was used to compute the slope of the sorption isotherm from a plot of amount sorbed ($\mu\text{g kg}^{-1}$) versus concentration in solution ($\mu\text{g L}^{-1}$); this corresponds to the sorption coefficient, K_d . Isotherms were also analyzed using nonlinear regression analysis. The data were fit to the Freundlich model $x/m = K_F C_e^n$, where x/m is the concentration in soil, C_e is the liquid-phase concentration, K_F is the Freun-

dlich sorption coefficient, and n is an indicator of isotherm curvature; the 95% confidence interval for n was calculated.

Desorption Rate Model

Sorption and desorption processes in soils have commonly been described using a model with both equilibrium and kinetically limited sites (Brusseau and Rao, 1989a; van Genuchten and Wagenet, 1989; Gamedainger et al., 1990). There is recent evidence, however, that some fraction of the sorbed material either does not desorb at all, or only desorbs very slowly (Fu et al., 1994; Kan et al., 1994; Tomson and Pignatello, 1999; Park et al., 2001, 2002). In this study, a recently developed three-site desorption model was used to analyze experimental data by assuming that (i) the solid is composed of equilibrium, nonequilibrium, and nondesorption sites; (ii) sorption equilibrium can be described by a linear isotherm; and (iii) the rate of release from nonequilibrium sites is proportional to the concentration gradient between these sites and the liquid phase (Park et al., 2001, 2002).

Mathematically, equilibrium and nondesorption partitioning are described by:

$$S_{eq} = f_{eq}K_dC \quad [1]$$

$$S_{nd} = f_{nd}K_dC_e \quad [2]$$

while the release from nonequilibrium sites follows the first-order expression:

$$dS_{neq}/dt = \alpha(f_{neq}K_dC - S_{neq}) \quad [3]$$

where S_{eq} , S_{neq} , and S_{nd} ($\mu\text{g kg}^{-1}$) are the sorbed concentrations in equilibrium sites, nonequilibrium sites, and nondesorption sites, respectively; K_d (L kg^{-1}) is the sorption distribution coefficient; C ($\mu\text{g L}^{-1}$) is liquid-phase concentration; C_e is liquid-phase concentration at sorption equilibrium; t is the desorption time; α (min^{-1}) is the first-order desorption rate coefficient for nonequilibrium sites; f_{eq} is the equilibrium site fraction; f_{neq} is nonequilibrium site fraction; and f_{nd} is nondesorption site fraction. These three terms are related to the total sorbed-phase concentration (S):

$$S_{eq} + S_{neq} + S_{nd} = S \quad [4]$$

The term K_d was calculated from the linear sorption iso-

therm; f_{nd} corresponds to the plateau of the desorption rate profile; and f_{eq} , f_{neq} , and α were estimated by nonlinear regression analysis of desorption data, with the constraint that:

$$f_{eq} + f_{neq} + f_{nd} = 1 \quad [5]$$

RESULTS

Sorption of ethylene dibromide and chlorobenzene did not exhibit statistically different (at the 0.01 level) increases in sorption from 1 to 30 d (Table 1), while 2,4-D did show a statistically significant ($P = 0.001$) increase in K_d values between the 1- and 30-d equilibrium times (Table 1). After 14 mo of aging, 2,4-D and ethylene dibromide both showed an increase in K_d from the corresponding values at 1 and 30 d ($P = 0.001$ for both), whereas K_d for chlorobenzene was unchanged. Atrazine showed a statistically significant decrease in K_d at 30 d. There appears to be reasonable agreement between organic matter-normalized sorption coefficients ($K_{oc} = K_d/f_{oc}$) obtained from experimental K_{oc} (calculated from measured K_d and fractional soil organic carbon content, f_{oc}) and those estimated from the compound's K_{ow} value according to the regression equation of Chiou et al. (1983) (Table 1).

The Freundlich isotherm regressions indicated some degree of nonlinearity for certain soil-compound-aging combinations as indicated by Freundlich coefficient n values different than 1.0. The isotherms demonstrating the highest degree of linearity were 2,4-D at the 1-d aging time ($n = 0.939$ – 1.18 ; 95% confidence interval), ethylene dibromide at the 1-d aging time ($n = 0.966$ – 0.995), and chlorobenzene at the 30-d aging time ($n = 1.00$ – 1.03). All of the Freundlich isotherm parameters are listed in Table 1. When the data were fit using the linear model, all isotherms had r^2 values of 0.993 or greater (Table 1).

Apparent desorption equilibrium was reached within a few hours for all of the compounds evaluated (Fig. 1).

Table 1. Linear sorption ($x/m = K_dC_e$), organic carbon-normalized sorption (K_{oc}), and Freundlich isotherm ($x/m = K_fC_e^n$) parameters for ethylene dibromide, chlorobenzene, atrazine, and 2,4-D sorption by Capac soil.†

Chemicals	Aging time	K_d	r^2	K_{ow}	K_{oc}		K_f , 95% confidence interval	n , 95% confidence interval
					Experimental‡	Calculated§		
		L kg^{-1}			L kg^{-1}		$(\mu\text{g kg}^{-1})(\mu\text{g L}^{-1})^{-n}$	
Ethylene dibromide	1 d	0.73	1.0	58	22.1	11.2	0.76–1.00	0.966–0.995
	30 d	0.72¶	0.997				2.13–3.76	0.827–0.884
	14 mo	1.26#	0.999				2.32–2.81	0.915–0.935
Chlorobenzene	1 d	3.96	0.998	832	120.3	125.2	10.17–13.06	0.865–0.893
	30 d	3.37¶	1.0				2.44–3.13	1.004–1.032
	14 mo	4.15¶	0.999				9.33–9.61	0.905–0.908
Atrazine	1 d	3.24	0.998	363	98.4	59.1	5.21–7.22	0.875–0.926
	30 d	2.82††	0.993				4.83–11.75	0.772–0.901
	14 mo	ND‡‡						
2,4-D	1 d	0.62	0.998	–	–	–	0.10–0.74	0.939–1.180
	30 d	0.66#	0.999				1.06–1.79	0.905–0.953
	14 mo	0.91#	0.996				0.63–6.13	0.794–0.952

† Terms: C_e , liquid-phase concentration; K_d , linear sorption coefficient; K_f , Freundlich sorption coefficient; K_{oc} , organic matter-normalized sorption coefficient; K_{ow} , octanol-water partition coefficient; n , indicator of isotherm curvature; x/m , concentration in soil.

‡ Value = $(K_d, 1 \text{ d})/f_{oc}$, where f_{oc} is the fraction of organic carbon (i.e., % OC/100).

§ Value from $\log K_{oc} = 0.904 \log K_{ow} - 0.779$ (Chiou et al., 1983); $K_{oc} = K_{ow}/0.58$.

¶ No statistically significant increase in sorption from the 1-d sample at the 0.01 level.

A statistically significant increase in sorption from the 1-d sample at the 0.01 level.

†† A statistically significant decrease in sorption from the 1-d sample at the 0.01 level.

‡‡ Not determined.

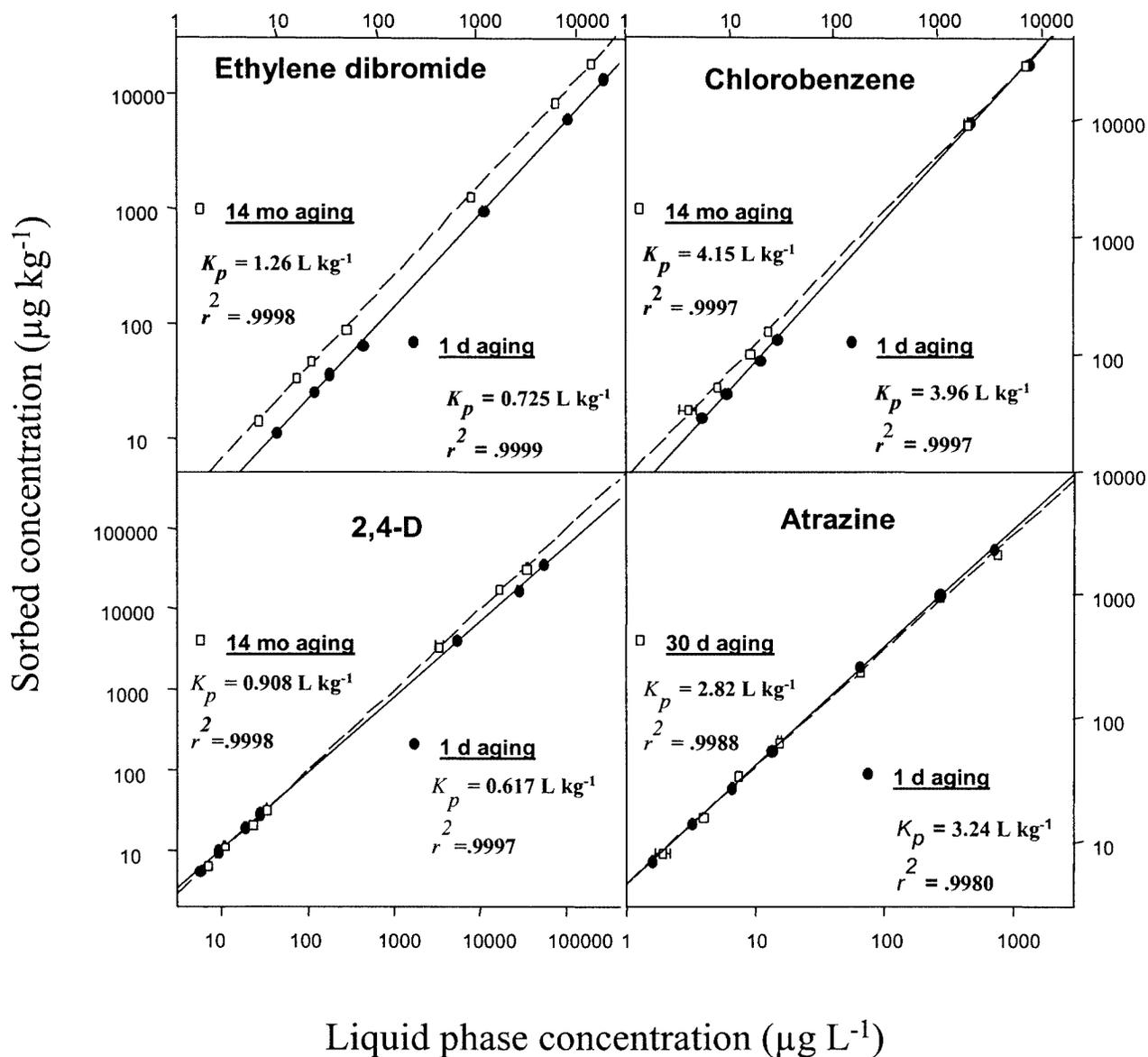


Fig. 1. Sorption isotherms of chlorobenzene, ethylene dibromide, 2,4-D, and atrazine after 1 d and 14 mo (or 30 d for atrazine) of aging.

The extent of desorption decreased markedly with aging time for all four compounds. This is reflected in the value of the nondesorption fraction (f_{nd}) from use of the three-site desorption model to fit the desorption data (Table 2). After 1 d of aging, f_{nd} ranged from 0.08 (2,4-D)

to 0.32 (ethylene dibromide). With prolonged aging (14 mo), f_{nd} ranged from 0.37 (chlorobenzene) to 0.64 (ethylene dibromide). The largest change in f_{nd} from the 1-d aging period to 30 d ($\Delta f_{nd} = 0.24$) or 14 mo ($\Delta f_{nd} = 0.41$) was for 2,4-D, which initially had the lowest nondesorp-

Table 2. Evaluated sorption-desorption parameters for desorption of ethylene dibromide, chlorobenzene, atrazine, and 2,4-D sorption on Capac soil after three different contact periods using the three-site desorption model.

Chemicals	Contact time	Desorbable fraction		Nondesorbable fraction, f_{nd}	Desorption coefficient, α	r^2
		Equilibrium, f_{eq}	Nonequilibrium, f_{neq}			
Ethylene dibromide	1 d	0.68 (0.03)†	0	0.32 (0.02)	0.14 (0.11)	0
	30 d	0.5 (0.01)	0.08	0.42 (0.008)	0.39 (0.11)	0.95
	14 mo	0.32 (0.009)	0.04	0.64 (0.02)	0.0053 (0.005)	0.59
Chlorobenzene	1 d	0.58 (0.05)	0.15	0.27 (0.02)	1.48 (0.73)	0.79
	30 d	0.53 (0.03)	0.12	0.35 (0.01)	1.34 (0.52)	0.9
	14 mo	0.58 (0.02)	0.05	0.37 (0.02)	0.07 (0.07)	0.52
Atrazine	1 d	0.56 (0.07)	0.17	0.27 (0.02)	2.16 (1.52)	0.66
	30 d	0.43 (0.05)	0.19	0.38 (0.04)	0.26 (0.15)	0.8
2,4-D	1 d	0.53 (0.05)	0.40	0.05 (0.02)	1.14 (0.28)	0.91
	30 d	0.52 (0.06)	0.27	0.21 (0.04)	0.14 (0.08)	0.80
	14 mo	0.25 (0.08)	0.30	0.45 (0.03)	1.23 (0.5)	0.78

† Standard deviations are listed in parentheses.

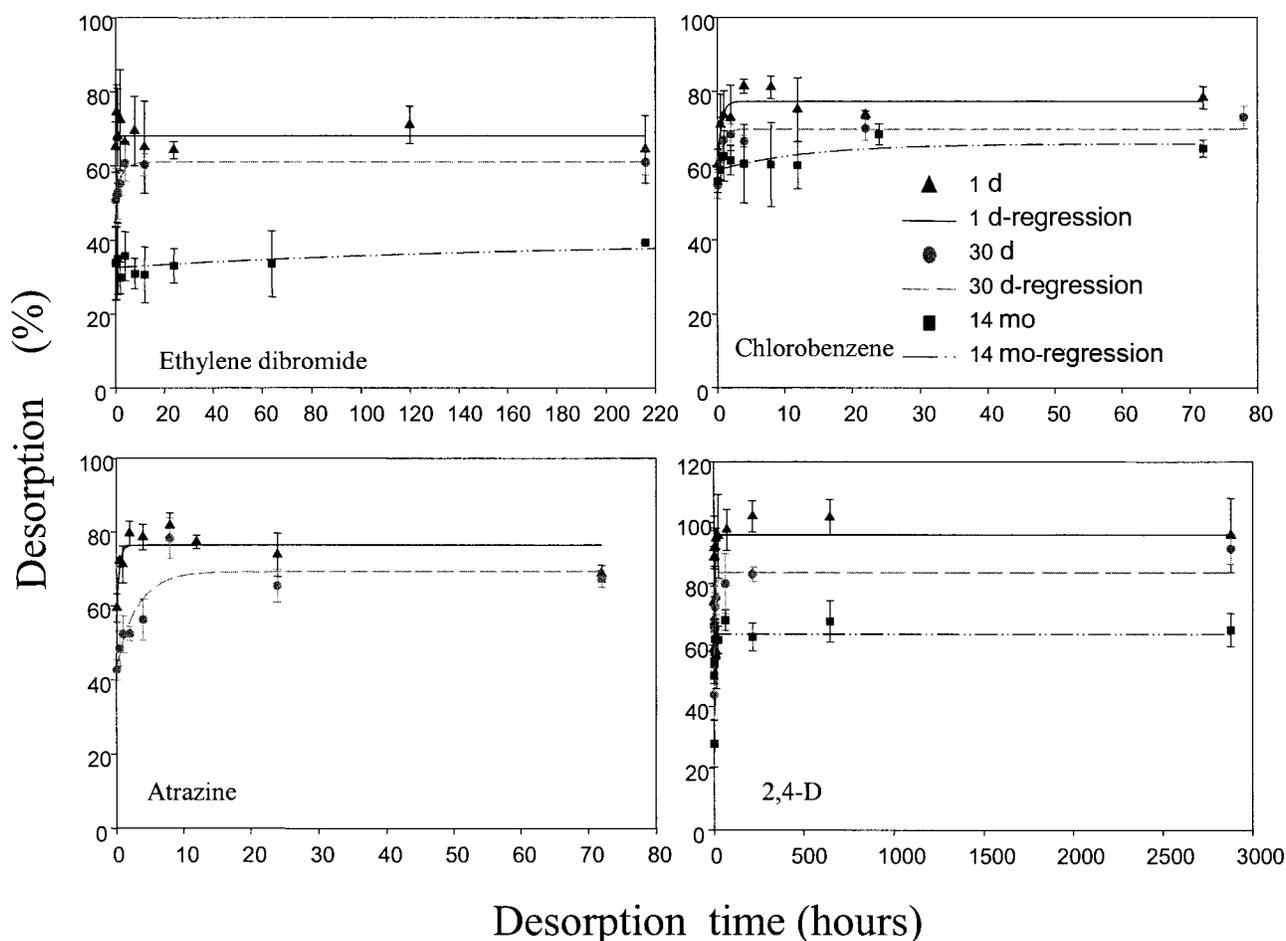


Fig. 2. Desorption kinetics of ethylene dibromide, chlorobenzene, atrazine, and 2,4-D on Capac A-horizon soil after aging periods of 1 d, 30 d, and 14 mo. Desorption is expressed as percent of the expected amount assuming complete reversibility.

tion fraction ($f_{nd} = 0.08$ after 1 d of aging). After the 1-d aging period, 2,4-D was the most reversible compound, desorbing approximately 92% of the amount expected assuming complete reversibility (Fig. 1). After 14 mo of aging, a considerably smaller fraction (51%) of 2,4-D desorbed. Chlorobenzene initially (1 d of aging) had a lower fraction desorbed (73%) than 2,4-D, but showed a more moderate increase after 14 mo of aging, after which 63% desorbed (highest among all compounds). Among the compounds studied, ethylene dibromide showed the smallest total desorbable fraction initially (68%) and after the 14-mo aging period (36%). Atrazine had similar but slightly lower values of f_{nd} after 1 and 30 d of aging compared with ethylene dibromide. All of the sorption site fractions (f_{eq} , f_{neq} , and f_{nd}) are reported in Table 2. Thus, results from the three-site desorption modeling demonstrate a clear reduction in the amount of chemical residing in the equilibrium sites for all compounds except chlorobenzene (Fig. 2), and a concomitant increase in the fraction of chemical residing in the nondesorption sites for all compounds with increased aging time (Table 2). The desorption rate coefficient (α) appeared to decrease with aging time for ethylene dibromide, chlorobenzene, and atrazine, but not for 2,4-D, which had essentially constant desorption coefficients throughout the aging regimes.

DISCUSSION

We observed a compound-specific effect of aging on the apparent sorption equilibrium condition as reflected by the sorption coefficient, K_d . The K_d values for ethylene dibromide and 2,4-D showed a significant increase from 30 d to 14 mo, for atrazine decreased from 1 to 30 d, and for chlorobenzene were essentially constant with aging. The limited data set provided here suggests that the effects of aging on sorption behavior may be inversely correlated to K_d . The largest increases in sorption on extended equilibration time were observed for 2,4-D and ethylene dibromide. These chemicals have the lowest soil sorption coefficients of the compounds studied. Chlorobenzene and atrazine have soil sorption coefficients that are approximately five times greater than ethylene dibromide and 2,4-D and there was little or no increase in sorption for these compounds after long equilibration times.

Agreement between experimental K_{oc} values and the corresponding values predicted using correlations to K_{ow} values (Table 1) is within the expected range of variation (a factor of 2 to 3) for measured K_{oc} values among soils (Kile et al., 1995). There is also good agreement between the K_{oc} values reported here for chlorobenzene and atrazine and those reported previously in the literature (Chiou et al., 1983; Montgomery, 1993). Previously re-

ported K_{oc} values for ethylene dibromide do not agree as well with our measured values. To illustrate, values for ethylene dibromide between 36.4 to 162.1 L kg⁻¹ are reported by Montgomery (1993) and between 103.3 and 134.5 L kg⁻¹ by Steinberg et al. (1987). These values are much larger than the values reported here, by an order of magnitude in some cases. An empirical equation (Chiou et al., 1983) based on K_{ow} predicts a K_{oc} for ethylene dibromide of 11.19 L kg⁻¹ (Table 1). The experimental value of 22.1 L kg⁻¹ reported here (1 d of equilibration) is much closer to the expected K_{oc} for ethylene dibromide than the values reported earlier.

Results from this study demonstrated no clear increase in nonlinearity with increased aging. The chlorobenzene sorption isotherm is more linear at 14 mo ($n = 0.905\text{--}0.908$) and 30 d ($n = 1.00\text{--}1.03$) than at 1 d ($n = 0.864\text{--}0.893$), whereas the ethylene dibromide isotherm is most linear at 1 d ($n = 0.966\text{--}0.995$) and least linear at 30 d ($n = 0.827\text{--}0.884$). Similar results have been observed for chlorobenzene sorption on several soil types (Sharer et al., unpublished data, 2003). These results are in contrast with those of Weber and Huang (1996) and Xing and Pignatello (1996), who reported increases in nonlinearity of isotherms for dichlorobenzene and dichlorophenol when comparing 1- and 180-d equilibrium times. This was rationalized in terms of a dual-mode sorption model where soil organic matter has both partition and adsorption domains. The adsorption domains are reached only after long soil–chemical contact times since these domains are internal to the soil organic matter matrix (Xing and Pignatello, 1996). The adsorption component gives the isotherm increasing nonlinearity that becomes more apparent with long soil–chemical contact times. The isotherms observed in this study do not exhibit consistent increases in nonlinearity with increased contact time, and in this sense do not appear to support a dual-mode sorption mechanism.

The desorption data shows that there is an increase in the nondesorbable fraction (f_{nd}) with increased aging time for all compounds tested (Table 2). This is in agreement with observations from a previous study (Sharer et al., unpublished data, 2003) where the nondesorbable fraction of chlorobenzene was found to increase in four soil types with increased aging time. Other studies have also found that the irreversible fraction increases with equilibration time (Pignatello, 1990; Pavlostathis and Mathavan, 1992). There does not appear to be a correlation between the magnitude of f_{nd} (at 14 mo) and K_d . The compound (chlorobenzene) with the largest K_d (4.75) has the smallest f_{nd} (0.37), and the compound (2,4-D) with the smallest K_d (0.9) has the next smallest f_{nd} (0.49). Likewise, there is no obvious relation between the relative increase in f_{nd} (Δf_{nd}) with longer aging times and K_d values.

Interestingly, a substantial fraction of the added chemical was rendered nondesorbable within 1 d. This observation is consistent with the findings of Kan et al. (1994, 1997, 1998) and Fu et al. (1994), who showed that the sorption of polycyclic aromatic hydrocarbons (PAHs) in soils was irreversible. The size of the irreversible fraction of PAHs was found to be 30 to 50% of the

total mass applied after seven days of sorption, with up to hundreds of days of desorption. The desorption-resistant fraction described here in the 1-d samples may be an indication that hindered diffusion is not the dominant mechanism controlling sorption–desorption behavior in this soil. Previous work has suggested that sorption and desorption of organic chemicals in soils is reversible in accordance with a retarded diffusion mechanism (Wu and Gschwend, 1986). The data presented here, along with data from other studies on the irreversibility of PAH sorption–desorption (Kan et al., 1994; Fu et al., 1994), suggest a different, perhaps additional, mechanism. The rapid formation of a desorption-resistant fraction suggests that a specific physical or chemical sorption interaction may be responsible, rather than slow diffusion. According to Xie et al. (1997), irreversible sorption of organic contaminants occurred in the humin fraction of soil. In their experiments, most irreversibly sorbed atrazine was found in the bound humic acid and mineral components of humin.

The desorption rate coefficient (α) in the nonequilibrium site shows that aging may have some effect on desorption rates. This coefficient decreased with aging for chlorobenzene, ethylene dibromide, and atrazine, but not for 2,4-D. These results would appear to partially support the findings of McCall and Agin (1985), who observed a decrease in the slow desorption rate constant with aging time. These results also partially support those of Carmichael et al. (1997), who found that the desorption rates (rather than rate constants) for fresh and field-weathered PAHs were different by several orders of magnitude.

One interesting aspect of this study is the difference in sorption–desorption behavior between chlorobenzene and ethylene dibromide on aging. Although there was no increase in K_d for chlorobenzene with increased aging time, a large increase in K_d was observed for ethylene dibromide subject to the same aging regimen (1 d to 14 mo). These results are surprising given that both compounds are halogenated hydrocarbons, are relatively nonpolar, and have similar molecular volumes (0.144 and 0.170 nm³ for ethylene dibromide and chlorobenzene, respectively). Furthermore, using the Wilke–Chang relationship, calculated diffusivities in water are nearly equal for these compounds (9.22×10^{-6} cm² s⁻¹ for chlorobenzene; 10.15×10^{-6} cm² s⁻¹ for ethylene dibromide) (Wilke and Chang, 1955). Based on these physical–chemical characteristics, one would predict similar effects of aging on sorption in soil. These compounds display significant differences in K_{ow} values (Table 1) and solubilities in water (S_w , 500 and 4250 mg L⁻¹ for chlorobenzene and ethylene dibromide, respectively). Consistent with previously developed relationships between S_w or K_{oc} and K_d (Chiou et al., 1983), chlorobenzene sorbs to soils five to six times greater than ethylene dibromide. Brusseau and Rao developed linear free energy relationships that predict that compounds with higher sorption coefficients (K_d) should have slower sorption–desorption behavior. Their relationship predicts that ethylene dibromide should have a log k (desorption rate coefficient) approximately five

times greater than chlorobenzene, which was not observed here. Our observation that chlorobenzene equilibrates more rapidly than ethylene dibromide contradicts this relationship and suggests that compound-specific interactions may be an important determinant of sorption kinetic behavior.

The larger magnitude of f_{nd} and its dramatic increase on aging for ethylene dibromide as compared with chlorobenzene provides more evidence of the behavioral differences between these compounds. While ethylene dibromide had the largest fraction bound to soil (after 14 mo of aging), and showed a significant increase in f_{nd} over the aging regime, chlorobenzene had the smallest irreversibly bound fraction and displayed a much more modest increase in f_{nd} over time. This was unexpected because of the similar physicochemical characteristics of ethylene dibromide and chlorobenzene as described previously. The differences in the measured f_{nd} values for these compounds is difficult to reconcile. It would seem that large f_{nd} values are more likely for 2,4-D and atrazine, which could enter into specific bonding relationships via their functional groups. In fact, atrazine and 2,4-D have relatively large f_{nd} values after long aging periods. However, ethylene dibromide has the largest f_{nd} value and chlorobenzene the smallest f_{nd} value, after 14 mo of aging. Interestingly, ethylene dibromide has been shown to have unexpected persistence in field soils (Steinberg et al., 1987) and results presented here indicate that ethylene dibromide exhibits sorption-desorption behavior that is consistent with this observation, albeit unpredicted based on its physical and chemical properties.

Spectral evidence has shown that compounds like ethylene dibromide and 1,2-dichloroethane exist as different conformational isomers in soils. This may help explain the unexpected behavior of ethylene dibromide observed in this study and in field studies (Steinberg et al., 1987). These compounds are known to associate more strongly with clay surfaces in the gauche conformer (Aochi et al., 1992) and with humics in the anti conformer (Aochi and Farmer, 1997). Sorption of these molecules is thought to occur by a pore-filling mechanism in soils as deduced from spectroscopic evidence (Aochi and Farmer, 1997). This pore-filling mechanism has been used to help explain the resistant fraction of 1,2-dichloroethane and ethylene dibromide observed in soils and clays. If chlorobenzene is unable to sorb via this mechanism, this could provide one possible explanation for the differences in behavior among these chemicals.

This study has demonstrated that aging causes an increase in sorption for some compounds but not for others on a common soil type. Ethylene dibromide and 2,4-D show clear indications of an increase in sorption, whereas atrazine does not during a 30-d sorption period, and chlorobenzene does not over a period of 14 mo. Aging appeared to affect the desorption rates of chlorobenzene, ethylene dibromide, and atrazine whereas it did not for 2,4-D. Aging does affect the amount of a compound desorbed. A nondesorbable fraction, present after only 1 d, increased with increasing aging time. This

trend was observed for all chemicals tested. It seems clear that some sorption-desorption characteristics of chemicals in soils can be compound specific and cannot be easily predicted from physicochemical characteristics. A much larger data set is needed to ascertain whether the behavior of ethylene dibromide is anomalous. Based on our results, generalizations about the effects of aging on the sorption-desorption behavior of organic chemicals in soils should be avoided.

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