

Desorption kinetics of neutral hydrophobic organic compounds from field-contaminated sediment

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“Capsule”: *Chemical release rates of neutral hydrophobic organic compounds are measured and biphasic desorption phenomena observed.*

Abstract

The chemical release rates from a field-contaminated sediment (Lake Charles, LA) using Tenax desorption were studied. Two dichlorobenzenes (*m*-, *p*-), hexachlorobutadiene, and hexachlorobenzene were investigated. Contrary to reports that sorption rates are inversely related to K_{OW} , the slow desorption rates were found to be similar for the four compounds. The data were modeled by a two-compartment irreversible adsorption and radial diffusion model. Desorption kinetics from the first irreversible compartment can be modeled by radial diffusion and assume an irreversible adsorption constant and soil tortuosity of 4.3. The desorption half-life is approximately 2–7 days. Desorption from the second irreversible compartment is very slow (half-life of approximately 0.32–8.62 years) presumably caused by entrapment in soil organic matter that increases the constrictivity of the solid phase to chemical diffusion. From the kinetic data, it is deduced that the diffusion pore diameter of the second irreversible compartment is approximately equal to the critical molecular diameter. The mass of chemicals in this highly constrictive irreversible compartment is approximately one-fourth of the maximum irreversible, or resistant, compartment. The slow kinetics observed in this study add additional support to the notion that the irreversibly sorbed chemicals are ‘benign’ to the environment. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Particles, or sediments, are the natural depository (and later sources) for contaminants of all kinds including metals, non-metals, and neutral organic hydrocarbons. The manner in which contaminants interact with and desorb from particles in natural waters has enormous consequences to all inhabitants of the aquatic environment. When hydrophobic chemicals such as petroleum products, industrial wastes, and municipal discharges are released into the coastal waterways, the primary fate in every case will generally be to attach to particles in the water column. The manner in which hydrophobic contaminants interact with particles can be either beneficial or detrimental depending upon the specifics of the equilibrium, the

kinetics and the mass transport of the adsorption and desorption processes. In the absence of more accurate information, companies and regulators tend to take a very conservative, or worst-case, approach to preparing fate models, setting clean-up end points, and designing control or treatment protocols to protect human health and the environment. This approach of taking the worst-case model, to be safe, because more realistic scientific answers are not known has enormous adverse economic consequences.

Mechanistic interpretation of sorption phenomena is crucial for prior prediction of contaminant fate in the environment. Even though a large amount of mechanistic laboratory research has been directed toward understanding and quantifying the fate of hydrophobic chemicals in contact with naturally occurring particles in the water column, the ability to predict fate and clean-up protocols is still quite poor. The problem is partly due to the complexity of the environment. Different types of soils, chemicals, contamination level, and

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environmental chemistry could affect the fate of contaminants significantly.

In this study, the primary interest is the sorption mechanism of trace level neutral organic hydrocarbons to soil containing a moderate amount of organic matter. Several conceptual models have been proposed in the literature to explain the anomalous sorption phenomena: (1) the existence of a condensed, glassy, organic polymeric matter as adsorbent. The adsorption to the condensed organic matter phase could be kinetically slow, site specific, and non-linear (Weber and Huang, 1996; Xing et al., 1996); (2) the presence of high surface area carbonaceous sorbent, e.g. soots. The adsorption to these high surface area carbonaceous materials could be non-linear, site specific, and limited in capacity (McGroddy et al., 1996; Chiou and Kile, 1998); and (3) the sorbed chemicals are irreversibly trapped in the humic organic matrix following sorption (irreversible adsorption) (Kan et al., 1998). The term 'irreversible' is used to imply that desorption takes place from a molecular environment that is different from the adsorption environment, and that desorption is essentially completely prevented. The irreversible compartment has been found to contain a finite maximum capacity (Kan et al., 1997). Neutral hydrophobic organic compounds desorb at a similar limit, regardless of the physical/chemical properties of the chemicals. The authors in 1985 (West et al., 1986) first proposed the notion of irreversible sorption as a new mechanism important for hydrocarbon transport.

Numerous researchers have shown that the adsorbent surface layer can undergo rearrangement upon adsorption and that this physical–chemical rearrangement can be the cause of non-reversible adsorption (Adamson, 1990). These ideas were tested with naphthalene (Fu et al., 1994; Kan et al., 1994, 1997, 1998). Recently, Huang and Weber (1997) concluded that the entrapment of sorbing molecules within condensed soil organic matter matrices contributes significantly to sorption–desorption hysteresis or sorption irreversibility. Schlebaum et al. (1988), presented compelling evidence to show that the anomalous sorption phenomena cannot be explained by the non-linear sorption to a condensed organic phase. Instead, the observations may be attributed to a change in conformation of the humic acid after adsorption, in agreement with the irreversible adsorption model proposed earlier. Chiou and Kile (1998) proposed that the specific-interaction to high surface area carbonaceous material could reconcile the outstanding features of the nonlinear and the competitive sorption. Interestingly, Chiou and Kile observed an apparent saturation capacity of similar magnitude to the irreversible capacity of Kan et al. (1997, 1998).

Kan et al. (1998) proposed that the sorption and desorption of organic chemicals to and from soil consisted of two compartments: (1) a labile desorption compartment, where the chemical can be readily and reversibly

desorbed; and (2) an entrapped and irreversible compartment, where the desorption is hindered by soil organic matter due to conformational changes in the soil organic matter following the adsorption. This suggests that there must be a rearrangement in order for there to be an irreversible fraction. Desorption from both the labile and irreversible compartments are limited by retarded intraparticle radial diffusion. Chemical desorption from the irreversible compartment shows a constant and different partition coefficient, $K_{oc}^{irr} \cong 10^{5.53}$ l/kg for chemicals of widely different hydrophobicities. It is proposed that the chemical in the irreversible compartment form an organic 'complex' with the organic colloids in the soil organic matter. Therefore, the physical–chemical nature of the adsorbate would be masked by the 'complex'. A similar conceptualization was proposed by Schulten and Schnitzer (1997) based upon molecular modeling. Both the kinetic and thermodynamic aspects of desorption, regardless of the chemical hydrophobicity, are expected to be similar. The possible existence of such a complex has been observed previously (Kan et al., 1998; Devitt and Wiesner, 1999). In this study, the long-term desorption kinetics of neutral organic hydrocarbons from field-contaminated sediment (Lake Charles sediment) were evaluated to further elucidate the mechanisms that control the resistant desorption.

2. Materials and methods

2.1. Sediments

The contaminated sediment was collected near the confluence of Bayou d'Inde and the lower Calcasium River at Lake Charles, LA, by personnel at US Geological Survey in 1995. The sediments were stored in clean plastic zipper bags and chilled to 4°C during shipment. Upon receipt, sediment samples were combined, mixed, and centrifuged at a low temperature to separate the pore water from the sediments, and the sediment was stored in a refrigerator. The sediment contains a large fraction of fine particles. The inorganic fraction of the sediment is mainly quartz, and the organic carbon content is 4.1%. Wet sediment, containing 31.2% moisture, was used exclusively in the experiments. In the following, the reported sediment weight is on a dry weight basis. Tenax TA beads (polymeric adsorbent beads, 20/35 mesh, Alltech Associates, Inc., Deerfield, IL, USA) were used in desorption experiments. Tenax beads were cleaned before use by successive Soxhlet extraction with acetone, acetone–hexane (1:1 by volume), methanol, and acetone, respectively, 48 h for each extraction step. After extensive cleaning, 1 g Tenax beads was extracted with 10 ml acetone. The acetone extract was analyzed by gas chromatography–electron capture detection (GC–ECD) to confirm the cleanliness. Clean Tenax was

then baked at 200°C overnight and stored in methanol. Used Tenax was cleaned and regenerated by the same procedure mentioned above. Prior to use, Tenax beads were removed from the methanol, baked at 200°C for at least 4 h in a clean glass vial. The vial was then sealed and allowed to cool to room temperature. Glassware was cleaned in heated 2% detergent solution (RBS 35 from Pierce Chemical Co., Rockford, IL, USA) overnight at 60°C. Then the glassware was brushed, rinsed with tap water, deionized water, acetone, and oven dried at 200°C.

2.2. Tenax desorption experiments

Five experiments were used to study the release of hydrocarbons for the Lake Charles sediments with the presence of Tenax beads as a sink for the contaminant to desorb. The procedure is similar to that used in the literature (Pignatello, 1990; Cornelissen et al., 1997). In a typical desorption experiment, 0.7 g sediment was suspended in a vial containing 40 ml electrolyte solution (0.1 M NaCl, 0.01 M NaN₃) and 0.5 g Tenax. The vial was capped with a Teflon septum and tumbled at 1 rpm for a designated period of time. Tenax was replaced at 2-, 10-, 20-, and 30-day intervals. A total of 151 days desorption time was monitored. At the end of each desorption period, the reactor vials were centrifuged for 30 min at 1000 g (IEC Centra MP4 Centrifuge, International Equipment Company, MA, USA). The Tenax beads were then carefully taken out with a clean stainless steel spatula and transferred to a pre-weighed 25-ml clear glass vial. Another 0.5 g clean Tenax beads were added into the vial to continue desorption.

The contaminated Tenax was extracted with 6 ml acetone in four successive extractions. The acetone extraction was done on a horizontal shaker (Yamato, Model 1290) overnight. ¹⁴C-labeled 2,2',5,5' tetrachlorobiphenyl (PCB) or 1,4-dibromobenzene were added to Tenax prior to acetone extraction to determine the extraction efficiency. The contaminant concentration in the acetone extract was analyzed by GC-ECD. Over three repetitive extractions, the cumulative recovery of PCB from Tenax was 98%.

2.3. Soxhlet extraction

The initial solid phase concentrations of selected chlorinated hydrocarbons on the sediments were determined with the Soxhlet extraction method followed by gas chromatography–mass spectroscopy (GC–MS) and GC–ECD analysis. Approximately 10 g of wet sediment was mixed with 10 g anhydrous sodium sulfate (baked at 460°C for 4 h), and refluxed with dichloromethane for 48 h. 1,2-Dibromobenzene, used as a surrogate standard, was added to the sediment before Soxhlet extraction. After extraction, the extract was passed through a 20-mm ID drying column containing about

10 cm of anhydrous sodium sulfate. The extraction flask and the sodium sulfate column were washed with 100 ml methylene chloride to complete the quantitative transfer of chlorinated hydrocarbons and the surrogate standard. The effluent was collected in a Kuderna-Danish concentrator and concentrated to 2 ml. The concentrated solution was cleaned with a SupelcleanTM LC-Florisil SPE tubes (Supelco Inc., Bellefonte, PA, USA) and a Nylon Acrodisc 13 syringe filter (0.45 µm pore size, Gelman Sciences, Ann Arbor, MI, USA). A portion of the final extract was further concentrated and analyzed by GC–MS to identify the compounds in the sediments. The rest of the extract was diluted with isooctane and quantified with GC–ECD (HP Ultra 2 fused silica capillary column, 25 ml×0.32 mm internal diameter, 0.52 µm film thickness). The injector temperature was set at 275°C and the detector temperature was set at 390°C. The temperature program was set at an initial temperature of 50°C, for 4 min, and increased by 8°C per minute to 280°C, and held at the final temperature for 4 min. Equal concentration of 2,5-dibromotoluene was added to the analyst prior to GC analysis as an internal standard.

2.4. Data analysis

Tenax desorption data was fitted with the empirical two compartment first-order kinetic model, used by Cornelissen et al. (1997): this empirical method to represent desorption rate data is used, because detailed mechanistic understanding of slow desorption rate is not yet available.

$$q_t/q_o = F_1 e^{-k_1 t} + F_2 \times e^{-k_2 t}, F_2 = 1 - F_1 \quad (1)$$

in which q_t and q_o (µg/g) are the sediment-bound contaminant concentrations at time t (days) and at the start of the experiment, respectively; F_1 , and F_2 are the fractions of contaminant present in the two kinetically different desorbing compartments, respectively; k_1 , and k_2 (day⁻¹) are the first-order rate constants for the two desorption compartments, respectively. The natural logarithmic form of Eq. (1) was fitted with experimental data by minimizing the squares of differences between experimental and calculated values of $\ln(q_t/q_o)$ using a non-linear least-square parameter minimization procedure (Wentworth, 1965). For the infinite bath condition, the first-order rate constant is related to retarded intraparticle radial diffusion coefficient (D_e) (Ball and Roberts, 1991; Schwarzenbach et al., 1993) as follows:

$$k \cong \frac{\ln 2}{t_{50\%}} \cong \frac{\ln 2}{0.03 R^2 / D_e} \cong \frac{0.693 \times \phi \times D_w / \chi_e}{0.03 \times R^2 (\rho_s \times (1 - \phi) \times OC \times K_{OC} + \phi)} \quad (2)$$

where D_e is the effective diffusivity, D_w (cm²/s) is the molecular diffusivity of the molecule, χ_e is the effective tortuosity, ρ_s is the solid density (g/cm), k is the first-order rate constant (s⁻¹), ϕ is the intraparticle porosity and R is the particle radius (cm), OC is the fractional organic carbon content, and K_{OC} (cm³/g) is the organic carbon-based partition coefficient. The effective tortuosity is a product of tortuosity factor and the inverse of a constrictivity factor (Ball and Roberts, 1991).

$$\chi_e = \chi/K_r, \quad (3)$$

where χ is the soil tortuosity and K_r is the constrictivity factor. Theoretically and experimentally proposed tortuosity in unconsolidated material generally ranges between 1.3 and 3 (Ball and Roberts, 1991). Constrictivity is a measure of the relative size of the molecule to the pore size. Satterfield et al. (1973) proposed the following correlation:

$$K_r = 0.98 \exp(-4.6\lambda), \quad (4)$$

where λ is the ratio of critical molecular diameter to pore diameter.

3. Results and discussion

Since the sediments were contaminated for over 30 years, the dissolution of the chlorinated compounds should have ceased long ago. Yet, a significant fraction of the contaminants still exist in measurable quantity. In Table 1 are listed the solid phase concentration and the physical–chemical properties of four predominant contaminants found in the Lake Charles sediment. As discussed in the Materials and methods section, considerable effort has been devoted to data and quality control to avoid experimental artifacts. Five desorption experiments were performed with five sediment samples. Wet sediments were used without deliberate homogenization to prevent any possible disturbance to the sediments that could affect the release of contaminants

from the natural sediments. Data from these five desorption experiments are very consistent (see below).

Fig. 1 shows the fractional desorption of four chlorinated hydrocarbons from the sediments by Tenax desorption over 151 days. The dotted lines were obtained by exponential curve fitting to the two compartment first-order kinetic model (Eq. (1)). The plot of fraction remaining versus time showed a progressive decrease in slope, indicating greater and greater resistance to desorption. The curve-fitted kinetic parameters are listed in Table 2. The numbers in parentheses are the standard deviations of the parameters.

The desorption data can be fitted well with the two-compartment model. The first kinetic rate constants (k_1) are between 0.093 and 0.309 day⁻¹ for the four compounds in Lake Charles sediments. The fractional mass of chemicals in the first compartment ranges from 0.7 to 37% for the two dichlorobenzenes and hexachlorobutadiene, but is negligible for hexachlorobenzene. The second kinetic rate constants (k_2) are between 0.00022 and 0.0026 day⁻¹ for the four compounds in Lake Charles sediments. The two kinetic rate constants for the three chlorinated benzenes are very similar regardless of the fact that their aqueous solubilities differ by four orders of magnitude. The desorption rates for hexachlorobutadiene are lower by a factor of 2–10 than that of the chlorinated benzenes. The significance of these differences between the desorption of the three chlorinated benzenes and hexachlorobutadienes is not known at this time. The reported two-compartment desorption rates are consistent with the previously reported irreversible adsorption data (Fu et al., 1994). Fu et al. (1994) reported a desorption rate of 0.113 and 0.0016 day⁻¹ for naphthalene desorption into water from a laboratory contaminated irreversibly adsorbed sediment.

It is generally agreed that Eq. (2) or one of the K_{OW} /kinetic-rate correlations (Karickhoff and Morris, 1985; Brusseau and Rao, 1989a; Brusseau et al., 1990, 1991) can model the rate of chemical uptake and release of the freshly adsorbed chemicals (Karickhoff and Morris, 1985; Wu and Gschwend, 1986; Brusseau and Rao,

Table 1
Concentrations and the physical–chemical properties of four predominant contaminants in Lake Charles sediment

Compound	Solid phase concentration (μg/g)	K_{OW}	Physical–chemical properties ^a		
			Aqueous solubility (M)	Molar volume ^b (cm ³ /mol)	Molecular diffusivity ² (cm ² /s)
1,3-Dichlorobenzene	4.67	10 ^{3.38}	10 ^{-3.05}	125.8	8.73 × 10 ⁻⁶
1,4-Dichlorobenzene	16.5	10 ^{3.38}	10 ^{-3.39}	125.8	8.73 × 10 ⁻⁶
Hexachlorobutadiene	3.4	10 ^{4.90}	10 ^{-4.90}	183.0	7.01 × 10 ⁻⁶
Hexachlorobenzene	49.5	10 ^{5.50}	10 ^{-7.69}	195.8	6.75 × 10 ⁻⁶

^a Data are from Schwarzenbach et al. (1993).

^b Estimated from equations in Schwarzenbach et al. (1993, pp. 198–199).

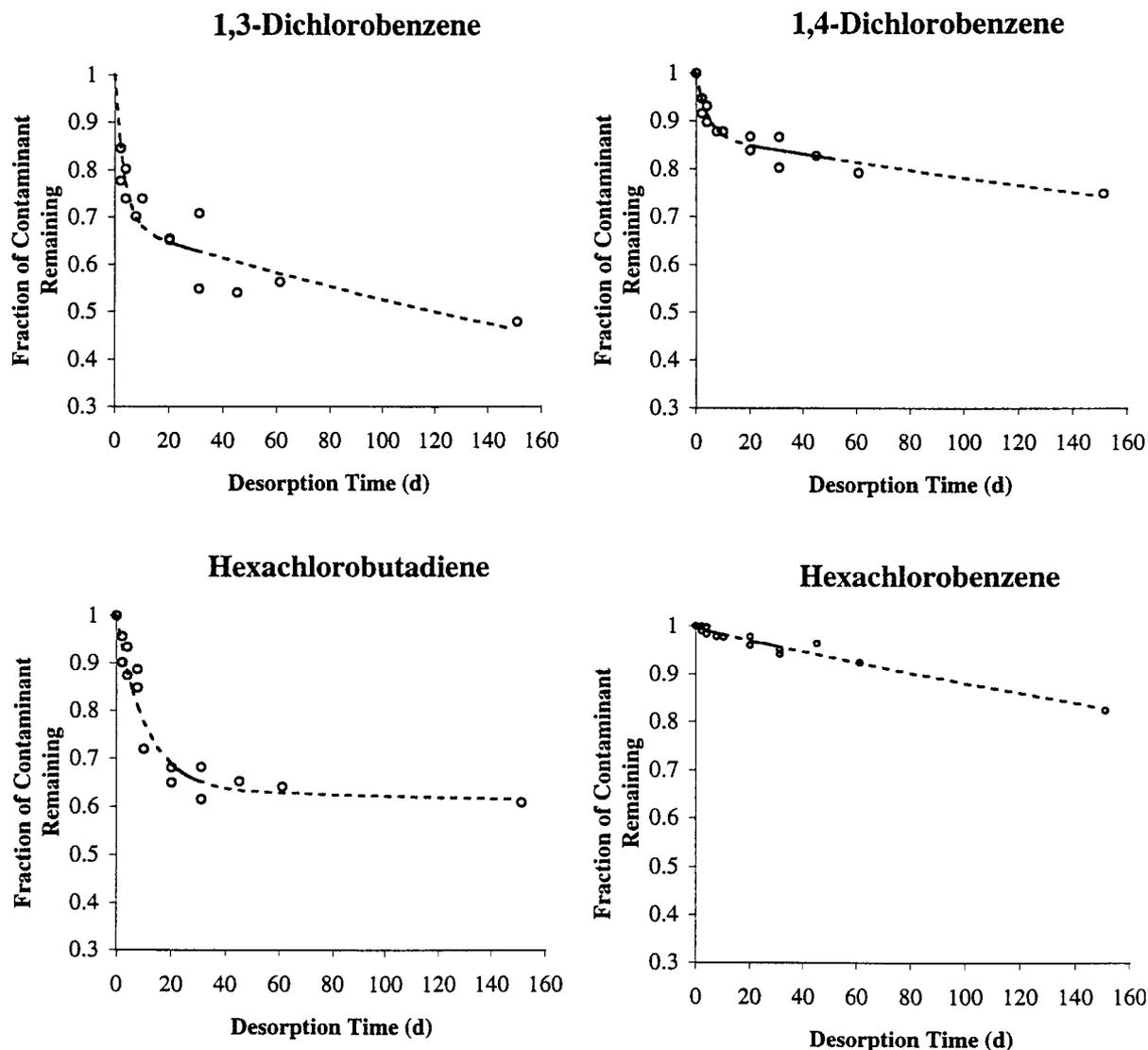


Fig. 1. Plots of the fractional mass of four contaminants on Lake Charles sediment versus desorption time (days) following desorption by Tenax beads. The four predominant chemicals in Lake Charles sediment are 1,3-dichlorobenzene, 1,4-dichlorobenzene, hexachlorobutadiene, and hexachlorobenzene.

1989a, b; Brusseau et al., 1990; Kan et al., 1998). The first-order rate constant based on radial diffusion model (Eq. (2)) predicts an inverse relation between the rate constants and chemical hydrophobicity (K_{OW}). Table 2 lists the calculated radial diffusion rate constants by assuming nominal soil parameters and K_{OC}/K_{OW} relationships ($\rho_s = 2.65/\text{g}/\text{m}^3$, $\phi = 0.05$, $R = 50 \mu\text{m}$, $\chi = 3$, and $K_r = 1$ and $K_{OC} = 0.63K_{OW}$) (Karickhoff et al., 1979). However, the K_{OC}/K_{OW} predicted sorption rate constants are about two to four orders of magnitude larger than the measured k_1 and k_2 (Table 2). Also, polymer diffusion theories have been proposed to explain such slow desorption kinetics (Carroll et al., 1994; Pignatello and Xing, 1996; Weber and Huang, 1996; Cornelissen et al., 1997). It will be shown in the following discussion that the slow desorption kinetics can also be explained with intraparticle radial diffusion

and the irreversible adsorption model, previously proposed by the authors.

Kan et al. (1988) proposed that the sorption and desorption of organic chemicals to and from soil consisted of two compartments: (1) a labile desorption compartment, where the chemical can be readily and reversibly desorbed; and (2) an entrapped, or irreversible compartment, where the desorption is hindered by soil organic matter due to the conformational changes in the soil organic matter following adsorption. It is further proposed that there existed two kinetically different regimes in the irreversible compartment. Previous work with naphthalene and phenanthrene (Kan et al., 1998) demonstrated that the adsorption and desorption to the labile compartment can be modeled by Eq. (2) and K_{OC}/K_{OW} relation. Since the Lake Charles sediment has been weathered and aged for over 30 years, it is proposed

Table 2
Solid phase contaminant concentrations and fractional distribution of the contaminants based on the release rates and the estimated release rate constants

Compound	Compartment 1 ^a		Compartment 2 ^a		k^b predicted from Eq. (2) and $K_{OC} = 10^{5.53}$	χ_e^c predicted from Eq. (2) with k_1 and $K_{OC} = 10^{5.53}$
	F_1	First-order rate constant (k_1 , day ⁻¹)	F_2	First-order rate constant (k_2 , day ⁻¹)		
1,3-Dichlorobenzene	0.321 (0.0087)	0.284 (0.021)	0.679	0.0026 (0.0002)	74.5	3.51
1,4-Dichlorobenzene	0.135 (0.0030)	0.229 (0.015)	0.865	0.0010 (0.00005)	74.5	4.35
Hexachlorobutadiene	0.366 (0.0077)	0.093 (0.013)	0.634	0.00022 (0.00013)	1.80	8.60
Hexachlorobenzene	0.007 (0.0013)	0.309 (0.186)	0.993	0.0012 (0.00002)	0.44	2.49

^a Numbers in parentheses are the standard deviations.

^b Predicted from Eq. (2) with $\phi = 0.05$, $\chi_e = 3$, $R = 50 \mu\text{m}$, and D_w from Table 1.

^c Predicted from Eq. (2) with measured k_1 , $\phi = 0.05$, $\chi_e = 3$, $R = 50 \mu\text{m}$, and D_w from Table 1. k_1 (day⁻¹) is Eq. (2) assumed equal to k_1 (day⁻¹)/(96,400 s/day) and $K_{OC} = K_{OC}^{irr} = 10^{5.53}$ ml/g-OC.

that the kinetic rates reported in Table 2 correspond to the rates of chemical release from the entrapped and irreversible compartment only, which will be further justified below. Kan et al. (1998) observed that most irreversibly adsorbed organic compounds had similar sorption and desorption equilibrium properties ($K_{OC}^{irr} \cong 10^{5.53}$ ml/g). Based upon an assumption of $K_{OC}^{irr} \cong 10^{5.53}$ and holding the other soil parameters constant ($\rho_s = 2.65$, $\phi = 0.05$, $R = 50 \mu\text{m}$, $\chi = 3$, and $K_r = 1$), a different diffusion rate would be predicted via Eq. (2). The K_{OC}^{irr} -based predicted rate constants are very similar to the measured k_1 for all four compounds (Table 2, column 7). The effective tortuosity (χ_e) can be calculated from Eq. (2) with the experimentally measured rate (k_1) and the same soil parameters ($\rho_s = 2.65$, $\phi = 0.05$, $R = 50 \mu\text{m}$, $K_{OC} \cong 10^{5.53}$). The calculated χ_e are between 2.5 and 8.6 with a geometric mean of 4.3, which is very close to the theoretically predicted soil tortuosity suggested by Wu and Gschwend (1986) and Satterfield et al. (1973). Therefore, it is proposed that chemical desorption from the first irreversible compartment can be modeled with simple intraparticle radial diffusion of an irreversibly sorbed compound. The effective tortuosity is similar to the soil tortuosity estimated previously for soil and other unconsolidated materials (Satterfield et al., 1973; Wu and Gschwend, 1986). Therefore, the constrictivity factor (Eq. (4)) is $K_r \cong 1.0$; i.e. the molecular size is small in comparison with the diffusion pore diameter. The desorption half-life from the first irreversible compartment is between 2 and 7 days.

The desorption rate (k_2) from the second irreversible compartment is two to three orders of magnitude slower than the first irreversible compartment desorption rate (k_1). In Table 3, k_2 values of this study are compared with five other literature reported desorption rate data. The chemicals listed in Table 3 include both polar (atrazine and metolachlor) and nonpolar compounds; the range of K_{OW} values varies by four orders of magnitude. Soil organic carbon contents range from 0.26 to 7.02%. However, the reported desorption rate constants in Table 3 varied by less than a factor of 3 (except for hexachlorobutadiene). It is proposed that a fraction of the irreversibly adsorbed chemical is trapped in the soil organic matter and that the diffusion from the entrapped compartment is limited by a constrictivity factor. In Table 3 are listed the effective tortuosities (χ_e) calculated from the desorption rate (k_2) and the irreversible isotherm $K_{OC}^{irr} \cong 10^{5.53}$. The geometric mean of the effective tortuosities (χ_e) is 458 for the 11 compounds, which is within the range of effective tortuosity reported by Ball and Roberts (1991) for Borden soil. Using the soil tortuosity from compartment 1 data, $\chi = 4.3$, the mean effective tortuosity (χ_e , Table 3, column 6) corresponds to a constrictivity factor, $K_r \approx 0.01$ (Eq. (3)).

According to Eq. (4), a value of $K_r \approx 0.01$ corresponds to $\lambda \approx 1$, i.e. the diffusion pore diameter is similar in size

Table 3
Comparison of reported long-term slow desorption rate constants

Contaminant	Soil/sediment OC content	Experiment	K_{OW}	First-order rate constant (day ⁻¹)	χ_e	Reference
Aroclor 1242	Lake Carnegie 2.6% OC	Laboratory-contaminated sediment, batch water desorption	$10^{5.3-6.4}$	0.003	351	Witkowski et al., 1988
Atrazine Metolachlor	Merrimac find sandy loam 2.6% OC	Field contaminated, Column water desorption	$10^{2.56}$	0.006 0.0019	194 615	Pignatello et al., 1993
2,2',3,4',5'-PCB 2,2',4,4',5'-PCB	Lake Ketelmeer 7.02% OC	Field contaminated, Tenax desorption	$10^{6.25}$ $10^{6.35}$	0.005 0.003	75 125	Cornelissen et al., 1997
PCBs	Hudson River 1–5% OC	Field contaminated, XAD-4 desorption	$10^{5.3-6.4}$	0.005	549	Carroll et al., 1994
Naphthalene	Lula fine sand 0.27% OC	Laboratory-contaminated sediment, batch water desorption	$10^{3.36}$	0.0016	2382	Fu et al., 1994
1,3-Dichlorobenzene	Lake Charles 4.1% OC	Field contaminated, Tenax desorption	$10^{3.38}$	0.0026	383	This study
1,4-Dichlorobenzene			$10^{3.38}$	0.001	997	
Hexachlorobenzene			$10^{4.90}$	0.00022	3634	
Hexachlorobutadiene			$10^{5.5}$	0.0021	641	
Geometric mean				0.0021	458	

to the critical molecular diameter. The desorption half-lives from the second irreversible compartment range from 0.32 to 8.62 years. Therefore, the second compartment represents a fraction that may persist in the environment for a long time, especially because the subsurface environment has much less turbulence than laboratory desorption simulations.

Kan et al. (1998) proposed that there is a maximum irreversible capacity that can be estimated by ($q_{\max}^{\text{irr}} \approx 10^{3.8} \times \text{OC}$). According to this relation, the maximum irreversible capacity for the Lake Charles sediment should be approximately 258 $\mu\text{g/g}$. The measured chemical concentration in Lake Charles sediment is 74.07 $\mu\text{g/g}$ (Table 1). Only $\sim 8\%$ of the total chemical mass in the solid phase belongs to the first irreversible compartment. Since the half-life of the first irreversible compartment desorption is only 2–7 days, it is proposed that the majority of chemicals in the first irreversible compartment had been desorbed over the past 30 years. The total chemical mass in the second irreversible compartment is 68.8 $\mu\text{g/g}$, which is approximately a fourth of the maximum capacity, which is consistent with the observed field persistence of those chlorinated compounds, one labile compartment and two resistant, or irreversible compartments.

In conclusion, three kinetically different desorption regimes are proposed to model the desorption of chemicals from soil (Table 4). First, a fraction of the adsorbed chemicals is labile and readily desorbs according to the

Table 4

Summary of three desorption regimes for chemical desorption from soil and the proposed soil and chemical parameters for the intraparticle diffusion coefficient estimation^a

Labile compartment	Irreversible compartments	
	1	2
$K_{OC} \cong 0.63 K_{OW}$	$K_{OC} \cong 10^{5.53}$	$K_{OC} \cong 10^{5.53}$
$\chi \cong 4.3$	$\chi \cong 4.3$	$\chi \cong 4.3$
$K_r \cong 1$	$K_r \cong 1$	$K_r \cong 0.01$

^a The terms χ and K_r represent intraparticle tortuosity and constrictivity, respectively.

radial diffusion model and K_{OC}/K_{OW} predictions. A second fraction of the adsorbed chemicals is entrapped by the soil organic matter, as proposed by the irreversible adsorption model. Two kinetic regimes are assumed within the irreversible compartment. A fraction of the entrapped and irreversibly adsorbed chemical desorbs kinetically with a half-life of approximately 2–7 days, which is predictable by the radial diffusion and $K_{OC}^{\text{irr}} \cong 10^{5.53}$ and a nominal soil tortuosity = 4.3. A second fraction of the entrapped and irreversibly adsorbed chemical desorbs with a half-life of 0.32–8.62 years, which is predictable by a radial diffusion and assumes an additional constrictivity factor of $K_r = 0.01$.

Regardless of the mechanism that governs the rate of chemical release, a thermodynamic equilibrium model provides an upper bound prediction for desorption. An

irreversible adsorption equation (Kan et al., 1998) has been proposed to model contaminant desorption and has been tested extensively with reported field data:

$$q = K_{oc} \times OC \times C + \frac{K_{OC}^{irr} \times OC \times q_{max}^{irr} \times f \times C}{q_{max}^{irr} \times f + K_{OC}^{irr} \times OC \times C}, \quad (5)$$

where q_{max}^{irr} ($\mu\text{g/g}$) is the maximum irreversible capacity, K_{OC}^{irr} (cm^3/g) is the irreversible compartment organic carbon-based partition coefficient, OC is the organic carbon content, C is the aqueous phase concentration ($\mu\text{g/ml}$), f ($0 < f < 1$) is the fraction of the irreversible compartment that is filled at the time of exposure, which is typically assumed to be equal to 1. The isotherm equation consists of two terms, the first is a linear term to represent reversible sorption and the second is a Langmuir-type term to represent irreversible sorption. With this equation and a value of OC , no additional site-specific or chemical-specific information is required to predict the contaminant fate. The isotherm predicts that a significant fraction of irreversibly sorbed chemicals does not desorb into the environment, as expected. Recently, several papers have shown evidence that the nondesorbing chemicals are not biodegradable (Cornelissen et al., 1998). If it can be shown that these irreversibly adsorbed chemicals are not bioavailable, one may assume that the irreversibly sorbed chemicals may be 'safe' in the environment. The additional kinetic results shown in this study would suggest that approximately a quarter of the irreversibly sorbed compounds is tightly trapped and that desorption is extremely slow. This kinetic effect will add an additional 'safety factor' to support the notion that no substantial risk to health or the environment will be added if trace level tightly bound contaminants are left in the soil.

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