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Demonstration of the "Conditioning Effect" in Soil Organic Matter in Support of a Pore Deformation Mechanism for Sorption Hysteresis

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Hysteresis, or isotherm nonsingularity, is a confounding issue in sorption research that undermines the commonplace assumption of reversibility in environmental fate and effects models for organic compounds in soil media. Until now, a molecular-level mechanism for true hysteresis when the sorbate is retrievable, structurally intact, has not been forthcoming. We show here that two organic soils exhibit the "conditioning effect", which refers to the enhancement in sorption of a compound following brief exposure of the sorbent to high concentrations of the same or a similar compound. The conditioning effect has been used in support of a pore deformation mechanism for hysteresis in glassy polymers. By this mechanism, the sorbate causes irreversible changes in the structure of internal nanopores (holes) in the organic matrix upon its sorption. Trichloromethane was the test solute for dichloromethane-conditioned Pahokee soil (44.6% organic carbon), and chlorobenzene and 1,2,4-trichlorobenzene were the test solutes for benzene-conditioned Mount Pleasant silt loam (4.5% organic carbon). In each case, the isotherm of the test solute in the conditioned soil was shifted upward of, and was less linear than, the corresponding isotherm in the nonconditioned control. Application of the polymer-based Dual-Mode (partitioning-hole filling) Model shows an expansion of the hole domain as a result of conditioning. The memory of the conditioning effect persists for longer than 96 days at 21 °C but is lost upon heating the sample at 100 °C. A three-step (sorption−desorption−resorption) experiment demonstrated hysteresis followed by enhanced resorption, implying a mechanistic relationship between hysteresis and the conditioning effect. The results indicate that irreversible pore deformation is a mechanism for hysteresis in natural organic matter materials and suggest that slow matrix relaxation may contribute to the often-observed long-term resistance of some contaminants to desorption.

Introduction

The sorption of organic compounds to natural solids often exhibits hysteresis, or nonsingularity, between the sorption and desorption branches of the isotherm (e.g., refs *1*−*13*). When hysteresis occurs, the sorbate characteristically shows greater apparent affinity for the solid in the desorption direction. Hysteresis has important implications for the fate and hazardous effects of pollutants. Models dealing with physical and biological availabilities of pollutants typically assume sorption to be reversible. The sorption coefficients used in such models are invariably based on forward-constructed sorption isotherms. If sorption is irreversible, these models may incorrectly predict the fate and biological effects of a pollutant. Although many researchers intend to develop models accounting for sorption hysteresis, no consensus on a mechanism exists.

Hysteresis may be true or due to artificial causes. Possible artifacts include nonequilibrium owing to intraparticle molecular diffusion limitations; removal of competing substances, such as colloids or cosolutes in the supernatant liquid just prior to the desorption step; and reaction to give covalently altered products that are either free or bonded to the sorbent (*2, 6, 13*). True hysteresis occurs in the absence of artifacts and when the parent compound is retrievable intact through extraction or other vigorous means. Many examples exist in the literature where hysteresis appears to be of the true kind. True hysteresis is also referred to as *irreversible* sorption. Irreversible here means not that the sorbate is irretrievable, but that sorption and desorption follow different mechanistic pathways. To date, a satisfactory explanation for true hysteresis in natural solids has not been advanced. Since it is not possible at equilibrium for a given solute concentration to correspond to more than one sorbed concentration, as implied by a nonsingular isotherm, true hysteresis must have a kinetic basis. Molecular diffusion comes to mind first; yet diffusion may not be the only process limiting rates. Hysteresis in reference solids has been attributed to formation of metastable states, network percolation effects, or irreversible pore deformation. The first two of these causes are characteristic of capillary liquid condensation in fixed mesopores (*14, 15*), whereas the last is characteristic of vapor sorption in the nanopores of glassy polymers (*16, 17*) and in dry clay (*18*) and organoclay (*19*) interlayers.

We provide evidence here linking hysteresis to a pore deformation mechanism in natural organic matter (NOM) solids. NOM can be modeled as an amorphous polymer-like material existing in a mixture of rubbery and glassy states (*20*−*24*). The glassy state, which is much less flexible and open than the rubbery state, is believed to contain nanovoids serving as adsorption or condensation sites that are interspersed in a solid-phase dissolution matrix. The presence of these voids, or holes, is due to the inability of the matrix to achieve the thermodynamic fully relaxed state owing to the stiffness of its macromolecules. Kan et al. (*10*) explained irreversible sorption by proposing that the sorbate undergoes equilibrium partitioning to a set of "high-affinity sites" generated by "rearrangement" of NOM upon sorption. The nature of such sites remains unclear considering that the test sorbates were apolar compounds capable of only weak intermolecular interactions. Moreover, evidence for "rearrangement" was not given. Our study places hysteresis in NOM in the context of a molecular-scale mechanism established for macromolecular reference systems.

A diagram illustrating the pore deformation mechanism in glassy organic solids appears in Figure 1. On sorption, holes may be forced to expand by the thermal motion of incoming sorbate molecules, creating new internal surface area in the solid. Molecules may even force their way into holes initially too small to accommodate them. On desorption, a lag can exist between sorbate molecules leaving their

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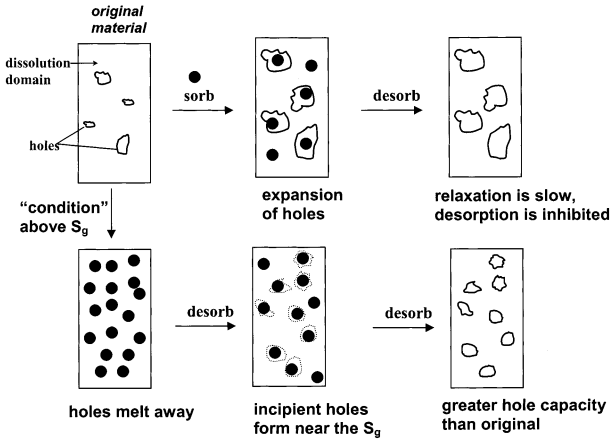

FIGURE 1. Conceptual diagram of the proposed mechanisms of isotherm nonsingularity and conditioning effect in natural organic matter based on glassy polymer theory. The glassy material initially contains holes interspersed in a solid-phase dissolution domain.

holes and relaxation of the surrounding matrix to its original state. This cycle results in irreversible sorption because sorption and desorption are occurring to/from different physical environments.

Glassy polymers also exhibit a related phenomenon known as the "conditioning effect", which has been demonstrated for vapor sorption of small hydrocarbon molecules (*16, 17*) (Figure 1). This refers to the effect on the isotherm brought about by infusing the sample with a sorbate at a concentration above the glass transition concentration of the sorbate, S_g, for that solid and then removing it. Conditioning first converts the sample to the rubbery state through the effect of plasticization and causes the holes to disappear. Then, as the conditioning agent is removed and S_g is approached from the high-concentration side, new holes are created in the solid. This leaves the conditioned sample with a greater hole capacity than the original sample. As a result, sorption on the conditioned sample is enhanced, and the isotherm in this case is more nonlinear than the original isotherm in the nonconditioned sample. Xia and Pignatello (*24*) observed a conditioning effect for trichloromethane (TCM) in a TCM-conditioned soil. If the mechanism is correct, the conditioning agent and test compound need not be the same.

We test this hypothesis here on two high organic matter soils. For the first soil, the same one used by Xia and Pignatello (*24*), we used dichloromethane (DCM) as the conditioning agent and TCM as the test compound. For a second soil, we used benzene (BZ) as the conditioning agent and chlorobenzene (CB) or 1,2,4-trichlorobenzene (TCB) as the test compound. The conditioning agents were selected for their volatility so they could be removed easily by sparging. Sorption isotherms for the original and the conditioned soils were compared. Pore deformation does not require high concentrations of a conditioning agent but occurs through action of the sorbing molecules themselves (Figure 1). We follow-up with sorption−desorption−resorption experiments linking the conditioning effect and hysteresis in the isotherm to a common mechanism.

Experimental Section

Materials. The two soils used are Pahokee peat (PP) and Mount Pleasant silt loam (MPSL). PP is a high-organic, highly humified reference soil from the International Humic Substances Society (*21*). MPSL is a forest soil collected near Mount Pleasant, NY, U.S.A. (*25, 26*). TCM (99.9%, HPLC Grade) and DCM (99.9%, GC Resolv) were from Fisher Scientific; BZ (99%), CB (99+%) and TCB (99+%) were from Aldrich Chemical Co. 1,3-Dibromopropane (98%) and 1,2-dichlorobezene (99%, HPLC Grade), both from Aldrich, were used as internal standards for gas chromatographic (GC) analyses. Information on the soils, test solutes, and conditioning agents is provided in Table 1. Water was distilled and passed through a Barnstead Nanopure system to remove ions and organic matter.

Conditioning Procedure. Conditioned PP was prepared by mixing 50 g of PP with 1 L of 10 g/L DCM in water. Conditioned MPSL was prepared by mixing 30 g of MPSL with 1 L of 1.75 g/L BZ in water. In both cases, a nonconditioned control sample was prepared at the same soil-to-water ratio and without the conditioning agent. In all subsequent steps, conditioned and nonconditioned samples were handled concurrently and, in every respect, identically to rule out artifacts due to physical handling. Note also that the conditioning agents were kept below their solubility limits while in contact with soils to eliminate potential artifacts due to solvent extraction of NOM components.

The suspensions were equilibrated with shaking on a platform circular orbital shaker at 50 revolutions per min (rpm) at 20 ± 2 °C for 6−7 days and then sparged with N_2 for 5−7 days. The solid and liquid phases were separated by centrifugation at 1800 rpm for 20 min in a swinging-bucket centrifuge. GC analyses indicated no detectable DCM or BZ in the supernatant of each respective conditioned soil. The wet soils were air-dried for 24 h; the resulting moisture contents (g water per g dry soil) were 0.46 for PP and 0.15 for MPSL. The air-dried, conditioned soils were examined for residual conditioning agent by hot methanol extraction (*27*) followed by GC analysis. Residual DCM was 0.9 mg/kg, and BZ was below the detection limit of 0.6 mg/kg.

Sorption Isotherms. Sorption was conducted in 12-mL glass screw-cap centrifuge vials with aluminum foil layered between the contents and the PTFE liner. The liquid phase was 0.005 M $CaCl_2$ with 200 mg/L NaN_3 to inhibit aerobic biodegradation. About 0.65 g of PP soil (for TCM), 0.9 g MPSL (for CB), or 0.1 g MPSL (for TCB) based on dry-weight was added, followed by enough liquid phase (approximately 11 mL) to almost eliminate the headspace. The water-to-soil ratios—about 18, 12, and 120 mL/g, respectively, for TCM, CB, and TCB systems—were adjusted to achieve 30−70% of total solute sorbed. Each experiment included three series of vials as follows: Series 1: conditioned soil; Series 2: nonconditioned soil; and Series 3: liquid phase without soil as controls. Each series comprised 22−36 samples.

After 24 h of soil prewetting time, the sorbate was added in methanol carrier to each vial except those with high concentrations near the water solubility, S_w, for which neat liquid sorbate was added. To eliminate cosolvent effects, methanol concentration was identical in all vials of a given experiment and was kept below a mole fraction of 0.001. The vials were shaken on an orbital shaker at 50 rpm at 20 ± 2 °C for 7 days in the dark. Preliminary tests indicated that 7 days was sufficient to reach apparent equilibrium. As an example, TCM-PP sorption−desorption kinetics are presented in Figure 2. See also ref *24*.

After equilibration, the vials were centrifuged at 1800 rpm for 20 min. An aliquot of 0.5−5 mL of the supernatant liquid was extracted with hexanes containing 2.5 mg/L of 1,3-dibromopropane (for TCM and TCB analyses) or 25 mg/L 1,2-dichlorobenzene (for CB analysis). TCM and TCB were analyzed by GC/ECD on a DB-624 capillary column; CB was analyzed by GC/FID on a DB-5 capillary column (both columns from J&W Scientific, Folsom, CA). Sorbed concentrations were calculated by mass difference. Series 3 samples were used to construct calibration curves over the same test concentration range.

Memory of the Conditioning Effect. This experiment was designed to determine the time scale of sorbent relaxation.

TABLE 1. Characteristics of Soils and Sorbates

expt	materials		abbr	particle distribution	% organic carbon	S_w[a] (mg/L)
#1	soil	Pahokee Peat	PP	<2 mm	44.6	
	conditioning agent	dichloromethane	DCM			19400
	sorbate	trichloromethane	TCM			7700
#2	soil	Mount Pleasant silt loam	MPSL	<2 mm; 24% clay, 5% sand, 71% silt	4.5	
	conditioning agent	benzene	BZ			1800
2−1	sorbate 1	chlorobenzene	CB			503
2−2	sorbate 2	1,2,4-trichlorobenzene	TCB			35

[a] Solubility in water from ref *28*.

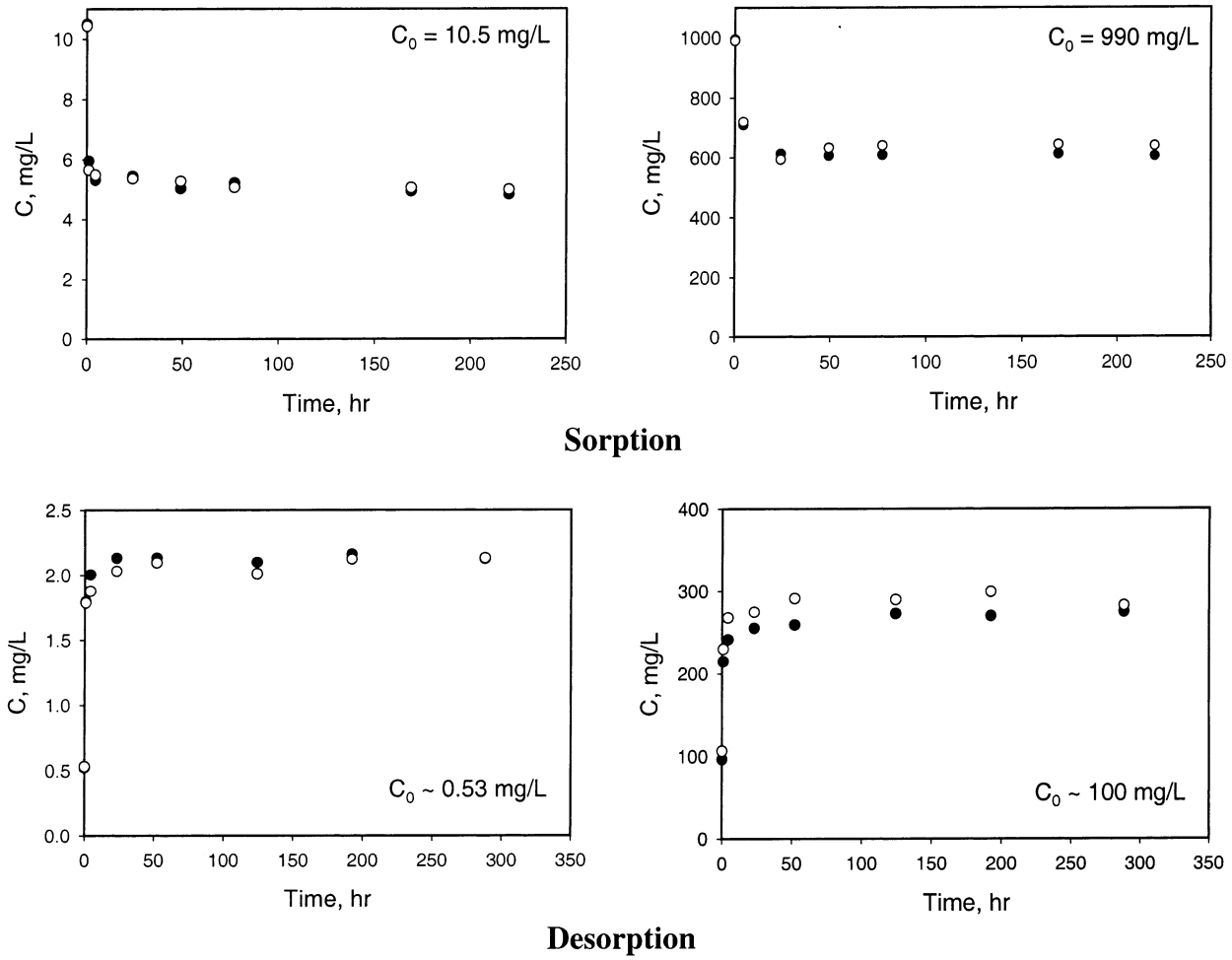

FIGURE 2. Rates of trichloromethane sorption and desorption to Pahokee Peat soil at low and high initial trichloromethane concentrations (C_0). Open and closed symbols represent duplicate runs. Water-to-soil ratios, ~12.2 mL/g. For desorption, there is a finite initial concentration at time zero due to residual supernatant from the sorption step.

PP soil was conditioned with DCM in the same manner as described above. A 6-day sparging period was used, and the soil was air-dried to a moisture content of 0.40 g water per g soil. Conditioned and nonconditioned soils were weighed into 12-mL vials and stored for various times at 21 °C in either the same air-dry condition (hereafter, "moist soil") or in a water-saturated condition (11 mL of liquid-phase added). All the vials were gastight capped so that the water contents of the air-dry soil samples were maintained over a long period of time. Prior to spiking the vials with TCM to determine equilibrium sorption, the vials containing the moist soils were charged with 11 mL of liquid phase (defined as above) and allowed to stand for 4 h. The initial test solute concentration used was 6.0 mg/L. Duplicate samples were analyzed. Samples of conditioned and nonconditioned soil were aged sealed in their vials for up to 90 days at 21 °C. To determine thermal effects sealed vials were heated overnight at 100 °C in a water bath and cooled at room temperature for 4 days before the test solute was added.

Sorption−Desorption−Resorption. An experiment comprising a three-step cycle (sorption−desorption−resorption) for a TCM-PP system was conducted in support of the hypothesis. Each step had a 7-day equilibration period. The method of sorption was the same as described in Sorption Isotherms except a water-to-soil ratio of 12.5 was used (0.9 g of PP and 11.3 mL of liquid phase). Five initial TCM concentrations were set up with five replicates at each concentration. After the first sorption period, desorption was achieved by withdrawing 80% of the supernatant and replenishing the samples with fresh liquid phase. After desorption equilibration, more sorbate was added to the mixture to effect resorption, targeting an equilibrium aqueous

phase concentration close to that in the initial sorption step.

Data Analysis. Sorption isotherms were fit to the simple Dual-Mode Model (DMM), which includes solid-phase dissolution (partitioning) described by a linear term and hole-filling described by a Langmuir term. The DMM is given by

$$q = K_D \cdot C + \frac{S^0 \cdot b \cdot C}{1 + b \cdot C} \quad (1)$$

where q [mg/kg] is the equilibrium sorbed concentration, C [mg/L] is the equilibrium solution phase concentration, K_D [L/kg] is the dissolution domain partition coefficient, and S^0 [mg/kg] and b [L/mg] are the capacity and affinity coefficient, respectively, of the hole-filling domain.

The isotherms were also fit to the Freundlich model to obtain information on the degree of nonlinearity. The Freundlich model is given by

$$q = K_F \cdot C^n \quad (2)$$

where K_F [(mg/kg)/(mg/L)^n] is the affinity coefficient and n is an exponential coefficient.

Results and Discussion

Sorption Isotherms and the Conditioning Effect. The isotherms spanning 3 to 4 powers of 10 in concentration are plotted on a log−log scale in Figure 3. The Freundlich model and DMM fitting parameters are listed in Table 2. Included for completeness in Table 2 are the corresponding isotherm parameters for TCM sorption on PP soil using TCM as the conditioning agent from Xia and Pignatello (*24*). Both models give good fits to individual isotherms (compare SEE), but the DMM captures the curved shapes. Only the DMM fits are shown in Figure 3.

The conditioning effect was found to be significant in all three sorbate-soil systems. This is supported by the following. (i) The isotherm in each conditioned soil is clearly shifted upward of the isotherm in the respective nonconditioned soil. (ii) Conditioning enhances nonlinearity. The Freundlich n may be used as an index of nonlinearity (decreasing with increasing nonlinearity). By this index, the isotherm in each conditioned soil is more nonlinear (Table 2). (iii) From inspection of eq 1 it can be seen that $S^0 \cdot b/K_D$ represents the intrinsic affinity of solute for the hole-filling domain relative to the dissolution domain in the limit of infinite dilution. The ratio $S^0 \cdot b/K_D$ increases upon conditioning (Table 2)—from 1.07 to 2.28 for TCM-PP (conditioning agent, DCM); from 1.25 to 1.55 for TCM-PP (TCM); from 1.12 to 1.57 for CB-MPSL (BZ); and from 1.85 to 2.28 for TCB-MPSL (BZ). These increases are highly significant in the case of PP systems (>99.9% confidence level for both conditioning agents) but much less so in the case of MPSL systems (82% and 75% for CB and TCB, respectively). It can also be seen that the increases are attributable mainly to changes in $S^0 \cdot b$ rather than changes in K_D. Worth mentioning too is that, since the hole domain is the locus of nonlinear behavior, $S^0 \cdot b/K_D$ constitutes another index of nonlinearity (increasing with nonlinearity), again, showing enhanced nonlinearity with conditioning.

Taken together, these results are consistent with expansion of the hole domain upon conditioning. It is noteworthy that for TCM sorption to PP a conditioning effect is observed regardless of whether the conditioning agent was the same compound or a different one (DCM).

The isotherms are replotted in Figure 4 as the soil-to-water distribution ratio

$$K_d = q/C \quad (3)$$

versus reduced solute concentration (C/S_w), where S_w is the saturated water solubility. Note that K_d is concentration dependent. Included (Figure 4b) are the isotherms corresponding to TCM in PP soil with TCM as the conditioning agent, as replotted from ref *24*. Except for CB on MPSL soil,

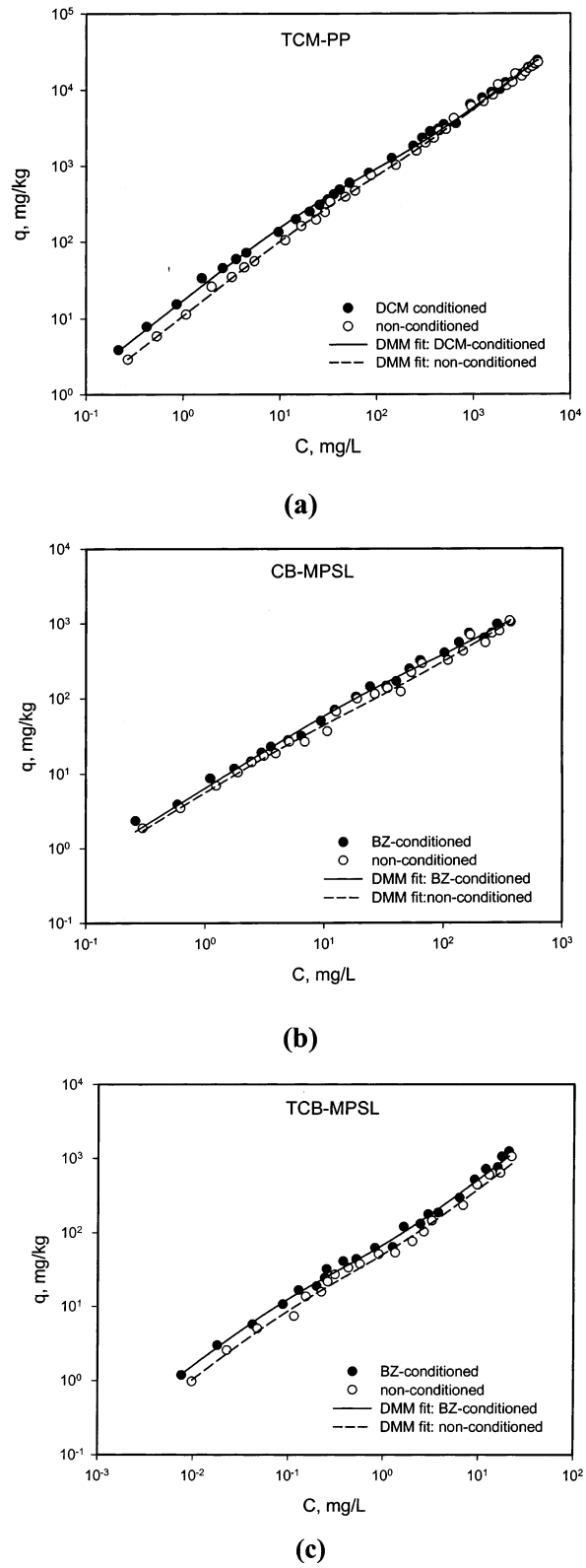

FIGURE 3. Comparison of sorption isotherms in conditioned and nonconditioned soils: (a) TCM in DCM-conditioned and nonconditioned PP; (b) CB in BZ-conditioned and nonconditioned MPSL; and (c) TCB in BZ-conditioned and nonconditioned MPSL. Curves are Dual-Mode Model fits. Abbreviations in Table 1.

TABLE 2. Freundlich Model and Dual-Mode Model Parameters for Sorption of TCM on PP, CB on MPSL, and TCB on MPSL[a]

sorbate on sorbent		Freundlich			Dual-Mode Model					
		K_F	n	SEE*[b]	S°, mg/kg	b, L/mg	K_D, L/kg	SEE*[b]	$(S^0 \cdot b)$, L/kg	$(S^0 \cdot b)/K_D$
TCM on PP	DCM-cond	18.5 ± 0.6[c]	0.847 ± 0.006[c]	0.101	585 ± 86	0.021 ± 0.004[c]	5.31 ± 0.15[c]	0.089	12.1 ± 2.7[c]	2.28 ± 0.52[c]
	noncond	11.4 ± 0.4	0.905 ± 0.005	0.093	359 ± 83	0.016 ± 0.004	5.24 ± 0.14	0.084	5.64 ± 1.93	1.07 ± 0.37
TCM on PP[d]	TCM-cond	29.7 ± 0.4	0.893 ± 0.003	0.091	580± 110	0.033 ± 0.007	12.4 ± 0.3	0.127	19.2 ± 5.3	1.55 ± 0.43
	noncond	17.1 ± 0.2	0.933 ± 0.002	0.111	21.9 ± 2.8	0.60 ± 0.08	10.5 ± 0.1	0.075	13.1 ± 2.7	1.25 ± 0.26
CB on MPSL	BZ-cond	7.2 ± 0.3	0.861 ± 0.012	0.123	191 ± 102	0.021 ± 0.010	2.53 ± 0.40	0.134	3.98 ± 2.90	1.57 ± 1.17
	noncond	5.7 ± 0.3	0.876 ± 0.016	0.158	36 ± 20	0.086 ± 0.053	2.75 ± 0.23	0.165	3.08 ± 2.57	1.12 ± 0.94
TCB on MPSL	BZ-cond	74 ± 3	0.829 ± 0.017	0.174	22.3 ± 5.8	5.1 ± 1.7	49.9 ± 2.8	0.133	114 ± 49	2.28 ± 0.98
	noncond	54 ± 2	0.843 ± 0.021	0.197	17.3 ± 7.0	4.0 ± 2.0	37.0 ± 3.1	0.168	68.7 ± 47.5	1.85 ± 1.21

[a] Obtained by weighted ($w = 1/q^2$) nonlinear regression. Abbreviations are in Table 1. [b] Standard error of estimates, which is the square root of the average weighted squared error from the regression line. [c] Standard deviations. Standard deviations of $(S^0 \cdot b)$ and $(S^0 \cdot b)/K_D$ are estimated from those of S^0, b, and K_D. [d] From ref *24*. The parameters for the nonconditioned soil differ from those in ref *24* because only data in the same concentration range as that of the TCM-conditioned soil was used in the regression here.

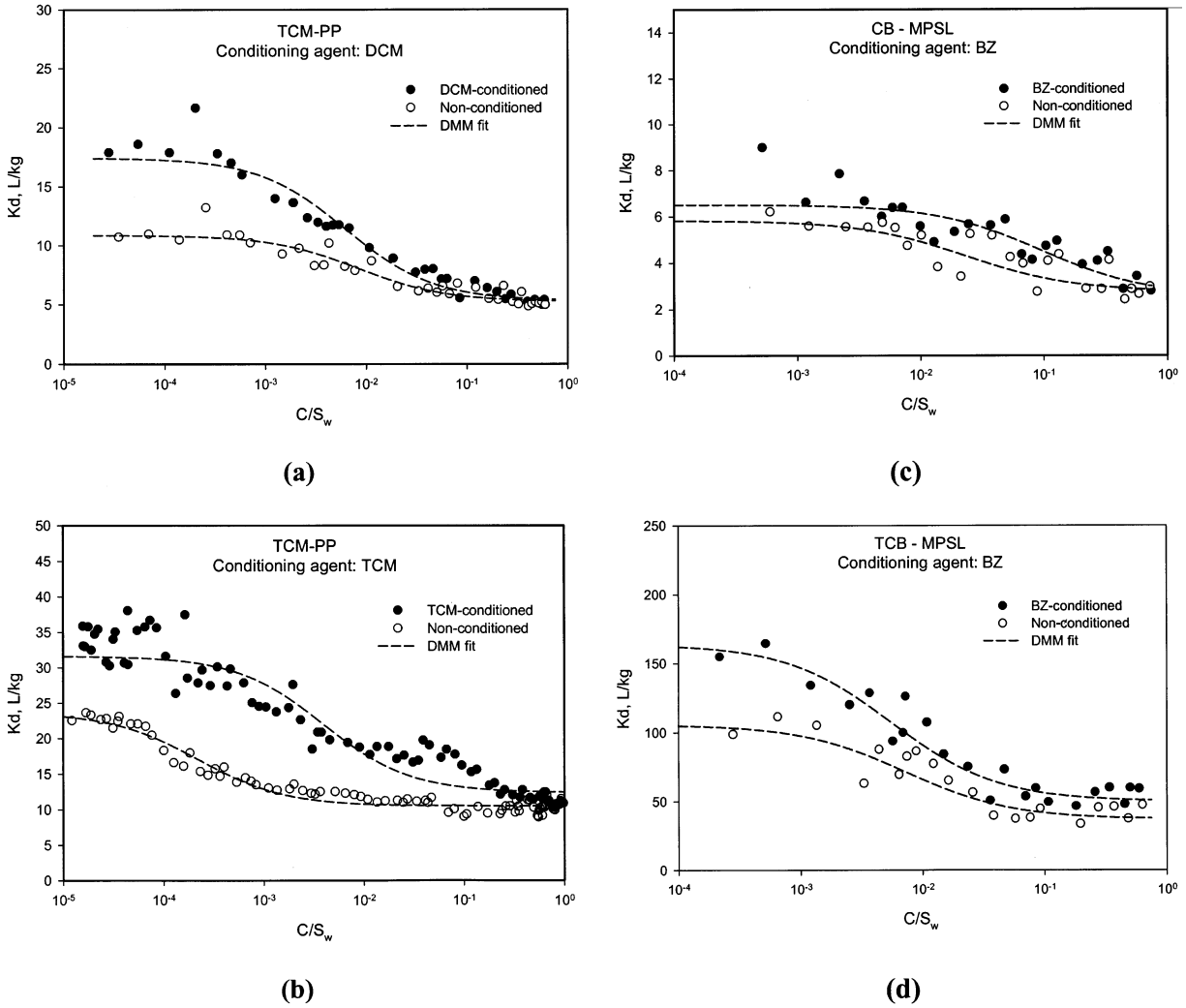

FIGURE 4. Comparison of apparent soil-to-water distribution ratios (K_d) for sorption in conditioned and nonconditioned soils: (a) TCM-PP (DCM conditioned); (b) TCM-PP (TCM conditioned, Xia and Pignatello (*24*)) (c) CB-MPSL; and (d) TCB-MPSL. Dashed lines represent Dual-Mode Model fits. For TCM-PP (TCM conditioned), only those data in the same solute concentration range as TCM-PP (DCM conditioned) were included in the model fit. The discrepancy of K_d values between the isotherm in nonconditioned PP in part a and in part b is most likely due to the use of different PP batches by different investigators. Abbreviations in Table 1.

where a higher degree of scatter in the data clouds interpretation, K_d approaches a constant at very low solute concentration and a second, smaller constant as solute concentration approaches S_w. Such a trend is implied by the DMM—that is, at low concentrations, the solute preferentially sorbs in the higher affinity hole-filling domain, while at high concentrations (e.g., approaching S_w), sorption in the lower affinity partition domain becomes dominant. In general, $K_{d,cond}$ (K_d for conditioned soil) is greater than $K_{d,noncond}$ (K_d for nonconditioned soil). The difference between $K_{d,cond}$ and $K_{d,noncond}$ is maximal at low to intermediate solute concentrations but tends to vanish as the solute concentration approaches S_w. This is consistent with the mechanism behind the DMM, because with increasing concentration holes

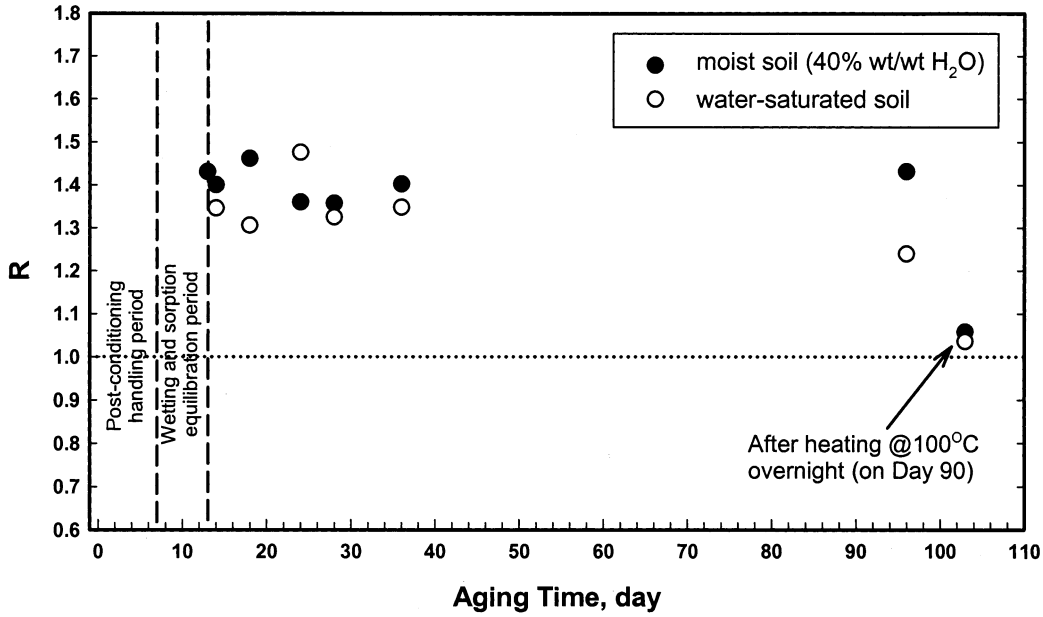

FIGURE 5. Conditioning effect of trichloromethane sorption in Pahokee Peat soil as a function of aging time. *R* is defined in eq 4. Each datum represents the average of duplicates. The errors of K_d and *R* average ±3.0% and ±6.3%, respectively. Aging time for each datum starts 1 day after sparging commenced and ends at termination of sorption. Aging time includes 7 out of 8 days total of the post-conditioning handling period, followed by a 0.125−0.167-day wetting period with the liquid phase, followed by a 7-day sorption equilibration period. Aging time for the heated samples includes, in addition, a 0.71-day heating time followed by a 4-day cooling time. The post-conditioning handling period (from day −1 to day 7) includes N_2 sparging (6 days) followed by soil separation and air-drying (2 days).

become filled and then eventually may disappear as sorbent plasticization occurs. Also discernible is that different conditioning agents show different conditioning effects—for example, DCM and TCM yield greater conditioning effects than BZ. Although it is possible that this is due to different pore deformation or plasticization abilities, it should be noted that benzene was used in a different soil than the chlorinated methanes.

Since residues of DCM were present in PP during sorption of TCM [see Experimental Section], an alternative explanation for $K_{d,cond}$ being greater than $K_{d,noncond}$ might be that the conditioning agent increases the hydrophobic character of the sorbent by providing a partitioning phase, such as a surface coating, or a condensate, in a small pore. Such an effect due to a small concentration of conditioning agent ought to be greatest at low test solute concentration and vanish at high. This explanation can be ruled out: since the test solute should be equally—if not more—effective than the conditioning agent at providing a hydrophobic coating or phase for itself, this explanation requires that the test solute in the nonconditioned soil exhibit a "concave up" isotherm (i.e., $n > 1$). Such an isotherm shape has never appeared in our studies and is only rarely found in other studies.

Memory of the Conditioning Effect. Decay of the conditioning effect over time was monitored by measuring the ratio *R* of distribution coefficients at a selected test solute concentration

$$R = \left.\frac{K_{d,cond}}{K_{d,noncond}}\right|_C \tag{4}$$

The system of choice for this experiment was TCM in DCM-conditioned PP, because, from Figure 4, it appeared to give the greatest conditioning effect among the systems tested. The equilibrium concentration *C* ended up being about 3.5 mg/L for the conditioned soil and 3.9 mg/L for the nonconditioned soils, which lie within the range giving the greatest conditioning effect. Although *C* for each member of the pair were slightly different, K_d values are not very sensitive to small changes in *C* (estimated < 3% in this case), and *R* even less so. Aging time was deemed to start 24 h after the beginning of N_2 sparging (at which point most of the conditioning agent had been removed) and to end when the TCM sorption period was over; while somewhat arbitrary, any reasonable definition of aging time would lead to the same conclusions presented below.

The evolution of *R* with time is shown in Figure 5. The memory of the conditioning effect remained strong and practically constant for at least 96 days at 21 °C. There was no significant difference in *R* between moist (40 wt %/wt H_2O) and water-saturated soils during the first 36 days (*R*, as mean ± standard deviation, are 1.40 ± 0.04 and 1.36 ± 0.07, respectively). At 96 days, *R* for the moist soil at 1.43 was still unchanged, while *R* for the water-saturated soil decreased to 1.24. The latter is slightly outside one-standard-deviation of the mean of the values for the first 36 days and may indicate that water-saturation accelerates matrix relaxation relative to a moisture content of 40%. However, the effect of water absence would have been more appropriately assessed using a dryer sample. In any case, the results suggest that pore deformation is highly irreversible and that matrix relaxation upon desorption could be a very slow process at 21 °C or below.

If a pore deformation mechanism is correct, elevated temperature is expected to reduce the memory of the conditioning effect by accelerating matrix relaxation. To test this, samples of conditioned and nonconditioned soil that had been aged for 90 days at 21 °C were heated overnight at 100 °C and allowed to rest at room temperature for 4 days before starting sorption. As shown in Figure 5, the conditioning effect was largely eliminated in both the moist and water-saturated soils after heating (*R* decreased to 1.06 and 1.04, respectively).

Like *R*, $K_{d,cond}$ and $K_{d,noncond}$ were substantially unchanged during 96 days at 21 °C (see Table 3, trend-line equations). The largest coefficient of time—but still small—corresponded

TABLE 3. Trends in Measured Distribution Coefficients (K_d) during Aging

PP soil samples	trend-line eq K_d = *a t (in days)* + *b*	mean K_d (over 96 d) for samples at 21 °C, L/kg	K_d for heated samples, L/kg
moist, cond	$K_d = 0.0096t + 14.4$ $r^2 = 0.119$	14.7 ± 0.8^a	11.6 ± 0.5^b
moist, noncond	$K_d = 0.0052t + 10.3$ $r^2 = 0.106$	10.5 ± 0.5	11.0 ± 0.2
water-saturated, cond	$K_d = -0.0163t + 14.9$ $r^2 = 0.245$	14.4 ± 1.0	12.0 ± 0.5
water-saturated, noncond	$K_d = (-5 \times 10^{-05})t + 10.7$ $r^2 = 0.00005$	10.7 ± 0.4	11.6 ± 0.1

[a] Standard deviation. [b] Estimated error defined as 1/2 the difference between duplicates.

to the water-saturated conditioned soil. Compared to the 96-day mean values for respective samples kept at 21 °C, $K_{d,cond}$ declined appreciably with heating, while $K_{d,noncond}$ increased slightly with heating. The net result is a decline in R to a value near 1, indicating almost complete loss of the conditioning effect. This indicates the conditioned soil reverts to a state close to the nonconditioned soil. The positive change in $K_{d,noncond}$ by heating at 100 °C is in the direction predicted by assuming that a "thermal conditioning effect", proceeding by a mechanism analogous to the chemical conditioning effect, is operative. If so, the thermal effect at 100 °C is weaker than the chemical effect at 21 °C. Humic and fulvic acids are reported to have glass transition temperatures below 100 °C (*29*); however, it is not known where the glass transition temperature (temperatures or temperature range) of these soils lie. Glass transitions are difficult to detect in whole soils; for example, we were unsuccessful with PP using scanning calorimetry (*21*). Studies to establish the effect of preconditioning temperature on K_d in the absence of chemical conditioning are clearly warranted.

Linking the Conditioning Effect and Hysteresis (Enhanced Resorption). We suggested that the conditioning effect observed in soil is a result of irreversible expansion of pores in glassy domains of NOM induced by the conditioning agent and further suggested that sorption−desorption hysteresis in NOM may, by analogy, be attributed to the same mechanism, wherein deformation is caused by the test sorbate molecules themselves during sorption. (This is evident from Figure 1, top row). Hence, we hypothesized that if we observe sorption−desorption hysteresis, and then by adding more chemical to the desorbed sample attempt to bring the solution phase concentration back to the initial point on the sorption branch, we should see enhanced sorption compared to the initial sorption, as a result of the expanded glassy hole domain yet to relax. Accordingly a sorption−desorption−resorption cycle was carried out to demonstrate this link between conditioning and hysteresis. In this experiment, we ruled out artifacts due to diffusive nonequilibrium [TCM sorption and desorption appear to cease within 2 days (Figure 1) and 7 and 21 day sorption isotherms were identical (*24*)]; degradation [TCM is chemically stable under the conditions and biotransformation was inhibited with NaN_3]; and the colloids effect [TCM affinity for particles is too low ($K_d \sim 10^1$) for this to be significant at ordinary colloid concentrations].

To accomplish this objective the sorption isotherm of TCM in PP was reconstructed over the concentration range 2−1300 mg/L using a 7-day equilibration period (Figure 6). Single-step, 7-day desorptions subsequently performed on samples corresponding to select points along the sorption branch reveal hysteresis extending over the entire concentration range. The K_d values of the desorption points are 30−40% above those expected based on the initial sorption branch. Recharging each of the desorbed samples with additional TCM for 7 days indeed resulted in enhanced sorption compared to the corresponding initial sorption at approximately the same solution phase concentration C. This result was observed over the entire concentration range examined. The K_d values corresponding to the resorption points are 15−20% greater than those corresponding to the initial sorption branch. The results validate the hypothesis put forth above based on the pore deformation mechanism. The extents of hysteresis and the conditioning effect are not necessarily quantitatively comparable, as the matrix may experience different degrees of deformation in the two cases.

Implications. In glassy polymers (*16, 17*) the conditioning effect originates from irreversible expansion and creation of holes in the matrix. It leads to an upward shift and increased curvature of the isotherm of a test compound in the conditioned sorbent. In this study we find analogous effects in NOM created by preloading the solid with a high concentration of a "conditioning agent", either the same or a related compound. (i) Conditioning is accompanied by enhanced sorption and a decrease in the Freundlich exponent parameter, indicating a decrease in linearity. (ii) The conditioning effect is greater at low concentration, while tending to diminish at high concentration as the solute approaches its water solubility and holes become fully occupied or melted away by plasticization. (iii) The DMM provides a good description of the isotherms for the soil-sorbate systems tested. Conditioning results in an increase in the intrinsic affinity of the solute for the hole domain ($S^0 \cdot b$) compared to that of the dissolution domain (K_D). (iv) The memory of the conditioning effect is nearly eliminated after the soil is heated. (v) Sorption−desorption hysteresis is accompanied by an enhanced resorption (following desorption).

Our results implicate pore deformation as a cause of the conditioning effect and sorption−desorption nonsingularity. Sorption is irreversible because sorption and desorption occur to/from different physical environments. It is not possible to explain the behaviors we observe in terms of sorption to a fixed-pore material. Carbonaceous materials are likely to be the only ones present in soils capable of having deformable pores, and the compounds of this study sorb predominantly to such materials. In the case of PP there is very little mineral material. It is also not possible to explain the conditioning effect and hysteresis by assuming only a solid-phase dissolution type of sorption. Hence, our findings offer support for the existence of glassy forms of soil organic matter. However, the possibility that other materials are present in soil that have a deformable pore structure cannot be ruled out.

The results further suggest that often-observed long desorption times of contaminants in soils, sediments, and aquifer solids may to some degree depend on matrix relaxation, apart from rate-limiting diffusion of the sorbate. When a system is suddenly displaced from stasis—for

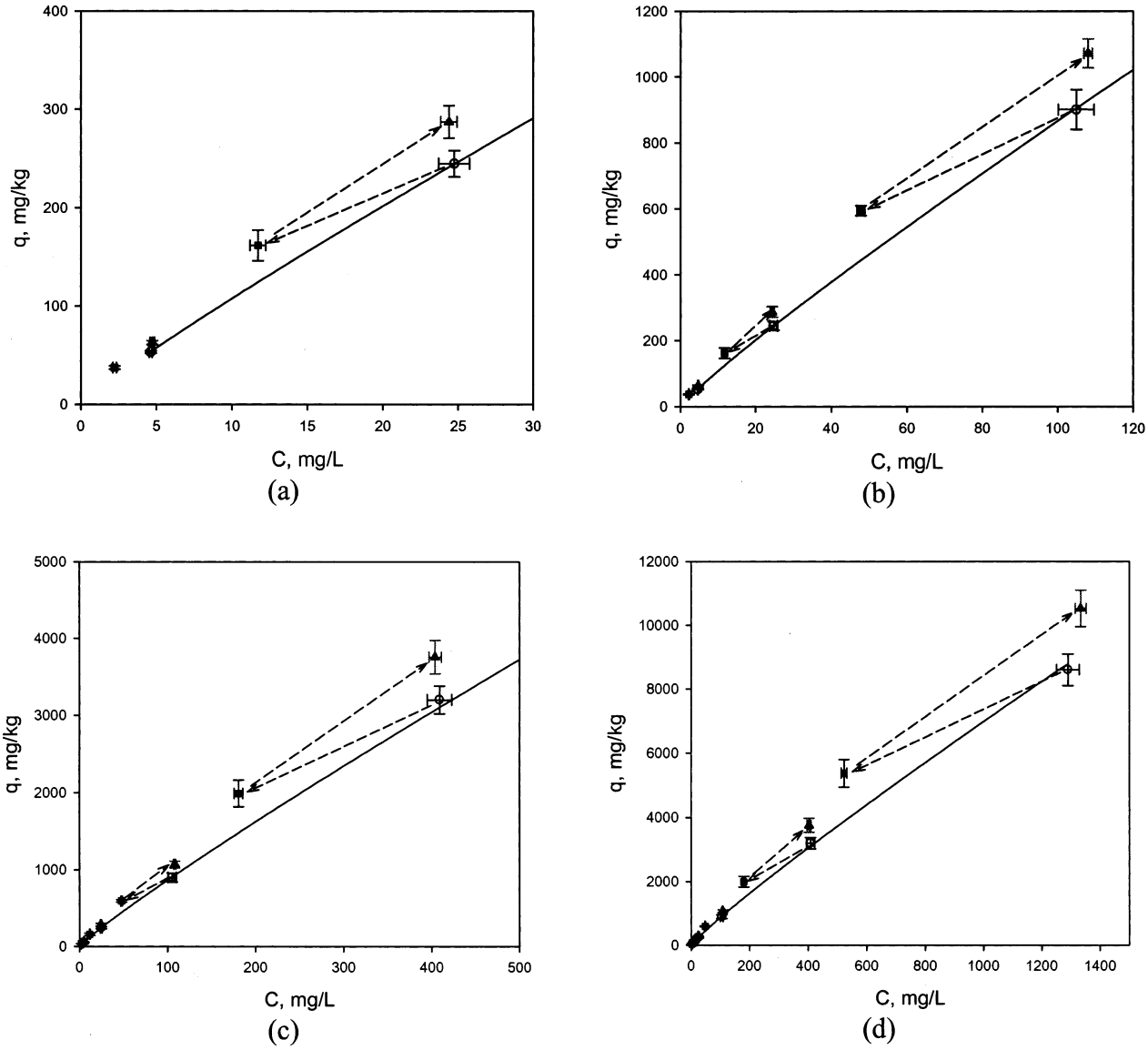

FIGURE 6. Trichloromethane sorption, desorption, and resorption in Pahokee Peat soil, demonstrating linkage of hysteresis and an enhanced resorption analogous to conditioning effect. Each graph represents a different concentration range. Error bars represent standard error of five replicates.

example, by dilution of the liquid phase—the re-equilibration time consists of the time needed for diffusion of the sorbate through the matrix and of the time needed for the matrix to relax to its original state, which may be even slower than the former. The aging experiment (Figure 5) implies that, when the sorbate is removed, matrix relaxation could be a very slow process at ordinary temperature. It is possible that desorption in such cases is rate-limited by physical changes in the sorbent, not by diffusion of the sorbate. In addition, sorbate molecules that have forced their way into pores initially smaller than their own thermal volume may become immobilized there until conformational changes in the matrix occur at some future time. From the standpoints of bioavailability and environmental fate and transport, a process that affects a significant percentage of sorbed contaminant (upward of 10%) cannot be ignored.

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