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# Temperature Dependence of Slow Adsorption and Desorption Kinetics of Organic Compounds in Sediments

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The purpose of the present study was to determine the temperature dependence of slow adsorption and desorption kinetics of some chlorobenzenes, polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs) in a lab-contaminated and a field-contaminated sediment. The kinetics of desorption were measured by means of a technique in which Tenax TA beads are used as "sink" for desorbed solute. A first-order kinetic model with three sediment compartments described the desorption of the test compounds from the sediments. Apart from a rapidly desorbing fraction, two sediment fractions were distinguished, one slowly desorbing with a rate constant of  $(1-4) \times 10^{-3} \text{ h}^{-1}$  and a very slowly desorbing one with rate constants approximately 10-50 times smaller. From temperature dependence studies, the activation enthalpies for slow desorption appeared to be 60-70 kJ mol<sup>-1</sup> for both the lab-contaminated and the field-contaminated sediments; the values were approximately constant for all compounds studied. From adsorption studies at two temperatures, enthalpies of sorption to the slow sediment compartment appeared to be slightly negative. Because slow desorption is much faster at elevated temperatures, the measurement of high-temperature desorption kinetics can provide information on long-term desorption kinetics and, probably, on the feasibility of bioremediation of aged contaminants.

## Introduction

A sometimes significant fraction of organic chemicals sorbed to soils and sediments is released slowly (months-years), whereas another part is released relatively rapidly (hours-days) (1-3). The existence of such slowly desorbing fractions can result in aqueous concentrations in (pore)water being lower than expected on the basis of short-term partition coefficients. These kinetic limitations and shifting partitioning may have consequences for many processes. For example, contaminant fluxes from contaminated sediment to ground-water and surface water are lower than expected from short-term partition coefficients. Also, amounts of chemical available for uptake by biota are lower, resulting in both lower bioaccumulation and biodegradation (2).

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Retarded diffusion is usually suggested to explain slow desorption. This retarded diffusion occurs either through the organic matter matrix or through and along the walls of narrow intraparticle pores, possibly with a hydrophobic wall coating (1). Brusseau et al. (4, 5) explained their findings on the basis of intra-organic matter diffusion. Ball and Roberts (6) as well as Wu and Gschwend (7) developed a pore diffusion model to describe their data. Steinberg et al. (8) suggested the entrapment in narrow pores in combination with slow pore diffusion.

Diffusion is an activated process, and therefore it is positively temperature-dependent in an Arrhenius-like way, as has been shown for the diffusion of several organic chemicals through polymer materials (9, 10). If retarded diffusion causes (de)sorptive rate limitations, an Arrhenius-like temperature dependence would also be expected for the rate constants of slow adsorption and desorption. By measuring the magnitude of the activation energy of slow adsorption and desorption, indications on the relative importance of organic matter diffusion [which can probably be regarded as polymer diffusion (11, 12)] and micropore diffusion to these processes may be obtained. Activation energies for the diffusion through polymer materials are typically above 60 kJ mol<sup>-1</sup> (11, 13), whereas they are mostly lower (approximately 20-40 kJ mol<sup>-1</sup>) for diffusion through liquids (11) and through the interior of micropores (14-16). Rates of slow desorption from sediments have been observed to increase strongly with increasing temperature; reported activation enthalpies are 66 (8), 46 (17), and -28 to +29 kJ mol<sup>-1</sup> (18).

In most studies on the slow desorption of organic contaminants from sediments, desorption experiments lasted less than 2 weeks, whereas field contamination may be a process with a time scale of years. Therefore, it is also important to know the kinetics of desorption on a longer time scale.

In the present study, slow adsorption and slow desorption have been investigated at various temperatures, with a 2-fold purpose: (i) to determine the enthalpy changes resulting from solute transfer into and out of the slowly exchanging sediment compartment via the determination of the activation enthalpies for slow adsorption and desorption and (ii) to determine the long-term desorption characteristics of lab-contaminated sediments as well as historically contaminated ones. These approaches will provide more insight into the character of the processes limiting contaminant exchange between sediment and water.

## Method

**Theoretical Model.** Desorption from sediment can be described by the following first-order model (4, 19, 20):

$$\frac{S_t}{S_0} = F_{\text{rap}} e^{-k_{\text{rap}} t} + F_{\text{slow}} e^{-k_{\text{slow}} t} \quad (1)$$

in which  $S_t$  and  $S_0$  (g) are the sediment-sorbed amounts at time  $t$  (h) and at the start of the experiment, respectively;  $F_{\text{rap}}$  and  $F_{\text{slow}}$  (-) are the fractions of contaminant present in the rapidly and slowly desorbing sediment compartment, respectively;  $k_{\text{rap}}$  and  $k_{\text{slow}}$  (h<sup>-1</sup>) are the rate constants of rapid and slow desorption, respectively.

$F_{\text{slow}}$  and  $k_{\text{slow}}$  were determined by exponential curve fitting ( $F_{\text{rap}}$  and  $k_{\text{rap}}$  were also fitted, but rapid desorption is not considered in the present study); the ln form of eq 1 was subjected to curve fitting. Fits were carried out by minimizing the squares of the differences between experimental and calculated values of  $\ln(S_t/S_0)$ .

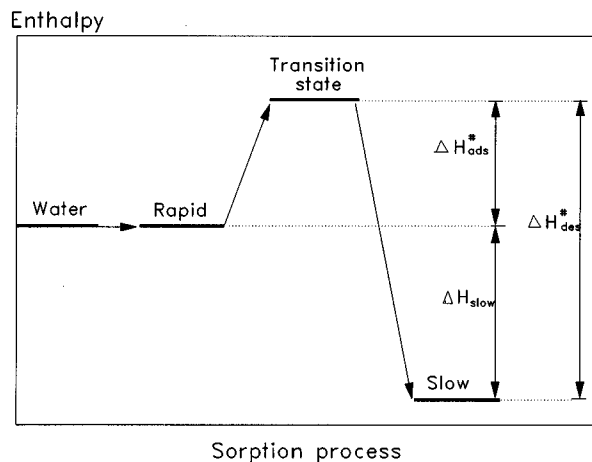


FIGURE 1. Enthalpy diagram for slow sorption.

**Enthalpies of Slow Adsorption and Desorption.** The enthalpy diagram for an organic compound going from water to the slowly exchanging sediment compartment is given in Figure 1. In Figure 1, the transfer from water to the rapidly exchanging sediment compartment is considered to be unactivated and thus not associated with a change in enthalpy, since short-term sorption enthalpies are approximately zero (13). The  $\Delta H_{\text{slow}}$  in Figure 1 represents the enthalpy difference between the rapid and the slow sediment compartments.  $\Delta H_{\text{des}}^{\ddagger}$  and  $\Delta H_{\text{ads}}^{\ddagger}$  are the activation enthalpies of slow desorption and adsorption, respectively.

Figure 1 shows that the relationship between equilibrium sorption enthalpies and the activation enthalpies for adsorption and desorption is

$$-\Delta H_{\text{slow}} = \Delta H_{\text{des}}^{\ddagger} - \Delta H_{\text{ads}}^{\ddagger} \quad (2)$$

where  $\Delta H_{\text{slow}}$  is defined in the "rapid" to "slow" direction. Assuming temperature-independent activation enthalpies and entropies, the following relationship between the activation enthalpy for slow desorption  $\Delta H_{\text{des}}^{\ddagger}$  and the rate constant  $k_{\text{slow}}$  is valid (21):

$$\ln k_{\text{slow}} = -\Delta H_{\text{des}}^{\ddagger}/RT + \text{constant} \quad (3)$$

in which  $k_{\text{slow}}$  is the rate constant of slow desorption. Thus, the activation enthalpy of slow desorption can be obtained via the slope of a plot of  $\ln k_{\text{slow}}$  vs  $1/T$ .

$\Delta H_{\text{slow}}$  can be calculated from the fractions desorbing rapidly and slowly after adsorption at different temperatures, with the integrated van't Hoff equation (see also refs 13, 18, and 22):

$$\Delta H_{\text{slow}} = -R \frac{\ln (K_{\text{SR},T_2}/K_{\text{SR},T_1})}{1/T_2 - 1/T_1} \quad (4)$$

where  $K_{\text{SR},T}$  is the ratio between the masses in the slow and the rapid fraction,  $(1 - F_{\text{rap}})/F_{\text{rap}}$ , respectively, after adsorption at temperature  $T$ .

**Materials.** 1,2,3,4-Tetrachlorobenzene (TeCB), pentachlorobenzene (QCB), hexachlorobenzene (HCB), 2,3,5,6-tetrachlorobiphenyl (PCB-65), 2,3',4,4',5-pentachlorobiphenyl (PCB-118), fluorene, anthracene, fluoranthene, and pyrene were obtained from various commercial sources. Tenax TA (60–80 mesh; 177–250  $\mu\text{m}$ ), a porous polymer based on 2,6-diphenyl-*p*-phenylene oxide, was obtained from Chrompack. Before use, the Tenax TA beads were rinsed with acetone (three times with 10 mL/g of Tenax) and hexane (three times with 10 mL/g of Tenax) and dried overnight at 75  $^{\circ}\text{C}$ .

The sediments were from Lake Oostvaardersplassen (OVP) and Lake Ketelmeer (KM), The Netherlands. The background

concentrations in the OVP sediment of the studied compounds proved to be <2% of the lab-added concentrations. The OVP sediment was dried (150  $^{\circ}\text{C}$ ; 5 days) in order to remove all possible volatile contaminants present, after which it was homogenized and dry-sieved. The 63–125- $\mu\text{m}$  fraction (organic carbon content (OC) 3.17%) was used in the experiments. The KM sediment (OC 7.02%) was historically contaminated with PCBs and chlorobenzenes (congener concentrations ranging from 45 to 319 ng/g). The compounds studied in the KM sediment were TeCB, HCB, 2,2',3,4',5-pentachlorobiphenyl (PCB-90), 2,2',4,4',5-pentachlorobiphenyl (PCB-99), 2,2',3,4,4',5-hexachlorobiphenyl (PCB-138), 2,2',4,4',5,5'-hexachlorobiphenyl (PCB-153), 2,3',4,4',5,5'-hexachlorobiphenyl (PCB-167), and 2,2',3,4,4',5,5'-heptachlorobiphenyl (PCB-180). A thick superficial layer was sampled (0–30 cm); this layer probably contained both aged and relatively recent contaminants. The wet KM sediment was passed through a 250- $\mu\text{m}$  sieve to remove all coarse particles and used without any further treatment in order to avoid disturbance of the sorption characteristics of the originally present contaminants.

**Temperature Dependence of Slow Adsorption.** Triplicate adsorption experiments were carried out with the OVP sediment. Prior to sorption studies, the OVP sediment was suspended in water and stored at 65  $^{\circ}\text{C}$  for 1 week, in order to reduce possible differences in structure between sediment portions incubated at different temperatures. The OVP sediment was loaded with the test compounds by suspending 0.6 g (dry weight) of the sediment in 250 mL of water spiked with 12.5  $\mu\text{L}$  of methanol containing the test compounds and 1.25 mg of  $\text{HgCl}_2$  to prevent microbial degradation. Suspensions were shaken for 34 days at both 20 and 65  $^{\circ}\text{C}$ . After 34 days, the sediment-solute system is probably not far from equilibrium, as indicated by Weber and Huang, who studied phenanthrene sorption to soils and sediments for reaction periods ranging from 1 min to 14 days (23).

For the determination of sediment-sorbed solute concentrations, sediment and supernatant water were separated by centrifugation at 2500 rpm for 20 min. The sorbed solutes were extracted by refluxing sediment with 50 mL of water and 60–70 mL of hexane for 6 h. The sediment-sorbed concentrations ranged from 0.1  $\mu\text{g g}^{-1}$  (PCB-118) to 20  $\mu\text{g g}^{-1}$  (TeCB). The supernatant water was analyzed by extracting 20 mL of water with 2 mL of hexane. The hexane was analyzed on GC-ECD for the chlorobenzenes and PCBs (Hewlett Packard 5890 with  $^{63}\text{Ni}$  ECD and HP 7673 autosampler; column: Chrompack, fused silica CP 8cb, length 50 m, diameter 0.25 mm; carrier gas: He, 1 mL/min). For PAH analysis, the hexane was evaporated until 1 mL and then dissolved in 10 mL of acetonitrile. The acetonitrile was subsequently evaporated to 1 mL and analyzed with HPLC-FCD (Hewlett Packard 1050 with fluorescence detector (FCD; HP 1046); column: reversed phase C<sub>18</sub>, Vydac 201TP54; gradient elution with acetonitrile and water).

The desorption kinetics of the OVP sediments loaded at 20 and 65  $^{\circ}\text{C}$  for 34 days were determined at 20  $^{\circ}\text{C}$  by means of the Tenax solid-phase extraction method described in a previous paper (20). Extraction with Tenax TA has been proved to be a very useful way of carrying out desorption kinetics experiments because of the high sorptive capacity (20, 24) and the very fast solute absorption from water to Tenax (20). Because of the rapid solute removal from the aqueous phase, backward re-adsorption during desorption is much slower than the slow desorption process (20); this is required for the validity of eq 1. During desorption, a mixture of Tenax TA (0.2 g), sediment (0.6 g), and Milli-Q water (100 mL) was constantly shaken in a 100-mL separation funnel. The Tenax was refreshed at set time intervals. Tenax was extracted with hexane; hexane was analyzed as described above.

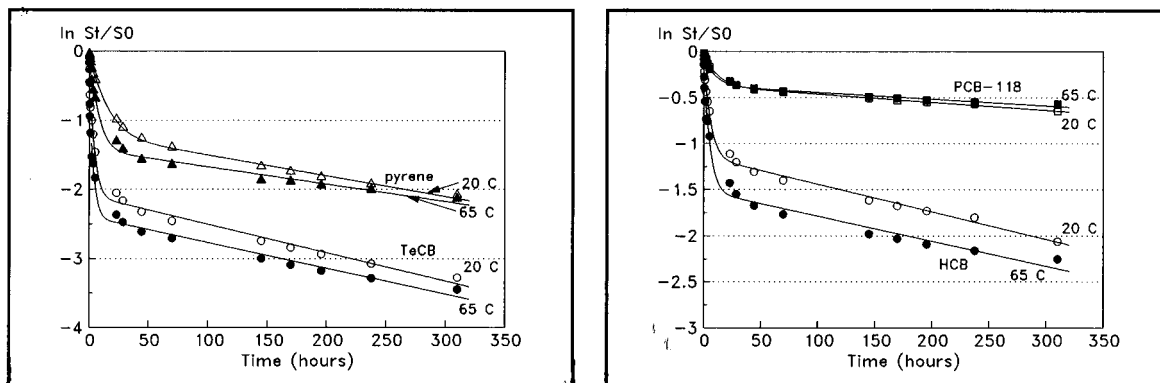


FIGURE 2. Desorption plots for OVP sediment equilibrated at 20 °C (open symbols) and 65 °C (solid symbols) for TeCB (circles), pyrene (triangles), HCB (circles), and PCB-118 (squares). Solid lines obtained by exponential curve fitting.

TABLE 1. Rapidly Desorbing Fractions and Rate Constants for Slow Desorption with 95% Confidence Intervals after Adsorption for 34 Days at 20 and 65 °C for OVP Sediment

compd	adsorption at 20 °C			adsorption at 65 °C			literature values	
	$K_p$ ( $10^3$ L/kg) <sup>a</sup>	$k_{slow}$ ( $10^{-3}$ h <sup>-1</sup> )	$F_{rap}$ (%)	$K_p$ ( $10^3$ L/kg) <sup>a</sup>	$k_{slow}$ ( $10^{-3}$ h <sup>-1</sup> )	$F_{rap}$ (%)	$k_{slow}$ ( $10^{-3}$ h <sup>-1</sup> )	$F_{rap}$ (%)
TeCB	0.54 ± 0.01	4.07 ± 0.18	87.1 ± 0.5	0.36 ± 0.04	3.99 ± 0.36	90.4 ± 0.7	1.9–6.5 (19), 19–170 (7)	83 <sup>b</sup> (19)
QCB	1.22 ± 0.04	2.96 ± 0.15	77.2 ± 0.7	0.70 ± 0.08	3.00 ± 0.47	83.7 ± 0.4	0.3–4.1 (19), 3.5–13 (37)	79–98 <sup>b</sup> (19), 22–29 <sup>c</sup> (37)
HCB	2.81 ± 0.10	3.03 ± 0.11	69.2 ± 1.7	1.61 ± 0.18	3.13 ± 0.61	76.8 ± 1.8	0–0.6 (19), 1.1–50 (37)	72–98 <sup>b</sup> (19), 11–35 <sup>c</sup> (37)
PCB-65	4.6 ± 0.5	1.72 ± 0.22	52 ± 3	4.0 ± 0.5	1.93 ± 0.54	62 ± 4		
PCB-118	6.6 ± 1.6	0.98 ± 0.08	34 ± 4	4.9 ± 1.3	0.97 ± 0.34	29.9 ± 1.3		
fluorene	0.39 ± 0.02	3.83 ± 0.26	91.1 ± 0.8	0.21 ± 0.04	4.08 ± 0.05	95.3 ± 1.0		
anthracene	1.78 ± 0.12	2.96 ± 0.22	76 ± 2	0.48 ± 0.06	2.62 ± 0.26	88 ± 4		
fluoranthene	4.56 ± 0.07	3.12 ± 0.28	60 ± 3	1.25 ± 0.16	2.98 ± 0.72	73.0 ± 2.0	$2 \times 10^{-4}$ (38)	
pyrene	6.3 ± 1.0	3.24 ± 0.17	64 ± 2	1.92 ± 0.22	2.74 ± 0.33	75.9 ± 0.4	6–31 (37), $2 \times 10^{-4}$ (38)	36–59 <sup>c</sup> (37)

<sup>a</sup> Not corrected for sorption to organic material in water. <sup>b</sup> Equilibration time 3–6 d. <sup>c</sup> Equilibration time 15–28 d.

After termination of desorption, the remaining sediment and supernatant water were refluxed with 60–70 mL of hexane for 6 h to extract and analyze all chlorobenzenes, PCBs, and PAHs still present in the sediment.

**Temperature Dependence of Slow Desorption.** OVP sediment (0.6 g) was loaded with the test compounds at 20 °C for 34 days, as described in the previous paragraph. The field-contaminated KM sediment (1–3 g dry weight) was used as such. The contaminated sediments were suspended in 100 mL of Milli-Q water. The desorption was studied as described in the previous paragraph.

The sediment was first desorbed at 20 °C for 24 h in order to remove the rapidly desorbing fraction. After this, desorption was continued at the three different desorption temperatures (5, 20, and 60 °C). All desorption experiments were carried out in triplicate. The 95% confidence intervals are presented along with all reported values. For parameters that had been determined directly from triplicate measurements, the calculation of the 95% confidence interval was based on the standard deviation in the triplicates; for parameters obtained by linear regression, the standard deviations in both the regression and in the triplicates are included in the 95% confidence intervals.

The mass balances (ratios between {total mass of solute desorbed and solute present after desorption} and the initial mass of solute) were 80–120% for the lab-contaminated OVP sediment and 70–110% for the field-contaminated KM sediment.

## Results

**Temperature Dependence of Slow Adsorption.** In Figure 2,  $\ln(S_t/S_0)$  vs time plots are given for the desorption at 20 °C

of TeCB, pyrene, HCB, and PCB-118 from OVP sediment equilibrated at 20 and 65 °C. Solid lines are obtained by exponential curve fitting to eq 1.

In Table 1, the rate constants of slow desorption and rapidly desorbing fractions are given for all nine compounds measured. Also, the partition coefficients ( $K_p$ ; L/kg) after 34 days of equilibration are presented.  $K_p$  is the ratio of  $c_s$  (the solute concentration in the sediment; g/kg) and  $c_w$  (the total solute concentration in the water; g/L). In Table 1, literature values for  $k_{rap}$  and rapid fractions are also given. Most  $k_{slow}$  values are reasonably in accordance with the ones presently found; the values of the rapid fractions show a higher degree of variation, probably because of different contact times used in different experiments. The rate constants of slow desorption after equilibration at 65 °C are not significantly different from those after equilibration at 20 °C ( $t$ -test at 95% confidence level). The fast fractions are larger after adsorption at 65 °C than after adsorption at 20 °C, by a factor of 1.4–2.3 (mean 1.8), PCB-118 excepted.

**Temperature Dependence of Slow Desorption.** In Figure 3,  $\ln(S_t/S_0)$  vs time plots are given for lab-contaminated OVP sediment (TeCB) and field-contaminated KM sediment (PCB-99 and PCB-180) at various desorption temperatures. Note that for the first 24 h of the experiments, desorption was carried out at 20 °C; after 24 h, different desorption temperatures were used. Also in Figure 3  $\ln(S_t/S_0)$  vs time is given for long-term desorption from OVP sediment (TeCB, QCB, HCB, PCB-65, and PCB-118) and KM sediment (PCB-90 and PCB-99) at 20 °C. The values for  $k_{slow}$  for nine compounds in OVP sediment and for eight compounds in KM sediment are given in Table 2. These rate constants for slow desorption increase strongly with increasing temperature.

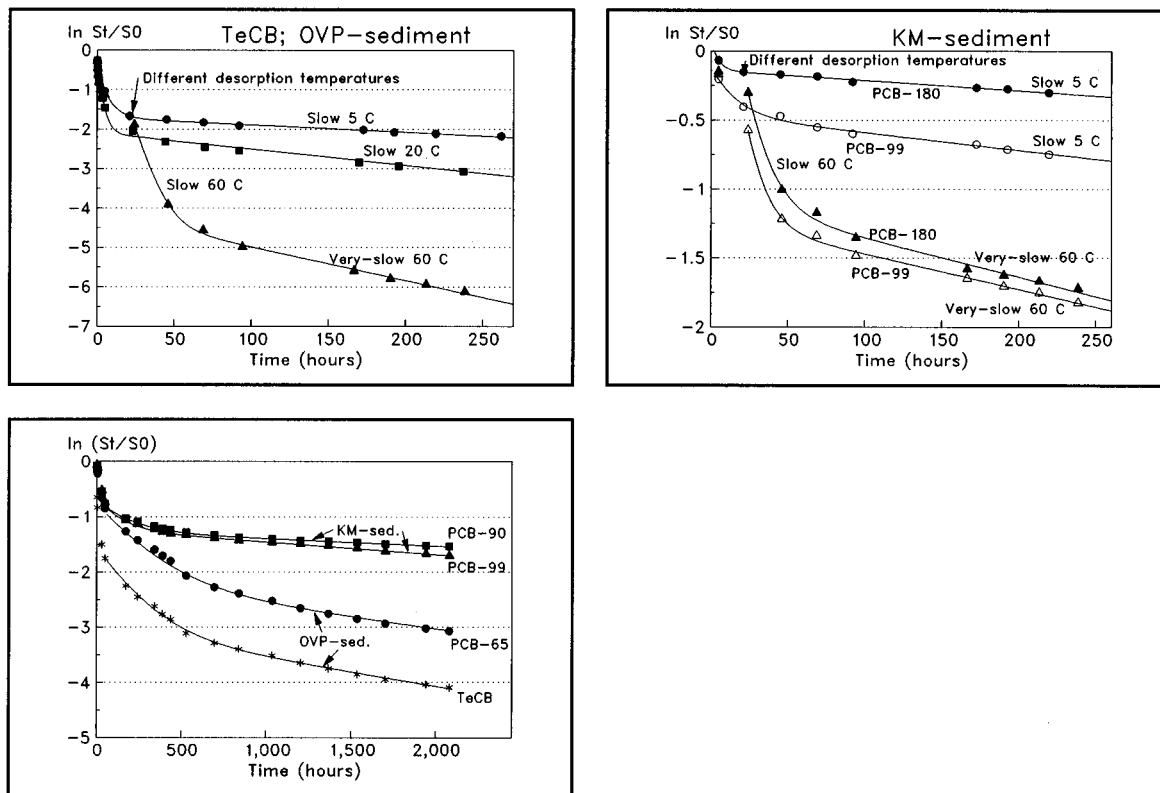


FIGURE 3. Desorption of TeCB from lab-contaminated OVP sediment at 5, 20, and 60 °C, and of PCB-99 and PCB-180 from field-contaminated KM sediment at 5 and 60 °C. Long-term desorption at 20 °C for TeCB, PCB-65 (OVP sediment), PCB-90, and PCB-99 (KM sediment). Solid lines obtained by exponential curve fitting; the parts of the curves representing slow and very slow desorption are indicated.

TABLE 2. Rate Constants of Slow Desorption ( $k_{slow}$ ,  $10^{-3} h^{-1}$ ) with Their 95% Confidence Intervals at 5, 20, and 60 °C for Lab-Contaminated OVP Sediment and Field-Contaminated KM Sediment

compd	OVP sediment (lab-contaminated)			KM sediment (field-contaminated)		
	5 °C	20 °C	60 °C	compd	5 °C	60 °C
TeCB	1.82 ± 0.04	4.07 ± 0.18	118 ± 2	TeCB	0.96 ± 0.10	55 ± 21
QCB	1.49 ± 0.06	2.96 ± 0.15	116 ± 3	HCB	0.37 ± 0.10	56 ± 6
HCB	1.60 ± 0.10	3.03 ± 0.11	122 ± 2	PCB-90	0.90 ± 0.08	87 ± 4
PCB-65	0.99 ± 0.04	1.72 ± 0.22	112.0 ± 0.6	PCB-99	1.31 ± 0.09	95 ± 2
PCB-118	0.63 ± 0.04	0.98 ± 0.08	93 ± 9	PCB-153	1.07 ± 0.16	84 ± 10
fluorene	1.7 ± 0.3	3.83 ± 0.26	184 ± 20	PCB-138	1.09 ± 0.15	80.1 ± 1.4
anthracene	1.3 ± 0.2	2.96 ± 0.22	170 ± 10	PCB-167	0.47 ± 0.02	63 ± 7
fluoranthene	1.2 ± 0.4	3.12 ± 0.28	128 ± 37	PCB-180	0.88 ± 0.15	67 ± 17
pyrene	1.2 ± 0.4	3.24 ± 0.17	153 ± 6			

The long-term desorption plots at 20 °C show nonlinear behavior after 100 h of desorption, for both OVP and KM sediments; this is also observed for the 60 °C-plots after 50 h of desorption (Figure 3). This implies that one single rate constant of slow desorption is not adequate to describe the whole "slow" part of these plots. Therefore, an additional rate constant has been used to describe these plots; this rate constant, which applies to the last part of the long-term 20 °C plot and to the 60 °C plots, is termed  $k_{vs}$ , the "very slow" desorption rate constant. The relevant parts of the curves (after 24 h) are therefore fitted with a slow sediment compartment and a very slow compartment and their corresponding rate constants  $k_{slow}$  and  $k_{vs}$ . The solid lines in Figure 3 have been obtained by exponential curve fitting to an equivalent of eq 1.

Different stages of desorption are thus discerned: a stage in which the rapid fraction desorbs during the first 10 h (see also ref 20), a second stage in which the intermediate slow fraction desorbs during the first weeks, and a last "very slow" stage that is only observed after months at 20 °C or earlier at elevated temperatures. The values of the very slow desorption rate constant at 20 and 60 °C are presented in

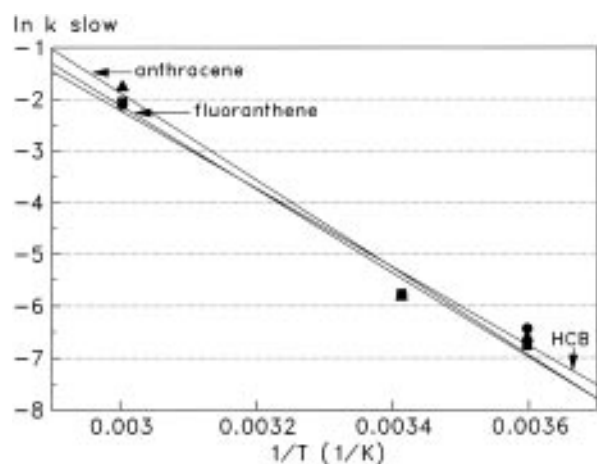
Table 3, along with the very slow fractions determined at 20 and 60 °C. The very slow fractions determined at 20 and 60 °C are only slightly different, with the exception of PCB-118. The slow fractions observed in the 300-h experiments at 5 and 20 °C (Table 1 and Figures 2 and 3) include the slow as well as the very slow fractions. From these (slow + very slow) fractions and the very slow fractions, separate slow and very slow fractions can be calculated. The slow fractions not including a very slow part are also given in Table 3. In cases where the very slow fraction was only measured at 60 °C, one value for the slow fraction is given; if the very slow fraction was measured at both 20 and 60 °C a range is given. The slow fractions cannot be directly determined from the y-intercept of the slow desorption parts in the 60 °C desorption curves because desorption was carried out at 20 °C between 0 and 24 h.

The values of the very slow fractions for the PAHs are very small and inaccurate. This is because the amounts released during the very slow phase were approaching or exceeding HPLC-FCD detection limits. These problems were not encountered with the measurements of concentrations of the PCBs and chlorobenzenes with GC-ECD.

**TABLE 3. Rate Constants for Very Slow Desorption Plots ( $k_{vs}$ ; Measured at 60 °C) along with Fractions Desorbing with These Rate Constants<sup>a</sup>**

	OVP sediment (lab-contaminated)					KM sediment (field-contaminated)					
	$k_{vs}$ ( $10^{-3} \text{ h}^{-1}$ )		very slow fraction (%)		slow fraction (%)	$k_{vs}$ ( $10^{-3} \text{ h}^{-1}$ )		very slow fraction (%)		slow fraction (%)	
	20 °C	60 °C	20 °C	60 °C		20 °C	60 °C	20 °C	60 °C		
TeCB	0.52 ± 0.08	8.5 ± 0.2	4.7 ± 0.7	1.2 ± 0.2	8.0–11.7	TeCB	2.5 ± 0.4		47 ± 5	20 ± 7	
OCB	0.40 ± 0.04	7.8 ± 0.2	7.0 ± 0.8	4.3 ± 0.2	15.8–18.5	OCB	1.60 ± 0.12		63 ± 2	22 ± 5	
HCB	0.48 ± 0.03	2.6 ± 1.3	8.9 ± 1.1	11.3 ± 3.2	20–21	PCB-90	0.14 ± 0.03	2.26 ± 0.02	28 ± 2	26.6 ± 0.4	35.1–36.5
PCB-65	0.43 ± 0.07	2.21 ± 0.07	11.2 ± 1.4	15.4 ± 0.6	33–37	PCB-99	0.23 ± 0.02	2.51 ± 0.06	29 ± 2	26 ± 2	34–37
PCB-118	0.30 ± 0.07	1.02 ± 0.11	16 ± 2	47.4 ± 2.3	19–50	PCB-153		1.87 ± 0.12	24.6 ± 0.3	50 ± 2	
fluorene		3.8 ± 1.9		0.5 ± 0.2	8.4 ± 1.1	PCB-138		2.22 ± 0.04	24 ± 3	54 ± 4	
anthracene		6 ± 2		1.8 ± 0.3	22 ± 3	PCB-167		1.5 ± 0.3	50.4 ± 1.1	37 ± 3	
fluoranthene		4.1 ± 1.2		3.4 ± 1.3	37 ± 4	PCB-180		2.5 ± 0.4	33 ± 2	51 ± 5	
pyrene		6.6 ± 0.8		2.4 ± 0.1	34 ± 2.2						

<sup>a</sup> Slow fractions corrected for the “very slow” fractions are also given as well as 95% confidence intervals. All values are given for OVP sediment (chlorobenzenes, PCBs, and PAHs) and KM sediment (chlorobenzenes and PCBs).



**FIGURE 4.**  $\ln(k_{slow})$  vs  $1/T$  for fluoranthene (squares), HCB (circles), and anthracene (triangles) for OVP sediment. Solid lines obtained by linear regression.

**Enthalpies of Slow Sorption.** In Figure 4, plots of  $\ln k_{slow}$  vs  $1/T$  are given for three of the compounds (for the OVP sediment). Values for  $\Delta H_{des}^\ddagger$  (calculated with eq 3) and  $\Delta H_{slow}$  (calculated with eq 4) are given in Table 4 as well as the values of  $\Delta H_{ads}^\ddagger$  calculated from  $\Delta H_{des}^\ddagger$  and  $\Delta H_{slow}$ , with eq 2. Also, activation enthalpies for desorption from the very slow fraction ( $\Delta H_{vs}^\ddagger$ ) could be calculated from the  $k_{vs}$  values at 20 and 60 °C (eq 3); values are given in Table 4 as well.

## Discussion

**Desorption Rate Constants and Slow Fractions.** For the field-contaminated KM sediment, the slow ( $k_{slow}$  approximately  $10^{-3} \text{ h}^{-1}$  at 20 °C) and the very slow fractions ( $k_{vs}$  approximately  $10^{-5}$ – $10^{-4} \text{ h}^{-1}$  at 20 °C) each contributed significantly to the total amount sorbed. For the lab-contaminated OVP sediment, the slowly and very slowly desorbing fractions were lower than for the KM sediment because slowly desorbing fractions increase with increasing contact time (20, 24, 25) and the contact time of 34 days (OVP sediment) is shorter than field contact times (KM sediment). McGroddy et al. (26) found that all sorbed PCB-138 and PCB-101 in sediment cores was available for partitioning, in contrast to two PAHs that were available for only 1–40%. The present observation that a significant part of the sorbed PCBs desorbs slowly is in contrast with McGroddy’s observation.

Desorption rate constants for the OVP and KM sediments were surprisingly similar (Table 2, both 5 and 60 °C). For the OVP sediment,  $k_{slow}$  slightly decreases with increasing solute size (Tables 1 and 2). Assuming diffusion as the explanation for slow desorption, this observation can be explained by

slower diffusion for larger solutes. Fast fractions decrease with increasing solute hydrophobicity (Tables 1 and 3), possibly reflecting a more hydrophobic character of the slowly exchanging sediment compartment relative to the rapidly exchanging one (20).

Many authors have described their results with a two-compartment model involving rapid and slow sediment compartments (4, 18, 25, 27, 28). The present results show that such a description is not always adequate to describe the whole desorption range, especially for aged contaminated sediments; for the last phase of desorption an additional very slow rate constant is needed. The desorption curves at 5 and 20 °C do not show a very slow part because the desorption time of 300 h in these experiments was not long enough to deplete the slow fraction.

The extraction of aged contaminants may be incomplete (1, 2, 25), even with a powerful extraction method such as hexane refluxing. Recoveries of about 80% have been reported for hexane reflux extraction of PCBs from certified reference materials (29). Incomplete extraction of sorbed residues after desorption may affect the numerical values of the parameters of slow desorption, especially for the aged field-contaminated sediment for which extraction yields are probably lowest. Therefore, our data only refer to hexane-extractable fractions.

**Thermodynamic Parameters.** The values for  $\Delta H_{des}^\ddagger$  are in the order of 60–70  $\text{kJ mol}^{-1}$  for both the lab-contaminated OVP sediment and the field-contaminated KM sediment (Table 4), in spite of potential differences in sediment characteristics, contaminant origin, and aging. The observed  $\Delta H_{des}^\ddagger$  values are approximately constant for all compounds studied, in spite of the variation in LeBas molar volume (from 179.6  $\text{cm}^3/\text{mol}$  for TeCB to 330.9 for PCB-180 (31)). The observed values for the activation enthalpies of slow desorption are roughly in accordance with values found in other studies. Steinberg et al. (8) found an activation energy of  $66 \pm 11 \text{ kJ mol}^{-1}$  for the slow desorption of 1,2-dibromoethane from field-contaminated aquifer material aged for at least 19 years. They used a gas-purge technique to carry out desorption experiments at five temperatures between 40 and 97 °C. Uzgiris et al. (17) reported a  $\Delta H_{des}^\ddagger$  value of  $46 \text{ kJ mol}^{-1}$  for the desorption of PCBs from a clay soil, but they employed an unconventional desorption technique in which PCBs were desorbed into the gaseous phase at rather high temperatures (125–300 °C). Piatt et al. (18) derived desorption rate constants from batch and column experiments with naphthalene, phenanthrene, and pyrene sorbed to a 0.02% OC aquifer sediment, at 4 and 26 °C. Equilibration times were relatively short, 100 h or less. From their data, we calculated  $\Delta H_{des}^\ddagger$  to be 6–29  $\text{kJ mol}^{-1}$  for phenanthrene and pyrene and, remarkably, –6 to –28  $\text{kJ mol}^{-1}$  for naphthalene. It should be noted, however, that the

TABLE 4. Activation Enthalpies ( $\text{kJ mol}^{-1}$ ) with 95% Confidence Intervals for Slow Adsorption and Desorption as Well as for Very Slow Desorption, Determined for Lab-Contaminated (OVP) and Field-Contaminated (KM) Sediment

KM sediment (field-contaminated)			OVP sediment (lab-contaminated)				
compd	$\Delta H^{\#}_{\text{des}}$	$\Delta H^{\#}_{\text{vs}}$	compd	$\Delta H^{\#}_{\text{des}}$	$\Delta H^{\#}_{\text{vs}}$	$\Delta H^{\#}_{\text{ads}}$	$\Delta H_{\text{slow}}$
TeCB	57 ± 9		TeCB	60 ± 8	57 ± 1	54 ± 10	-6 ± 2
HCB	70 ± 7		OCB	63 ± 10	60 ± 1	56 ± 12	-7 ± 2
PCB-90	64 ± 4	56 ± 2	HCB	63 ± 11	34 ± 12	56 ± 13	-7 ± 2
PCB-99	60 ± 3	49 ± 3	PCB-65	69 ± 14	33 ± 2	62 ± 18	-7 ± 4
PCB-153	61 ± 4		PCB-118	74 ± 17	25 ± 5	77 ± 19	+3 ± 2
PCB-138	60 ± 5		fluorene	68 ± 10		56 ± 15	-12 ± 5
PCB-167	68 ± 4		anthracene	70 ± 11		55 ± 15	-15 ± 4
PCB-180	61 ± 8		fluoranthene	67 ± 7		57 ± 11	-10 ± 4
			pyrene	69 ± 8		59 ± 13	-10 ± 5

$k_{\text{slow}}$  values reported in these three studies are at least 1 order of magnitude higher than ours.

**Mechanistic Interpretation.** The magnitude of the activation enthalpies of slow desorption ( $60\text{--}70 \text{ kJ mol}^{-1}$ ) seems to be in the polymer diffusion range ( $>60 \text{ kJ mol}^{-1}$  (1, 9, 11, 13)) rather than in the pore diffusion range [ $20\text{--}40 \text{ kJ mol}^{-1}$  (11, 14–16)]. Therefore intra-organic matter diffusion may better explain the slow desorption from the sediments used by us than pore diffusion.

It is not directly clear what the physical-chemical explanation is for the two slow fractions observed for the lab-contaminated sediment as well as for the field-contaminated one. One explanation is that the slow compartment is associated with bulk amorphous organic matter whereas the very slow compartment is associated with microcrystalline organic matter; the rapid compartment is then the outer sphere of the organic matter. Three compartments (domains I, II, and III) have been proposed by Young, Weber, and Huang in their "distributed reactivity model" (23, 32). Domain I is suggested to be inorganic material, domain II is suggested to be amorphous organic matter, and domain III is suggested to be microcrystalline organic matter. A roughly similar model with "dual-mode" sorption like in glassy polymers was proposed by Xing et al. (33). Analogous to dual-mode glassy polymer sorption, the slow fraction in sediments could be explained by a partitioning mechanism, and the very slow fraction could be explained by a hole-filling mechanism.

The physical-chemical explanation for the negative  $\Delta H_{\text{slow}}$  values (exothermic enthalpy effect of transfer from the rapid to the slow sediment compartment) probably lies in the removal of solute from water: in the rapid sediment fraction solute may still be in contact with water whereas in the slowly exchanging hydrophobic, organic compartment it may not be the case. Removal of a hydrophobic solute molecule from water results in an exothermic (favorable) enthalpy effect because of the restoration of aqueous H-bridge bonding (30). Sorption enthalpies anticipated in this way would be  $-18$  to  $-30 \text{ kJ mol}^{-1}$  (30) and roughly constant for the large nonpolar molecules used in the present study. The  $\Delta H_{\text{slow}}$  values we determined are also negative and roughly equal for the different compounds used ( $-10 \pm 3 \text{ kJ mol}^{-1}$ ; Table 4). If removal from the water indeed causes the exothermic character of  $\Delta H_{\text{slow}}$ , a mechanistic implication is that solute in the slowly exchanging sediment compartment is not in contact with water; the slow sediment compartment therefore probably consists of remote organic regions and not of narrow water-saturated pores.

In a recent review by our group (13), it was found that the average value of the sorption enthalpies found in 21 different studies was  $-4 \pm 19 \text{ kJ mol}^{-1}$ . In these 21 studies, equilibration times had been short so this sorption enthalpy value mainly addresses sorption to the rapidly exchanging sediment fraction. The present values for  $\Delta H_{\text{slow}}$  ( $-10 \pm 3 \text{ kJ mol}^{-1}$ ) address the enthalpy change resulting from solute transfer from the rapid to the slow sediment compartment. The

enthalpy change for the transfer from water to the slow sediment compartment is then approximately  $-14 \pm 22 \text{ kJ/mol}$ , indicating an exothermic process but with a very wide confidence interval. It has to be noted, however, that  $\Delta H_{\text{slow}}$  includes not only slow sorption but also very slow sorption because the  $\Delta H_{\text{slow}}$  values have been calculated with slow fractions including very slow fractions (Table 1). For the OVP sediment, however, the very slow fractions are smaller than the slow fractions (with the exception of PCB-118, see Table 3), so the most significant contribution to  $\Delta H_{\text{slow}}$  stems from the slow fraction.

**Implication.** A perspective offered by the strong temperature dependence of slow desorption is that indications of long-term desorption behavior can be obtained rapidly from desorption experiments at elevated temperatures. This is because slow fractions observed in a 300-h experiment at  $60^\circ\text{C}$  only slightly differed from the ones observed in a 2080-h experiment at  $20^\circ\text{C}$ .

During bioremediation, it is often observed that fractions of contaminants are degraded very slowly or not at all. Slow desorption of these compounds is probably the cause of these remedial limitations, so desorption experiments at elevated temperatures may give rapid information on the feasibility of bioremediation of contaminated soils and sediments. It is not clear whether these poorly degradable fractions encountered during bioremediation consist of only the very slow fraction or of both the slow and the very slow fractions. An indication that this may be the very slow one is offered by the observation that very slow desorption rate constants ( $10^{-5}\text{--}10^{-4} \text{ h}^{-1}$ ) are in the same order of magnitude as rate constants for biodegradation of aged residues (e.g., refs 34–36).

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