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Triphasic Desorption of Highly Resistant Chlorobenzenes, Polychlorinated Biphenyls, and Polycyclic Aromatic Hydrocarbons in Field Contaminated Sediment

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Pollutants in aged field sediments seem to differ from spiked sediments in their chemical and biological availability. Biphasic desorption is often used as an explanation. In the present study, desorption kinetics and partitioning of chlorobenzenes (CBs), polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs) in long term field contaminated sediment cores and top layer sediment were measured by gas-purging. Desorption from sediment was deduced to be triphasic: fast, slowly, and very slowly desorbing fractions were distinguished. In both the sediment core and the top layer sediment no detectable fast fractions were present for all the compounds studied, so these were estimated as upper limits from the desorption curves. This observation coincided with very high in situ distribution coefficients for several PCBs and PAHs: 10−1000 times higher than literature values for short contact time experiments. Rate constants were (3−8) × 10^{-3} h^{-1} for slow desorption and (0.16−0.5) × 10^{-3} h^{-1} for very slow desorption. In some cases only a very slowly desorbing fraction was detectable. Desorption from field contaminated sediments with extended contact times may not be readily estimated from laboratory experiments in which contaminants have contact times with the sediment in the order of weeks.

Introduction

The sediments of the lower stretches of the rivers Rhine and Meuse in The Netherlands are polluted with hydrophobic organic compounds such as CBs, PCBs, PAHs and with heavy metals. Especially the older layers of sedimentation areas of the river Rhine have been shown to be heavily polluted due to a high input in the 1960s and 1970s, caused by industrial activities upstream (*1*−*4*). There are several indications in the literature that aged pollution in sediments is less available for mild extraction (*5*−*7*), biodegradation (*6*−*10*), and uptake by organisms (*9*−*11*). These findings may be explained by the commonly observed biphasic desorption behavior of organic pollutants. Desorption experiments often reveal both a fast and a slowly desorbing fraction in both spiked and field contaminated sediments. An explanation for the decreasing availability of a chemical with aging is the decreasing amount of the chemical present in the fast desorbing pool with prolonged contact time.

Desorption kinetics in suspensions have been studied extensively in the past years, using either the gas-purge technique (*5, 12*−*16*) or extraction methods with Tenax (*17, 18*) or XAD (*19*). These studies all show a biphasic desorption of hydrophobic organic micropollutants from suspended particles in aquatic systems. The fast and slowly desorbing pools have rate constants of 0.1−1 and 10^{-3} h^{-1} respectively (*5, 12, 15*−*17*). Recently, very slowly desorbing fractions have been shown to exist in field sediments and sediments spiked with PAHs, CBs, and PCBs. This very slowly desorbing fraction has rate constants of 10^{-4}−10^{-5} h^{-1} (*20*).

In a previous study we determined very low concentrations of di and trichlorobenzenes in porewater from a sediment core sampled in lake Ketelmeer (*4*). This may have been caused by the presence of large slowly desorbing fractions. We concluded that only a small fraction of the compound was released to porewater. In another study from our group, in situ distribution coefficients of CBs were shown to be quantitatively in agreement with fast desorbing fractions in a polluted harbor sediment (*21*). High in situ distribution coefficients were also observed by McGroddy for PAHs but not for PCBs (*22, 23*). Association between PAH and sedimentary soot could explain this difference (*22*−*24*).

Most studies using field contaminated sediments or soils have shown variable fractions of fast and slowly desorbing compounds. In the present study the desorption kinetics for several CBs, PCBs, and PAHs were determined in aged field sediments (both core and top layer) from lake Ketelmeer, The Netherlands (*4*), and interpreted in terms of triphasic desorption.

Materials and Methods

Materials. Freshwater sediment was collected from Lake Ketelmeer, The Netherlands. For PAH desorption studies, we used the 30−60 cm section from a core sampled in February 1992. For CB and PCB desorption studies, the 40−120 cm section from a core sampled in March 1995 was used. These polluted layers were formed in the 1960s and 1970s. CB desorption studies were also done on the 5−10 cm top layer sampled in 1989 with a grab sampler. The sediments were wet-sieved (<500 μm) to remove coarse material and stored under water at 5 °C until further use. Desorption experiments were performed within a few weeks after sampling. Organic carbon (oc) content for the sieved sediment fraction was determined to be 7.41% (30−60 cm layer), 6.71% (40−120 cm layer), and 4.3% (top sediment) using an element analyzer (Carlo Elba NA 1500) after removal of carbonates with phosphoric acid. The compounds studied in these sediments were dichlorobenzenes (DCB), trichlorobenzenes (TCB), tetrachlorobenzenes (TeCB), pentachlorobenzene (QCB), and hexachlorobenzene (HCB), 2,4,4′-trichlorobiphenyl (PCB-28), 2,3′,4,4′,5-pentachlorobiphenyl (PCB-118), naphthalene (NAPH), biphenyl (BiPHEN), 2-meth-

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TABLE 1. Concentrations of CBs, PCBs, and PAHs (μg/kg dry weight) in Top Layer Sediment and Sediment Cores of Lake Ketelmeer[a]

top layer sediment		sediment core	
compound	concn	compound	concn
12-DCB	367	12-DCB	580; 630
13-DCB	149	14-DCB	710; 740
14-DCB	459	123-TCB	24.5; 24.7
123-TCB	13	124-TCB	471; 480
124-TCB	111	135-TCB	137; 144
135-TCB	59	1234-TeCB	19; 27
1234-TeCB	9.7	QCB	25; 28
1235-TeCB	5.5	HCB	37.0; 39.1
1245-TeCB	18	PCB-28	280; 340
QCB	28	PCB-118	50; 58
HCB	38	BiPHEN	960; 1290
		2-MN	7960; 9930
		FLUE	1488
		PHE	3990; 4750

[a] Duplicate measurements for most compounds.

ylnaphthalene (2-MN), fluorene (FLUE), phenanthrene (PHE), fluoranthene (FLUO), and pyrene (PYR).

Desorption Experiments. Duplicate sediment samples of about 25 g wet weight were suspended in the purge vessels. Each suspension had a total volume of approximately 1 L, and the headspace above the suspension was minimal. Water with a composition resembling that of freshwater was prepared as described earlier (*25*). Mercury(II) chloride (1 mL of a 5 g L^{-1} solution in water) was added to prevent microbial degradation. The thermostated purge and (Tenax) trap system used is described elsewhere (*26*). A gas flow of 600−1000 mL min^{-1} was applied and measured regularly. The sediment suspensions were continuously stirred and kept at 20.0 ± 0.05 °C. Tenax traps were changed 15 times for PAHs desorption, 9 times for CBs and PCBs on desorption from the 40−120 cm layer, and 18 times for CBs on top layer desorption. Total purging time was 756 h (PAHs), 624 h (CBs and PCBs in the 40−120 cm layer), and 1848 h (CBs and PCBs in the top layer). Mass balances were calculated by dividing the total mass at the end of an experiment (mass in suspension plus cumulative mass desorbed) by the total mass in the suspension measured at the beginning of the experiment. The mass balances were 107 ± 22% for the PAHs, 150 ± 26% for CBs and PCBs (40−120 cm layer), and 155 ± 27% for CBs (top layer). These mass balances mainly reflect the variations in concentration in the sediment suspension (see Table 1). There were no large differences in the mass purged in the duplicate desorption experiments.

Extraction and Cleanup. The sediment extraction procedure for CBs and PCBs (refluxing with hexane) is described elsewhere (*4*). The same extraction procedure was used for the PAHs; but after refluxing with hexane, the solvent was concentrated to 0.5 mL under a gentle nitrogen flow and the resulting extract was combined with 5 mL of acetonitrile. The total volume was reduced to 1 mL and filtered using a Millex 50 μm filter. For CBs in the top layer, sediments were extracted with hexane at room temperature (*27*). No significant differences in measured concentrations were found when using both extraction methods for CBs and PCBs in field contaminated sediments.

For PAHs, Tenax traps were eluted with hexane and acetonitrile. The hexane eluate was concentrated to 0.5 mL under a gentle nitrogen stream and combined with the acetonitrile eluate. The total volume was reduced to 1 mL as described above. For CBs and PCBs, Tenax traps were eluted with 10 mL of hexane. The total volume was reduced to 1 mL, followed by a cleanup step with 2 g of deactivated Al_2O_3 (11%). The volume of the eluate was reduced to 0.5 mL and combined with 4 mL of isooctane. The total volume was reduced to 1 mL.

Recovery experiments were performed for both CBs/PCBs and PAHs to quantify losses during extraction and cleanup. Losses during storage of aqueous solutions of PAHs were negligible. The average recoveries for the sediment extraction ranged from 73 to 92% (PAHs) and 91−121% (CBs and PCBs). Recoveries for the Tenax extraction ranged from 74 to 140% (PAHs) and 65−92% (CBs and PCBs). The recoveries for the concentration step with nitrogen ranged from 89 to 96% (PAHs) and >95% (CBs and PCBs). No correction for the method recoveries was made because for most compounds these recoveries were high. Recoveries for PAHs were corrected for blanks (see below).

Chemical Analyses. CBs and PCBs were analyzed with a GC-ECD (*27*). PAHs were analyzed by HPLC with fluorescence detection on a reversed phase C18 column as described previously (*28*). A correction was made for blanks because Tenax contains fluorescent material that coelutes with the compounds of interest. The relative influence of blanks was highest during the first few (relatively short) measurement intervals: blanks accounted for 10−30% of the measured mass. For the longer intervals blanks accounted for 1−5% of the mass measured. For most PAH compounds the interference from the Tenax material was constant for the batch used for the PAH desorption experiments (triplicate measurement, standard deviation 5−15%). For FLUO and PHE a larger variation was observed.

Data Handling. In our experiments single phase desorption was observed for most PAHs and several CBs. The mass transfer during gas purging in the case of single-exponential depletion is described by

$$G \xleftarrow{k_0} W \underset{k_2}{\overset{k_1}{\rightleftarrows}} S \tag{1}$$

in which G, W, and S (g) are the mass of compound in the gas phase, water phase, and sediment phase, respectively; k_0 (h^{-1}) is the volatilization rate constant from water, and k_1, k_2 (h^{-1}) are the rate constants of adsorption and desorption, respectively.

If the mass recovered from Tenax does not change with time, the water concentration in the purge vessel can be assumed constant during the time interval studied. For several PAHs and CBs depletion rates were constant on (prolonged) depletion. Thus we approximated dW/dt by

$$0 = \frac{dW}{dt} = -(k_0 + k_1)W + k_2 S \tag{2}$$

From (*2*) it follows that

$$\frac{S}{W} = \frac{k_0 + k_1}{k_2} \tag{3}$$

The total mass present in the purge vessel is described by

$$M_t = W + S \tag{4}$$

The mass recovered from Tenax reflects the change of mass in the purge vessel:

$$\frac{dM_t}{dt} = \frac{dW}{dt} + \frac{dS}{dt} = \frac{dS}{dt} = k_1 W - k_2 S \tag{5}$$

This approach is valid when $dW/dt = 0$ or $dW/dt \ll dS/dt$. With the assumption that $M_0 = S_0$ and combining (5) with (3) and (4) this yields after integration

$$\frac{M_t}{M_0} = e^{-k_0k_2/(k_0 + k_1)t} \tag{6}$$

in which M_0 = mass present at $t = 0$. Thus, the slope of a plot of $\ln(M_t/M_0)$ with time is equal to $-k_0k_2/(k_0 + k_1)$. Three cases can be distinguished:

1. $k_0 \gg k_1$: the slope of $\ln(M_t/M_0)$ vs t reduces to $-k_2$ and $S/W = k_0/k_2$. Only kinetic information can be obtained;
2. $k_0 = k_1$: the slope of $\ln(M_t/M_0)$ vs t reduces to $-k_2/2$ and $S/W = 2k_1/k_2$. Both kinetic information and distribution coefficients can be obtained;
3. $k_0 \ll k_1$: the slope of $\ln(M_t/M_0)$ vs t reduces to $-k_0k_2/k_1$ and $S/W = k_1/k_2$. Only distribution coefficients can be obtained.

Table 2 compares volatilization rates (k_0) and adsorption rates (k_1) of the compounds studied. These rates were calculated from literature data. For the CBs and PCB-28, k_1-values were considerably smaller than k_0-values: the desorption curves provided kinetic information. For BiPHEN, 2-MN, and FLUE the volatilization rates in this system were of the same magnitude as the adsorption rates. An order of magnitude estimate of k_2 was obtained from the desorption experiments, because only estimates of the adsorption rates were available (see Table 2).

For PCB-118, PHE, FLUO, and PYR the volatilization rates were much lower than the adsorption rates. For these compounds sediment-water distribution coefficients were calculated (see below).

On biphasic desorption (no constant depletion rates) the desorption curves are described by the sum of two exponential functions equivalent to eq 6, assuming $C_1 \gg C_2$

$$M_t/M_0 = F_1e^{-C_1t} + F_2e^{-C_2t} \tag{7}$$

where F_1 and F_2 (−) represent the mass fraction of pollutant present in the two sediment pools at the start of the experiment. The two coefficients C_1 and C_2 (in h^{-1}) combine k_0 (h^{-1}), k_1 (h^{-1}), and a desorption rate constant k_{des} (either fast, slow, or very slow desorption, also in h^{-1}) similar to eq 6: C_1 (or C_2) = $k_0k_{des}/(k_0 + k_1)$.

Results and Discussion

Desorption Curves. Plots of $\ln(M_t/M_0)$ vs t were obtained for the CBs, PCBs, and PAHs studied. The assumption of a constant concentration in water during (part of) the desorption experiments was tested by plotting the calculated concentrations in water vs time. C_w was calculated from $C_w = M_{tenax} \times V_{gas}^{-1} \times (H')^{-1}$, with C_w = concentration in water (ng L^{-1}); M_{tenax} = mass of compound sorbed to Tenax during the time interval studied (ng); V_{gas} = average volume of gas purging the suspension during the time interval studied (L); H′ = Henry coefficient (−).

Examples of the plots of the concentration in water vs time (duplicates for each compound) are presented in Figure 1 for three compounds. For most PAHs and some CBs, this concentration was relatively constant with time. Exceptions were PYR and FLUO for which a large decrease in the water concentration was calculated during the first few time intervals (for pyrene from 470 ng L^{-1} to approximately 7.5 ng L^{-1} and for FLUO from 2700 ng L^{-1} to approximately 25 ng L^{-1}). These large decreases corresponded to half-lives that were much higher than those observed for FLUO and PYR in water-only experiments, suggesting the presence of other (more volatile) compounds that could not be separated from the compounds of interest. No GC-MS analysis of these samples could be performed to confirm this speculation. Because of the high depletion rates of these possibly interfering compounds and the relative constant water concentration after more than 100 h of purging, their influence was assumed to be negligible for the last part of the experiments. Only the last part of the curve was used for data interpretation for these compounds.

TABLE 2. Calculated[a] Volatilization Rates (k_0) and Calculated[b−d] Adsorption Rates (k_1) in h^{-1} of CBs, PCBs, and PAHs Using Available Literature Data

chloro-benzenes	k_0[a]	k_1	PCBs, PAHs	k_0[a]	k_1
12-DCB	2.48	<0.02[b]	PCB-28	0.56	0.052
13-DCB	3.70	<0.02[b]	PCB-118	0.16	0.1−0.2[b]
14-DCB	3.10	<0.02[b]	BiPHEN	0.65	0.1−0.3[d]
123-TCB	1.47	0.02[c]	2-MN	1.04	0.5[d]
124-TCB	3.90	≤0.02[b]	FLUE	0.15	0.4[d]
135-TCB	1.49	0.0035[c]	PHE	0.066	0.6[d]
1234-TeCB	1.28	0.048[c]	FLUO	0.025	5.5[d]
1235-TeCB	2.04	0.03−0.05[b]	PYR	0.02	7.1[d]
1245-TeCB	2.09	0.03−0.05[b]			
QCB	1.20	0.034[c]			
HCB	0.82	0.05[c]			

[a] From $k_0 = H \cdot F \cdot R^{-1} \cdot T^{-1} \cdot V^{-1}$ (h^{-1}); F = flow; R = 8.31451 Pa·m^3·mol^{-1}·K^{-1}; T = temperature (293.15 K); H from various sources: (*12, 26, 28, 43*). [b] Estimated from the observation that adsorption rate constants for CBs are related to their hydrophobicity (*15*). [c] From (*15*). [d] Calculated from $K_p = k_1/k_2$ for a 10 g/L suspension. K_p(−), k_2 from (*17*).

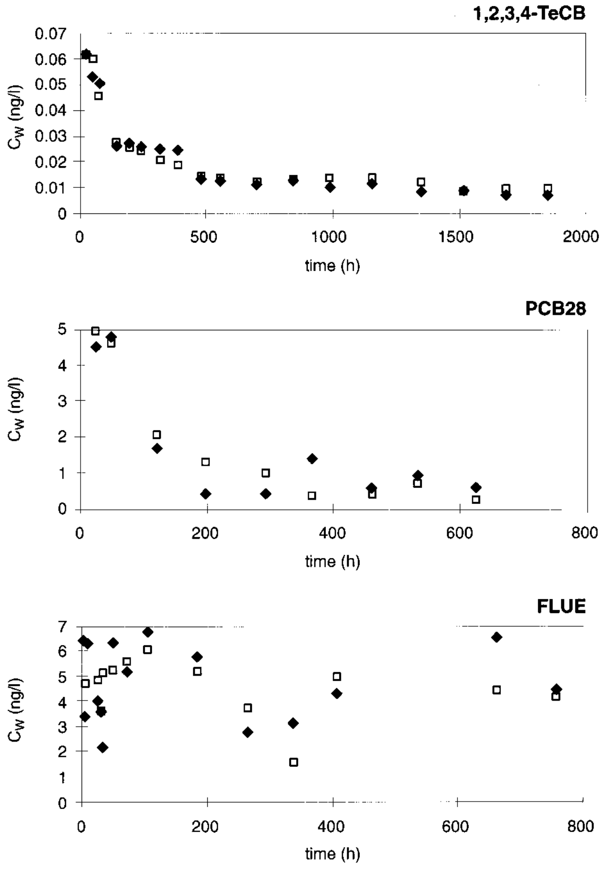

FIGURE 1. Concentrations of 1234-TeCB (top layer); PCB-28 and FLUE (both sediment core) in water during the duplicate desorption experiments.

For several CBs and PCBs the concentration in water declined during the first 100−400 h of purging. The change of mass in the water phase was small compared to the total mass purged from the system during a measurement interval (i.e. for the more soluble DCBs: $dM_t/dt \cong 0.5$ ng h^{-1}, $dW/dt \cong 0.001$ ng h^{-1}). This indicates that for calculating rate constants the change in concentration in the water phase may be neglected. However, for the calculation of distribu-

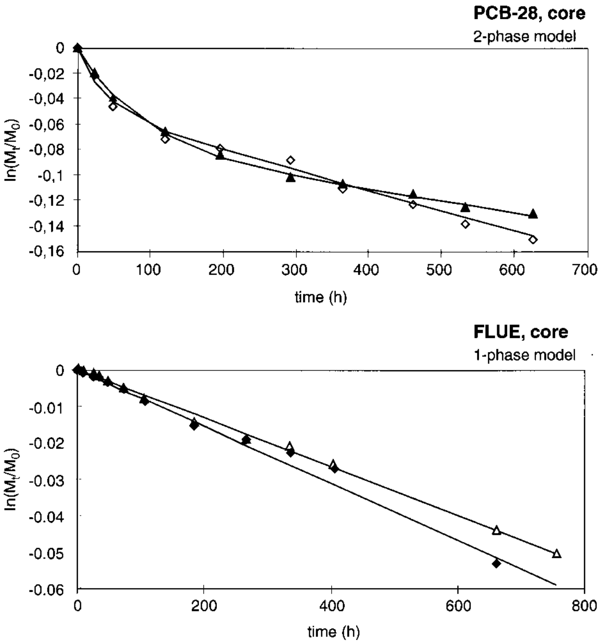

FIGURE 2. Duplicate desorption plots (ln M_t/M_0 = mass fraction remaining in suspension) for PCB-28 and FLUE in the sediment core. Measurements are indicated by symbols and model fits by solid lines.

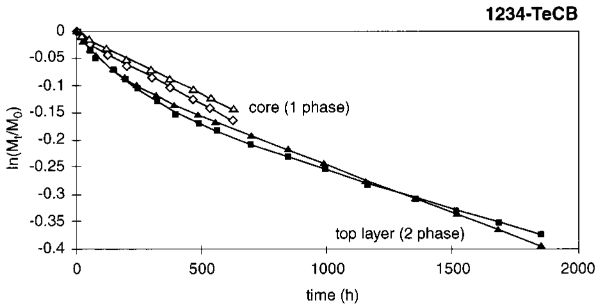

FIGURE 3. Duplicate desorption plots (ln M_t/M_0 = mass fraction remaining in suspension) for 1234-TeCB in the top layer sediment and sediment core. Measurements are indicated by symbols and model fits by solid lines.

tion coefficients, the variation in concentrations in water directly reflected the variation in distribution coefficients. For these calculations only that part of the desorption curve was used for which relatively constant concentrations were calculated.

For the CBs, PCBs, and three PAHs plots of ln(M_t/M_0) versus t were fitted with the single-stage (most compounds in the sediment core) and two-stage (most compounds in the top layer sample) desorption models presented above, using linear or nonlinear regression. Examples of the measured and fitted desorption curves are shown in Figures 2 and 3. The validity of the use of one or two-compartment models was tested using an F-test on least squares of eqs 6 and 7 (α = 0.05). In several cases the use of a two compartment model did not show a significant improvement.

Desorption Rates Constants. In Table 3, the desorption rate constants for CBs, PCBs, and three PAHs are presented. The magnitude of observed desorption rate constants demonstrates that only slowly and very slowly desorbing fractions were detectable in top layer and sediment core. Rate constants for fast desorption are expected to be in the range of 0.5–5 × 10^{-1} h^{-1} (*15–17*). No measurable fast desorbing fraction was present, yet we estimated these as upper limits, as is explained later on.

Desorption rate constants were (3–8) × 10^{-3} h^{-1} for the slow fraction and (0.9–1.7) × 10^{-4} h^{-1} for the very slow fraction. For those compounds showing one-phase desorption one very slowly desorbing fraction was observed (desorption rate constants (1–7) × 10^{-4} h^{-1}). The ratios of rate constants for the slowly and very slowly desorbing fractions were 20–170 for CBs and PCBs in the core and 20–60 for CBs in the top layer sediment. This is in accordance with findings by Cornelissen et al. (*20*) who found a ratio of 10–50. The rate constants for the slowly and very slowly desorbing fractions were relatively constant for all the compounds studied. No clear trend with hydrophobicity or molar volume was observed. This is in accordance with the findings of Schrap (*15*) but contrary to those of others (*17, 29, 30*).

Fast and Slow Fractions. For several compounds in the top layer, amounts present in slowly and very slowly desorbing fractions were obtained from a fit of the measured data with eq 7. We did not observe fast desorbing fractions for any of the compounds studied, but their presence (in small amounts) cannot be ruled out. We estimated the magnitude of the fast fraction from the amount desorbed during the first 24 h of the purge experiment. This estimation is supported by a calculation of the percent removal of compounds from the fast fraction during this time interval. For compounds with high volatilization rates (such as CBs) the depletion rate from the suspension is equal to the fast desorption rate (case 1 for eq 6). For the less volatile CBs these desorption rates vary between 0.2 and 0.4 h^{-1}, resulting in half-lives of 3.5–1.7 h. In 24 h the majority (>99%) of the fast desorbing fraction is removed from the suspension. For compounds with k_0-values that are too low to measure desorption kinetics (case 3 for eq 6) the observed depletion rate is k_0/K_p. For these compounds half-lives are much longer than 24 h, so no fast fractions can be estimated from the desorption curves. For compounds having approximately equal values for k_0 and k_1 half-lives are less than 10 h, resulting in >85% removal from the fast fraction. For QCB no estimate of the fast fraction could be made because in the first 24 h no measurable amount of mass desorbed.

For the slowly desorbing fraction the average desorption rate constant is 0.5 × 10^{-2} h^{-1} resulting in a half-life of 138 h. During a 300 h. time interval more than 75% of the slowly desorbing fraction is removed. Therefore, for compounds showing only one-phase desorption, the slowly desorbing fraction was estimated from the mass desorbed between 24 and 300 h of purging. The calculated slowly desorbing fractions for several CBs differed less than 10% from the fractions that were obtained from the data analysis with the two-phase model.

Mass fractions in fast, slowly, and very slowly desorbing fractions in top layer and sediment core samples are presented in Figure 4. Duplicate data points are presented. The SE of the fractions obtained by curve-fitting are not shown because these were small compared to the differences between duplicates. Figure 4 shows that relatively small amounts are present in the fast and slowly desorbing fractions, both in the top layer sediment and in the sediment core. The absence of detectable fast desorbing fractions was observed for all the compounds studied, including the highly volatile CBs. Therefore these observations were not caused by the kinetics of purging.

The presence of small fast desorbing fractions in field contaminated sediments and soils has been reported by others. Small fast fractions can be deduced from the data on ethylene dibromide (*31*) and were also reported for native atrazine and metolachlor (*32*). In contrast no differences in desorption rates of freshly applied and aged residues of trifluralin were found 10 months after treatment (*33*).

TABLE 3.

a. Duplicate Desorption Rate Constants (±SE) of the Slowly (k_s) and Very Slowly (k_{vs}) Desorbing Fractions for CBs and PCBs in the Top Layer Sediment[a,b]

CBs	k_s (in 10^{-3} h^{-1})	k_{vs} (in 10^{-3} h^{-1})	CBs	k_s (in 10^{-3} h^{-1})	k_{vs} (in 10^{-3} h^{-1})
12-DCB[b]	8.0 ± 0.6 5.7 ± 0.5	0.131 ± 0.003 0.093 ± 0.004	1234-TeCB[b]	4.6 ± 0.4 7.0 ± 0.8	0.14 ± 0.005 0.176 ± 0.003
13-DCB[a]		0.35 ± 0.02 0.30 ± 0.018	1235-TeCB[a]		0.360 ± 0.011 0.385 ± 0.012
14-DCB[b]	5.1 ± 0.6 3.4 ± 0.4	0.16 ± 0.02 0.10 ± 0.02	1245-TeCB[a]		0.192 ± 0.009 0.213 ± 0.007
123-TCB[a]		0.567 ± 0.01 0.547 ± 0.005	QCB[a]		0.264 ± 0.003 0.286 ± 0.002
124-TCB[b]	4.5 ± 0.4 4.5 ± 0.3	0.132 ± 0.005 0.115 ± 0.003	HCB[b]	3.7 ± 0.2 3.2 ± 0.3	0.134 ± 0.003
135-TCB[b]	6.1 ± 0.9 5.0 ± 0.6	0.152 ± 0.006 0.100 ± 0.007			

b. Duplicate Desorption Rate Constants (±SE) of the Very Slowly (k_{vs}) Desorbing Fraction for CBs, PCBs, and PAHs in the Sediment Core[d]

CBs	k_{vs} (in 10^{-3} h^{-1})	HCB, PCBs, and PAHs	k_{vs} (in 10^{-3} h^{-1})
12-DCB	0.55 ± 0.03 0.45 ± 0.02	HCB	0.288 ± 0.009 0.283 ± 0.014
14-DCB	0.57 ± 0.03 0.51 ± 0.03	PCB-28	0.21 ± 0.02 0.19 ± 0.02
123-TCB	0.34 ± 0.02 0.300 ± 0.005	BiPHEN[c]	0.32−0.4 0.37−0.45
124-TCB	0.245 ± 0.013 0.240 ± 0.007	2-MN[c]	0.17 0.16
135-TCB	0.24 ± 0.02 0.214 ± 0.011	FLUE[c]	0.31 0.27
1234-TeCB	0.246 ± 0.011 0.223 ± 0.006		
QCB	0.339 ± 0.007 0.39 ± 0.02		

[a] Data for these compounds were obtained with a one-compartment model. [b] Data for these compounds were obtained with a two-compartment model. [c] Order of magnitude estimate of k_{vs} (see text). [d] Data were obtained using a one-compartment model.

Low desorption rate constants for field contaminated sediments were reported earlier: values of $(2-7) \times 10^{-4}$ h^{-1} were reported for DDD, DDE, and DDT (*34*); for PCBs in a historically contaminated sediment rate constants were $(1.27-3.62) \times 10^{-3}$ (*13*). Most studies with field contaminated sediment containing chlorinated compounds show measurable amounts desorbing from the fast fraction: Oliver (*12*) observed fractions of 20% and Cornelissen (*20*) found fractions of ±30%. More recent evidence that desorption from field contaminated sediments is slow compared to freshly added compounds has been presented by Chen et al. (*35*) and Lamoureux et al. (*36*). This supports our observations of slow desorption.

Although in most of the cases described above substantial amounts of slowly desorbing fractions were present in field contaminated sediments, a direct comparison between these observations is difficult. This can be attributed to the use of different techniques to study desorption, but the total contamination of the studied field sediments may also influence desorption kinetics. Recently it has been shown that sediment has a limited resistant sorption capacity. When this desorption resistant compartment is filled, any excess contaminant present will desorb rapidly (*37*−*39*). The presence of other contaminants (such as oil) may perhaps explain why in some of the cases presented above substantial fractions desorbed rapidly, while in our case no measurable fast desorbing fractions were found, even after equally long contact times in the field. The variations in organic matter origin and history between the sediments studied may also explain some of the differences.

Because the very slowly desorbing compartment seems to increase with contact time in the field (see Figure 4), it may be concluded that this sorbed state is thermodynamically more favorable than the slow compartment. $\Delta G°$ for transition from the slowly to the very slowly desorbing compartment was calculated from the observed ratio of slowly and very slowly desorbing fractions using $\Delta G° = -RT \ln K$ (in which K is the ratio of slowly and very slowly desorbing fractions from Figure 4, T = absolute temperature, and R = gas constant: 8.314 Pa m^3 mol^{-1} K^{-1}). For CBs and PCBs $\Delta G°$-values averaged -5.2 ± 0.8 kJ/mol for the top layer sediment and -10.99 ± 0.13 kJ/mol for all compounds in the sediment core. These values indicate that in the sediment core CBs and PCBs are closer to equilibrium than in the top layer sediment. Furthermore $\Delta G°$-values show much less variation between compounds in the core than in the top layer sediment.

The presence of large very slowly desorbing fractions may be caused by the presence of different (more dense) regions in the organic carbon of the sediment from which “trapped” contaminants cannot be easily desorbed. The relatively constant desorption rates we observed for different types of compounds points to a mechanism that is driven by sediment properties and not by compound properties. Our data on very slow desorption do not support a diffusion process because in that case a trend with molecular weight or hydrophobicity is expected, and we did not observe this.

Field Distribution Coefficients. For PCB-118 and all PAHs organic carbon normalized sediment-water distribution coefficients (K_{oc} in L (kg oc)$^{-1}$) were calculated from the concentration in sediment and the part of the desorption curve for which a constant concentration in water was calculated. The decrease in sorbed concentrations caused by purging the suspension and the variation in water

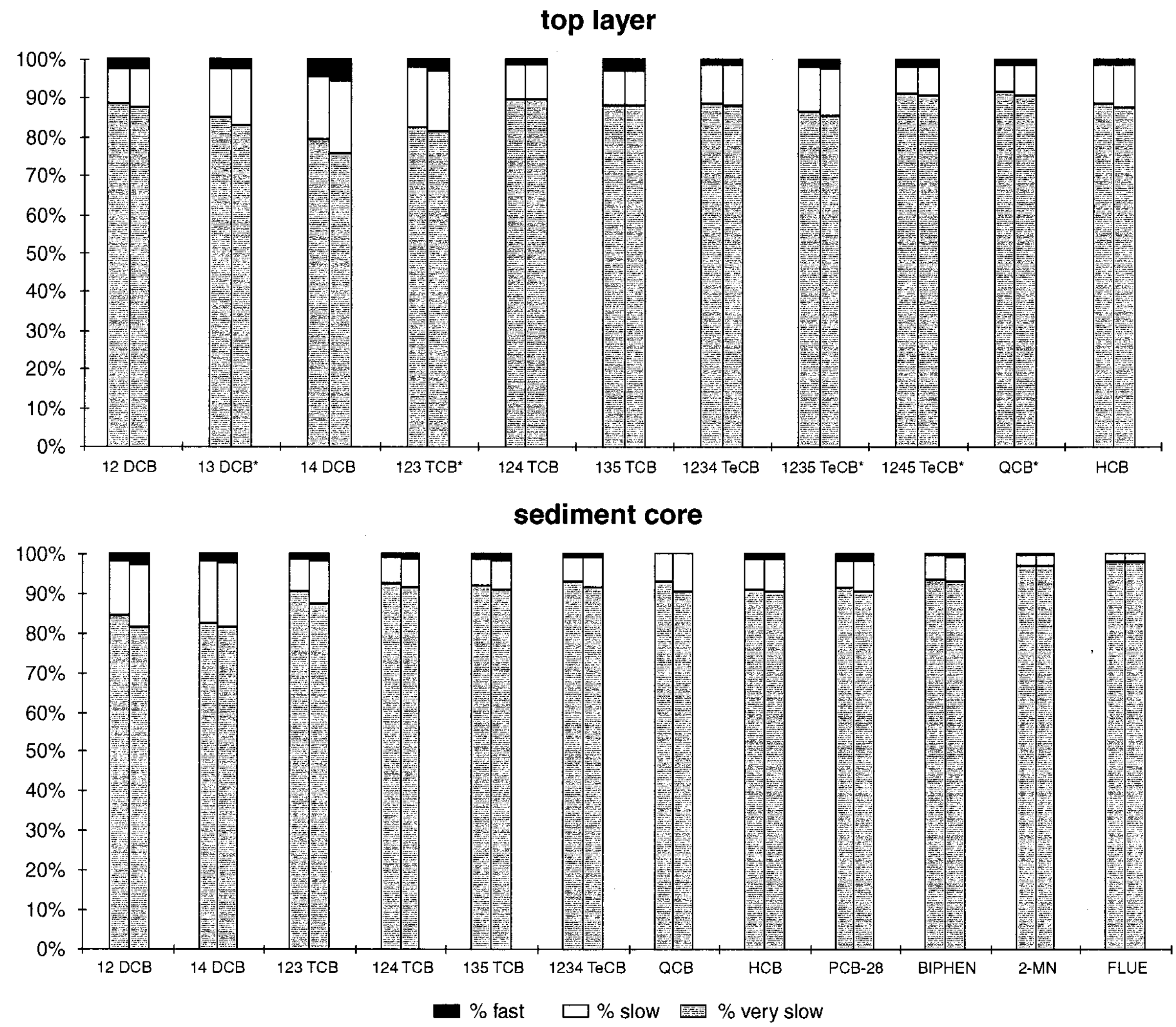

FIGURE 4. Fast, slow, and very slow fractions (duplicates) for CBs, PCBs, and PAHs in the top layer sediment and sediment core. All fast fractions were upper limits, deduced from the desorption curves. For the sediment core and top layer compounds indicated by * slow fractions were also estimated as upper limits. All other fractions were obtained directly from one- or two-phase models (see text).

TABLE 4. Field Distribution Coefficients (log K_{oc}, in log(L (kg oc)$^{-1}$) and Selected Literature Values for log K_{oc} for Six PAHs and PCB-118^a

	log K_{oc}	n	literature	method
BiPHEN	6.10 ± 0.14	15	3.03 (*40*)	batch equilibration, average for 5 soils
	5.99 ± 0.18	15		
2-MN	7.05 ± 0.14	15	3.93 (*41*)	batch equilibration (2 days)
	7.00 ± 0.17	15	3.40 (*42*)	batch equilibration (2 h)
FLUE	6.52 ± 0.15	15	4.07 (*43*)	average of compiled values
	6.45 ± 0.15	13	4.11 (*17*)	batch equilibration (2 days), DOC corrected
PHE	6.65 ± 0.14	12	4.36 (*44*)	batch equilibration (2–3 days), average for 12 soils and sediments
	6.53 ± 0.19	12	4.22 (*28*)	batch equilibration (2 days) with Ketelmeer sediment, DOC influence negligible
			4.28 (*42*)	batch equilibration (2 h)
FLUO	6.44 ± 0.14	9	5.56 (*17*)	batch equilibration (2 days), DOC corrected
	6.23 ± 0.16	9	5.4 (*25*)	gas purge with Ketelmeer sediment
			4.89 (*28*)	see remark at PHE
PYR	6.98 ± 0.20	8	4.95 (*28*)	see remark at PHE
	6.61 ± 0.29	8	5.13 (*42*)	batch equilibration (2 h)
PCB-118	6.93 ± 0.04	3	5.81 (*45*)	batch equilibration (2–19 h)
	6.79 ± 0.08	5	5.92 (*17*)	batch equilibration (2 days), DOC corrected

concentration were taken into account. The distribution coefficients were calculated for each measurement interval separately and averaged.

Log K_{oc}-values are presented in Table 4, together with literature values. Literature values were selected based on experiments in which sediments or soils were spiked and short contact times were employed, so that a large fraction of the added components was expected to be present in the fast desorbing pool (*17*). In an earlier study we have shown that higher in situ partition coefficients can be explained by the presence of slowly exchanging fractions (*21*). The methods used for measuring the log K_{oc} values are indicated in Table 4. The calculated distribution coefficients were 1−3 orders of magnitude higher than literature values, suggesting the presence of a very small, fast desorbing fraction both for PAHs and PCBs (*4*). This is in accordance with the observations in our desorption experiments for the compounds with high volatilization rates, in which no detectable fast fractions were present, and very small fast fractions were deduced from the desorption curves.

Comparison of the results from our study with results from other studies indicates that desorption from field sediments may not readily be predicted from results obtained in lab experiments: the presence of large amounts of very slowly desorbing fractions has only been reported once in a study using lab contaminated sediment and an elevated temperature (*16*). Our findings demonstrate that after very long contact times (decades) the resistant fraction may consist mainly of a (thermodynamically more favorable) very slowly desorbing fraction (rate constants of $10^{-4}-10^{-5}$ h^{-1}). This may apply to all (hydrophobic) contaminants that are introduced into aquatic sediments.

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