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DESORPTION KINETICS OF CHLOROBENZENES, POLYCYCLIC AROMATIC HYDROCARBONS, AND POLYCHLORINATED BIPHENYLS: SEDIMENT EXTRACTION WITH TENAX® AND EFFECTS OF CONTACT TIME AND SOLUTE HYDROPHOBICITY

GERARD CORNELISSEN,† PAUL C. M. VAN NOOT† and HARRIE A. J. GOVERS‡
†Institute for Inland Water Management and Waste Water Treatment, Lelystad, The Netherlands
‡Department of Environmental and Toxicological Chemistry, ARISE, University of Amsterdam, Amsterdam, The Netherlands

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Abstract—A technique using Tenax TA® beads as “sink” for desorbed solute was employed to measure the kinetics of desorption of chlorobenzenes, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons from laboratory-contaminated sediment. First-order rate constants of rapid and slow desorption were in the order of 10^{-1} to 10^{-2} h^{-1} and 10^{-2} to 10^{-3} h^{-1}, respectively. The rate constants of slow desorption correlate well with the molecular volumes of the compounds used and decrease between 2 and 34 d of equilibration. Slowly desorbing fractions increase with both increasing solute hydrophobicity and increasing equilibration time.

Keywords—Desorption kinetics  Sediment  Aging  Organic compounds  Sorption coefficients

INTRODUCTION

The desorption of organic chemicals from sediments is often considered to occur in two stages, the rapid release of a “labile” sorbed fraction, followed by the slow release of a “nonlabile” fraction. The mechanistic explanation usually suggested to account for the kinetic limitations in the desorption of the nonlabile fraction is slow diffusion within the sediment particles [1]. The two ways of diffusional retardation considered most realistic are intraorganic matter diffusion, which is diffusion through the organic matter matrix [2–4], and micropore diffusion, which is diffusion through and along the walls of narrow intraparticle pores that are possibly coated with hydrophobic material [5,6]. Also, slow desorption has been attributed to entrapment in micropores in combination with slow diffusion through such narrow pores [7]. In all diffusion mechanisms, the rapidly desorbing fraction is interpreted to be present in the outer regions of the sediment aggregates, i.e., the parts in close contact with the aqueous phase. Recently Pignatello and Xing [1] published a clear review on these mechanistic aspects.

There is a high degree of variation in the magnitude of reported rate constants for rapid and slow desorption. Reported rate constants for the desorption from the nonlabile phase range from 10^{-1} to 10^{-2} h^{-1} [6,8–11] to 10^{-3} to 10^{-4} h^{-1} [12,13]. Other authors reported values between these extremes [3,14–19]. For the desorption of the labile fraction, some researchers assumed equilibrium between the water in a sediment suspension and the rapidly desorbing fraction [2–4,20]. Others, however, considered the kinetic aspects of the desorption of this rapidly desorbing fraction and reported rate constants of approximately 10^{-1} h^{-1} [15].

The two purposes of the present study were to determine rapid and slow desorption kinetics after two different equilibration times and to relate slow desorption rate constants to molecular properties.

Desorption kinetics are given for a range of compounds, including chlorobenzenes, polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs). Especially for the higher-molecular-weight PAHs, hardly any data on the kinetics of slow desorption have been reported so far because these nonvolatile compounds are not well extractable with conventional gas-purge desorption techniques. We therefore used an extended version of a very rapid extraction method reported by Pignatello [21] in which the aqueous phase is kept solute-free by means of extraction with Tenax TA® beads. A similar method was used by Carroll et al. [22], who used XAD-4 resin as a PCB adsorbent.

EXPERIMENTAL METHODS

We used 1,2,3,4-tetrachlorobenzene (TeCB) (>98% pure) and pentachlorobenzene (QCB) (>98% pure) from E. Merck (Amsterdam, The Netherlands); hexachlorobenzene (HCB) (>97% pure) and fluoranthene (99%) from Aldrich Chemical Company (Bornem, Belgium); 2,3,5,6-tetrachlorobiphenyl (PCB-65) (99% pure), 2,3’,4’,5-pentachlorobiphenyl (PCB-118) (98% pure), hexane and acetone (both nanograde), as well as acetonitrile (high-performance liquid chromatography [HPLC] grade) from Promochem (Molsheim, France); fluorene, anthracene, and pyrene (all >99% pure) from Sigma Chemical Company (St. Louis, MO, USA); methanol (HPLC reagent) and HgCl2 (Baker grade) from J. T. Baker, Inc. (Deventer, The Netherlands); and Tenax TA (60–80 mesh; 177±263 mm) by Chrompack (Bergen op Zoom, The Netherlands). Tenax is a porous polymer based on 2,6-diphenyl-p-phenylene oxide. Prior to use, the Tenax TA beads were rinsed with acetone (3 × 10 ml/g Tenax) and hexane (3 × 10 ml/g Tenax) and dried overnight in the air at 75°C.

The sediment was from Lake Oostvaardersplassen (OVP), The Netherlands. The sediment was dried at 150°C for 5 d to remove remaining organic contaminants as well as a number of unidentified components that disturb the chromatographic analyses. The organic carbon content remained unchanged upon drying. The background amounts of the test compounds in the OVP sediment still present after drying proved to be
far lower (1% or less) than the laboratory-added concentrations. After drying the sediment was homogenized and dry-sieved. The 63- to 125-µm fraction was used. This was done to prevent differences resulting from possible particle size differences between subsamples. However, this renders the translatability to the whole sediment more difficult. The fraction of organic carbon, \( f_{\text{oc}} \), of the used sediment fraction was determined to be 3.17 ± 0.05% using an element analyzer (Carlo Elba NA 1500, Milan, Italy) after removal of carbonates with phosphoric acid.

All experiments were carried out at 20°C. Water was contaminated at test compound levels of 1 to 100 µg/L by means of spiking with 50 µL/L methanol containing the test compounds. Sediment (0.6 g) was brought together with 250 ml of contaminated water in 250-ml conical flasks, leaving only approx. 10 ml of headspace. In this way, evaporation was avoided (less than 20% of the compound masses was lost in 34 d, giving mass balances above 80% for the incubations). HgCl₂ (1.25 mg) was added to prevent microbial degradation. Contact times were 2 and 34 d. During equilibration the flasks were shaken continuously. It is assumed that the low amounts of methanol and HgCl₂ do not affect sorption kinetics; the former because methanol has only a low tendency to accumulate in sediment, and the latter because the number of metal ions present in 600 mg of sediment is probably large compared with the added amount of HgCl₂ (1.25 mg).

Sediment and supernatant water were separated by centrifugation at 2,500 rpm for 20 min. Aqueous contaminant concentrations were determined by extracting 20 ml of water with 2 ml of hexane and subsequently analyzing the hexane with gas chromatography–electron capture detection (GC–ECD) for the chlorobenzenes and PCBs (Hewlett Packard 5890 with 63Ni ECD and Hewlett Packard 7673 autosampler; column: Chrompack, fused silica CP sil 8cb, 1 m, φ = 0.25 mm; carrier gas: He [Groenband high-purity], 1 ml/min; makeup gas: N₂ [Groenband high-purity], 60 ml/min). For the PAHs, the hexane was evaporated until 1 ml was left and then dissolved in 10 ml of acetonitrile. The acetonitrile was subsequently evaporated to 1 ml. Analysis was carried out with HPLC–fluorescence detection (Hewlett Packard 1050 with fluorescence detector; Hewlett Packard 1046); column: reversed-phase C₁₈ [Vydac 210TP54]; gradient elution: with acetonitrile and water). The dissolved organic carbon (DOC) content of the supernatant water was determined in separate sediment suspensions without methanol or test compounds using a Beckman 914B total organic carbon (TOC) analyzer. It is assumed that the low amounts of methanol in the spiked solutions do not affect the generation of DOC because of the low organic carbon affinity of methanol.

For the determination of mass balances and sediment/water distribution ratios \( K_{\text{oc}} \), the total concentration in the sediments was measured for half of the incubated sediments (triplicate measurements). The other sediment suspensions were used for the measurement of desorption kinetics. To measure the total sediment concentrations, the sediment residues were reflushed with 50 ml of hexane for 6 h; the hexane was analyzed by GC–ECD and HPLC–FCD as described above. \( K_{\text{oc}} \) values (L/kg) are the ratios of sediment and aqueous concentrations, normalized to the actual \( f_{\text{oc}} \) values after incubation. These \( f_{\text{oc}} \) values differ from the original \( f_{\text{oc}} \) values because of DOC release during incubation. They are calculated from the original \( f_{\text{oc}} \) and the amounts of DOC released. \( K_{\text{oc}} \) values were corrected for sorption by DOC. Equation 5 in Koelmans [23] was used to calculate the distribution ratios between DOC and water, \( K_{\text{DOC}} \). This assumes that the DOC-corrected \( K_{\text{oc}} \) value, \( K_{\text{oc}}^{\text{app}} \), is the same in two sediment suspensions with different DOC contents (see Eqn. 5 in Koelmans [23]). In this case, \( K_{\text{oc}}^{\text{app}} \) probably does not remain completely constant between 2 and 34 d because of aging effects. However, the effect of this uncertainty will probably be insignificant for the resultant DOC-corrected \( K_{\text{oc}}^{\text{app}} \) values.

The kinetics of desorption were determined by means of the Tenax extraction method described in the next section. After approx. 300 h, desorption was terminated, and the remaining sediment suspensions were reflushed with 50 ml of hexane for 6 h to extract and analyze all chlorobenzenes, PCBs, and PAHs still present in the sediment. The hexane was analyzed as described above.

**Desorption experiments using Tenax beads**

Desorption kinetics were measured in duplicate. Contaminated sediment (0.6 g), 100 ml of water, 1.25 mg of HgCl₂, and 0.2 g of Tenax beads were brought into a separation funnel. The funnel was continuously shaken at 20°C at such a rate that the sediment and Tenax beads were well dispersed.

At selected times, the Tenax was separated from the sediment suspension and analyzed; fresh Tenax was added to the sediment suspension. Separation of Tenax from the sediment suspension was easy and rapid because the sediment sank to the bottom, whereas the Tenax beads floated on top and adhered to the glass wall of the separation funnel during separation. The Tenax residues were extracted by shaking with 10 ml of hexane, after which the hexane was analyzed as described. Amounts of organic carbon (measured as TOC) remaining with the Tenax residues and extracted along with the Tenax were below 0.2% of the total amount of organic carbon present.

Rates of extraction from the aqueous phase, \( k_{\text{extr}} \) (per h), were measured in separate experiments without any sediment. In these experiments, we used 100 ml of water contaminated at levels comparable to those used in the desorption experiments (1–100 µg/L). Extractions were carried out with 0.2 g of Tenax for 5 min and in triplicate. After 5 min, Tenax and water were separated; the Tenax and water were extracted as described above, and values for \( k_{\text{extr}} \) were calculated. The values for \( k_{\text{extr}} \) were 15 to 21/h.

Recoveries for the extraction of Tenax with hexane were determined by extracting Milli-Q® water containing known solute concentrations with Tenax (triplicate measurements). The Tenax was separated from the water and extracted with hexane for analysis. Recoveries were 90 to 110%.

For the desorption experiments, the mass balances (ratios between the sum of the masses of solute desorbed and solute present after desorption and total initial mass of solute) were 80 to 120%.

**Sorption capacity of Tenax TA**

Pignatello [21] has shown that the sorption capacity of Tenax beads is adequate to serve as sink for compounds desorbed from sediment. In the present study, the added amount of 0.2 g of Tenax rendered sufficient adsorption capacity to extract organic compounds from 0.02 g of organic carbon present in 0.6 g of sediment because the compound affinity for Tenax is approximately equal to that of organic carbon \( K_{\text{Tenax}} = 10^4 \) L/kg and the compound concentrations on Tenax remain low compared with those on the sediment because fresh
Desorption kinetics of chlorobenzenes, PCBs, and PAHs

Environ. Toxicol. Chem. 16, 1997 1353

Table 1. Log $K_{oc,app}$ (L/kg) values after 2 and 34 d of equilibrationa

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<td>4.67</td>
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<td>5.19</td>
</tr>
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<td>5.50</td>
</tr>
<tr>
<td>Fluorene</td>
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<td>Pyrene</td>
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a Batch-measured values and values corrected for DOC solubility enhancements, along with literature values, are presented.

b HCB = hexachlorobenzene; PCB 65 = 2,3,5,6-tetrachlorobiphenyl; PCB 118 = 2,3',4,4',5-pentachlorobiphenyl; QCB = pentachlorobenzene; TeCB = 1,2,3,4-tetrachlorobenzene.

c Batch measured and probably suffering from incomplete phase separation.

d Gas-purge measured and not suffering from incomplete phase separation.

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c Batch measured and probably suffering from incomplete phase separation.

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Tenax is added many times in each experiment. Aqueous concentrations in equilibrium with 0.2 g of Tenax can be calculated to be 100 to 700 times lower than aqueous concentrations in equilibrium with 0.02 g of organic carbon.

Data interpretation

The desorption from sediment is described with two sediment compartments and a water compartment in the following way:

$$ S_i/S_{oc} = F_{aq} e^{-k_{oc} t} + F_{rap} e^{-k_{rap} t} + F_{slow} e^{-k_{slow} t} $$  (1)

in which

- $S_i$ and $S_{oc}$ (μg) = the sediment-sorbed amounts at time $t$ (h) and at the start of the experiment, respectively
- $F_{aq}$ = the fractions of contaminant present in the aqueous phase and in the rapidly and slowly desorbing sediment compartment at time zero, respectively
- $k_{rap}$ and $k_{slow}$ (per h) = the rate constants of rapid and slow desorption, respectively

$k_{rap}$ is determined in separate experiments (see previous section). The water-dissolved fraction, $F_{aq}$, can be calculated with [24]

$$ F_{aq} = 1/(1 + K_f D) $$  (2)

where

- $D$ = the sediment concentration in water (kg/L)
- $K_f$ = the distribution ratio (L/kg), and
- $K_f D$ = the dimensionless distribution ratio

$K_f D$ values were calculated with the $K_{oc,app}$ values measured in the present study. The 2-d $K_{oc,app}$ values were used because these probably approximate short-term equilibrium in the best way.

Values of $F_{rap}$, $F_{slow}$, $k_{rap}$, and $k_{slow}$ were determined by minimizing the cumulative squared residuals between experimental and calculated values of ln($S_i/S_{oc}$) in Equation 1.

RESULTS

$K_{oc,app}$ values

The DOC concentrations were 11.4 ± 0.2 mg/L after 2 d and 45 ± 4 mg/L after 34 d of equilibration, respectively. The higher DOC concentration after 34 d shows that DOC is slowly released from the sediment during equilibration. The DOC concentrations of 11.4 and 45 mg/L in 250 ml of water show that a significant fraction of the initially present organic carbon is released into the aqueous phase during equilibration (15% after 2 d and 59% after 34 d, respectively). The calculated remaining $f_{oc}$ values are 2.70 ± 0.07% after 2 d and 1.30 ± 0.10% after 34 d. These $f_{oc}$ values were used for calculation of $K_{oc,app}$. The $K_{oc,app}$ values were also corrected for sorption by DOC. The calculated value for $K_{oc,app}$ (with Eqn. 5 from Koelmans [23]) used for this correction was 0.15 × $K_{oc}$. This value is in agreement with literature values for $K_{oc,app}$ of 0.1 × $K_{oc}$ [25], 0.14 to 0.20 × $K_{oc}$ [26], and 0.44 × $K_{oc}$ [16]. In Table 1, batch-measured and DOC-corrected $K_{oc,app}$ values are presented for the equilibration times of 2 and 34 d (triplicate measurements). Standard deviations in the measured values are cumulatives of the SDs in the triplicate measurements, in the original $f_{oc}$, and in the DOC values used to calculate $f_{oc}$ after equilibration.

Literature $K_{oc,app}$ values are also presented; these are all measured values for laboratory-contaminated sediments. For the literature values it is also indicated whether values were measured by the separation of sediment and water (batch technique; probably suffering from incomplete separation of the water and sediment phases) or by a gas-purge technique (not suffering from incomplete phase separation). The values measured in the present study are reasonably in accordance with the literature values, although different sediments were used.

Desorption kinetics

In Figure 1a and b, ln($S_i/S_{oc}$) versus time is given for the desorption of some of the studied compounds after 2 and 34 d of equilibration, respectively. The solid lines were obtained by curve fitting. In Figure 2, the first 6 h of the 34-d desorption curves are given. The rate constants for rapid and slow de-
Fig. 1. (a) \(\ln(S_t/S_0)\) as a function of time after 2 d of equilibration for 1,2,3,4-tetrachlorobenzene (TeCB), pentachlorobenzene (QCB), and 2,3',4,4',5-pentachlorobiphenyl (PCB-118). Solid lines are fits obtained with a two-compartment model. (b) \(\ln(S_t/S_0)\) as a function of time after 34 d of equilibration for TeCB, PCB-118, anthracene, and fluoranthene. Solid lines are fits obtained with a two-compartment model.

**Table 2.** Rate constants of rapid and slow desorption (\(k_{rap}\) and \(k_{slow}\), respectively) as well as the percentages slowly desorbing (\(F_{slow}\)) are presented in Table 2. Each value in Table 2 is the average of duplicate measurements; differences between duplicates were 10% or less.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(k_{rap}) (per h)</th>
<th>(k_{slow}) (10(^{-2})h)</th>
<th>(F_{slow}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 d</td>
<td>34 d</td>
<td>Literature</td>
</tr>
<tr>
<td>TeCB</td>
<td>0.369</td>
<td>0.317</td>
<td>0.16 [15]</td>
</tr>
<tr>
<td>QCB</td>
<td>0.312</td>
<td>0.285</td>
<td>0.067 [15]</td>
</tr>
<tr>
<td>HCB</td>
<td>0.243</td>
<td>0.216</td>
<td>0.045 [15]</td>
</tr>
<tr>
<td>PCB 65</td>
<td>0.058</td>
<td>0.117</td>
<td>—</td>
</tr>
<tr>
<td>PCB 118</td>
<td>0.045</td>
<td>0.112</td>
<td>—</td>
</tr>
<tr>
<td>Fluorene</td>
<td>—</td>
<td>0.404</td>
<td>—</td>
</tr>
<tr>
<td>Anthracene</td>
<td>—</td>
<td>0.320</td>
<td>—</td>
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<tr>
<td>Fluoranthene</td>
<td>—</td>
<td>0.202</td>
<td>—</td>
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<tr>
<td>Pyrene</td>
<td>—</td>
<td>0.163</td>
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</table>

* Literature values are also presented.

HCB = hexachlorobenzene; PCB 65 = 2,3,5,6-tetrachlorobiphenyl; PCB 118 = 2,3',4,4',5-pentachlorobiphenyl; QCB = pentachlorobenzene; TeCB = 1,2,3,4-tetrachlorobenzene.

\(^a\) Equilibration time = 3–6 d.

\(^b\) Equilibration time = 15–28 d.

\(^c\) Measured for 2,6,2',6'-tetrachlorobiphenyl.

**DISCUSSION**

**K\(_oc\)\(^{app}\) values**

\(K\(_oc\)\(^{app}\) values corrected for DOC effects are markedly higher after 34 d than after 2 d (by a factor of 1.3–2.9). Two reasons can be given for this observation, aging, leading to deeper penetration into remote sediment parts after prolonged equilibration (\(F_{rap}\) also decreases by a factor of 1.05–2.0), and a lower polarity of the sediment organic carbon after 34 d compared with 2 d because of the dissolution of relatively polar parts of the organic carbon. Increasing \(K\(_oc\)\(^{app}\) values with increasing equilibration time have been reported [7,11,27–30].

Sorption by DOC may have affected the magnitude of some literature \(K\(_oc\)\) values for QCB and HCB (Table 1); those measured by means of gas-purge (not sensitive to DOC effects) are higher than the ones measured by a batch technique.

**Desorption parameters**

The values for \(k_{slow}\) observed in the present study are in accordance with some literature values for pesticides and relatively volatile chlorobenzenes (HCB, QCB, and pyrene [10]; picloram [11]; chlorobenzenes [15]; TeCB and HCB [16]; and some pesticides [19]) but are rather high compared with others in the order of 10\(^{-5}\) to 10\(^{-7}\) h (PAHs [12,13] and naphthalene
In the case of relatively nonvolatile solutes, a reason for relatively low rate constants of slow desorption obtained by gas-purge experiments may be that the combination of Henry's constant and the magnitude of the gas flow sometimes is not high enough to render the sediment desorption rate the limiting factor in the purge rate.

The three compartments used to fit the data (water and two sediment compartments) can be distinguished in Figures 1 and 2. The initial part, roughly during the first 15 min, is the depletion of the aqueous phase; the second part, 15 min to 10 h, is the depletion of the rapid sediment compartment; and the last part, 10 to 300 h, depicts the desorption from the slow sediment compartment. The three compound classes (PAHs, PCBs, and chlorobenzenes) were observed to exhibit rate constants of rapid and slow desorption in the same order of magnitude.

For backward adsorption from the water to the rapid sediment compartment is negligible when measured rapid desorption rate constants are much lower than rate constants limited by Tenax extraction of the water. The maximum extraction rate constants by Tenax for sorbed solute are equal to \( k_{\text{app}} \) (see also Eqn. 2). These values are a factor of 3 to 10 higher than \( k_{\text{rap}} \). This means that rapid desorption, not Tenax extraction, is limiting during the rapid-desorption phase, but only by a factor of 3 to 10. As a result, backward adsorption to the rapid compartment cannot be completely ruled out, and, therefore, the reported values of \( k_{\text{rap}} \) (Table 2) should be regarded as somewhat lower limits.

For backward adsorption to the slow compartment to be negligible, the adsorption rate from the rapid to the slow compartment (\( k_{\text{ads}} A_{\text{rap}} \), where \( k_{\text{ads}} \) = the rate constant of slow adsorption and \( A_{\text{rap}} \) = the amount present in the rapid fraction) needs to be much lower than the desorption rate from the slow compartment (\( k_{\text{slow}} A_{\text{slow}} \), where \( c_{\text{slow}} \) = the amount present in the slow fraction). During the slow desorption phase, the rapid compartment is so far depleted that \( A_{\text{rap}} \) is in equilibrium with the aqueous phase, which in turn is in equilibrium with the Tenax. \( A_{\text{rap}} \) can be calculated from the amounts sorbed to the Tenax (which are low because the Tenax is refreshed several times), \( K_{\text{Tenax}} \) and \( K_{\text{app}} \). An estimate for \( k_{\text{ads}} A_{\text{rap}} \) can be obtained from the slow fractions after 2 and 34 d of equilibration. Because of potential desorption during the adsorption phase, these values for \( k_{\text{ads}} A_{\text{rap}} \) are lower limits. \( A_{\text{slow}} \) is the amount that is still sorbed after time \( t \), and \( k_{\text{slow}} \) is obtained from Table 2. It turns out that rates of slow adsorption (ng/h) are 10 to 400 times lower than rates of slow desorption (ng/h).

**Hydrophobicity effects**

The slow fractions, \( F_{\text{slow}} \), are observed to increase with increasing test compound hydrophobicity (Tables 1 and 2). In Figure 3 the logarithm of the ratio between the fractions in the slow and in the rapid sediment compartments, \( \log(F_{\text{slow}}/F_{\text{rap}}) \), is plotted as a function of \( \log K_{\text{oc}} \) (both after 34 d of equilibration). The plot shows that \( F_{\text{slow}}/F_{\text{rap}} \) increases with increasing hydrophobicity (\( r^2 = 0.96 \)). Assuming that a certain degree of equilibrium between the rapid and slow sediment compartments has been established after 34 d, this probably reflects a lower polarity of the slowly exchanging sediment compartment relative to the rapidly exchanging one. This is in accordance with the concept of the exterior of sediment particles as the rapidly exchanging compartment: organic material at the sediment–water interface is probably more polar than organic material that is not in direct contact with the water. The interior of relatively low polarity can be envisioned as the remote parts of the organic matter or as hydrophobic wall coatings in deep pores.

From the present study, it cannot be concluded whether \( k_{\text{slow}} \) is dependent on hydrophobicity or not, although the correlation between \( k_{\text{slow}} \) and \( K_{\text{oc}} \) is significant (t test at a 95% confidence level; \( r^2 = 0.58 \)). Schrap et al. [15] and Knaebel et al. [32] observed that \( k_{\text{slow}} \) hardly depended on hydrophobicity, whereas Brusseau et al. [2–4], Karickhoff and Morris [10] as well as Helmstetter and Alden [12] did report such a dependence.

If some kind of diffusion is the explanation for the slow desorption of organic compounds from sediment, \( k_{\text{slow}} \) should be dependent on the size of molecules because larger solutes diffuse more slowly through the macromolecular organic matter matrix or through narrow micropores [33–34]. \( k_{\text{slow}} \) does exhibit a correlation with the molecular volume (Fig. 4; molecular volume from Mackay et al. [35] and \( k_{\text{slow}} \) after 34 d; \( r^2 = 0.89 \)), so in this respect the current results are in accordance with a slow diffusion process.

![Fig. 3. log(Fslow/Frap), the ratio between the amounts in the slow and rapid sediment compartment, respectively, as a function of log Koc after 34 d of equilibration. The solid line and the correlation coefficient were obtained by linear regression.](image)

![Fig. 4. kslow (per h) versus molecular volume (cm³/mol) with the linear regression line and the correlation coefficient.](image)
Effect of equilibration time

$k_{\text{slow}}$ is observed to decrease with increasing equilibration time (by a factor 1.3–2.6 between 2 and 34 d; Table 2), while $F_{\text{slow}}$ slightly increases (by a factor 1.4–3.1; Table 2). The combination of an increase in $F_{\text{slow}}$ and a decrease in $k_{\text{slow}}$ for slow does not increase linearly in time between 2 and 34 d.

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REFERENCES

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