Mechanism and consequences of slow desorption of organic compounds from sediments

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Part II:

Slow desorption and sediment characteristics
Slow desorption of PCBs and chlorobenzenes from soils and sediments: relations with sorbent and sorbate characteristics

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Chapter 6

Abstract

The kinetics of slow desorption were studied for 4 soils and 4 sediments with widely varying characteristics (organic carbon (OC) content 0.5-50%, organic matter (OM) aromatic content 7-37%), for 3 chlorobenzenes and 5 PCBs. Slowly and very slowly desorbing fractions ranged from 1-50% (slow) and 3-40% (very slow) of the total amount sorbed, and were observed for all compounds and all soils and sediments. In spite of the wide variations in sorbate $K_{ow}$ (factor 1000) and sorbent characteristics, the rate constants of slow ($k_{slow}$, around $10^{-3}$ h$^{-1}$) and very slow ($k_{very slow}$, $10^{-5}$-$10^{-4}$ h$^{-1}$) desorption appeared to be rather constant among the sorbates and sorbents (both within a factor of 5). There was a good correlation ($r^2$ above 0.9) between the distribution over the slow, very slow and rapid sediment fractions and log $K_{OC}$, indicating that sorbate hydrophobicity may be important for this distribution. No correlation could be found between sorbent characteristics (organic carbon (OC), N, and O in the organic matter, polarity index C/(N+O), OC aromaticity as determined by CP-MAS $^{13}$C-NMR) and slow desorption parameters (slowly/very slowly desorbing fractions + corresponding rate constants). The absence of i) a correlation between $k_{slow}$ and $k_{very slow}$, respectively, and OC content, and ii) the narrow range of $k_{slow}$ and $k_{very slow}$ values, indicate that intra-organic matter diffusion is not the mechanism of slow or very slow desorption, because on the basis of this mechanism it would be expected that increasing OC content would lead to longer diffusion pathlengths and, consequently, to smaller rate constants.

In addition, it was tested whether Differential Scanning Calorimetry (DSC) would reveal a glass transition in the soils/sediments. In spite of the sensitivity of the equipment used (changes in heat flow in the micro-Watt range were measurable), a glass transition was not observed. This means that activation enthalpies of slow desorption can be calculated from desorption measurements at various temperatures; in the present study these values ranged from 60-100 kJ/mol among the various soils and sediments studied.

Introduction

In many studies, slow desorption kinetics of organic substances in soils and sediments have been reported. Even after short equilibration periods, significant slow desorption has been observed [Kan et al.1994, 1998, Cornelissen et al. 1997b]. It is presently unclear what process causes these kinetic limitations in the sorbent-water exchange.
Sorbent and sorbate characteristics

One hypothesis is slow diffusion through the sediment particle, including slow diffusion through micropores [Ball and Roberts 1991, Steinberg et al. 1987] or through the organic matter [Brusseau et al. 1991a,b], or entrapment in dead-end micropores [Steinberg et al. 1987]. A recently proposed alternative mechanism is the entrapment in (voids in) the glassy, microcrystalline regions of the organic matter present in soils and sediments [Huang et al. 1997a,b, LeBoeuf and Weber 1997, Xing and Pignatello 1996a,b, 1997]. This microcrystalline organic matter is hypothesized to be characteristically analogous to glassy polymers in which the polymer chains have low flexibility and low translational and rotational freedom.

Mechanistic studies addressing slow sorption phenomena include both adsorption and desorption studies. In most desorption studies, one sorbate and only one or a few sorbents are used. Therefore, in the present study we study desorption kinetics for 4 soils and 4 sediments, using nine test compounds. These experiments were carried out after two sorbent-contaminant contact times (14 and 63 days), and at two desorption temperatures (20 and 60 °C). Desorption parameters ($F_{\text{slow}}, k_{\text{slow}}$) were correlated to organic carbon (OC) content, N content of the organic matter (OM), O content of the OM, polarity index $C/(N+O)$, and OM aromaticity (studied through $^{13}$C-NMR) of the soils and sediments. With the study of these correlations, two aims were strived after: i) to gain information on the mechanism of slow desorption, and ii) to provide simple relationships to predict desorption behavior from simple sorbent and sorbate characteristics.

By studying desorption kinetics at 60°C, a distinction between slow and very slow fractions can be made [Cornelissen et al. 1997a]; here it was studied whether very slow fractions, as previously observed for two sediments [Cornelissen et al. 1997a], would occur in the various soils and sediments studied. Also activation enthalpies of slow desorption are determined from $k_{\text{slow}}$ at 20°C and 60°C; these values are also compared for the various sorbents. The desorption kinetics are studied with a method in which the aqueous phase was kept solute-free by means of Tenax beads that show very fast and efficient sorption of organic solutes [Cornelissen 1997b].

If entrapment in glassy OM regions plays a role in the process of slow desorption, there is probably a glass transition between the glassy state and the rubbery state (in which there is more chain movement and flexibility) possible for the glassy parts of the OM. For pure glassy polymers, glass transitions occur at certain, reasonably fixed temperatures. A glass transition has been reported for purified Aldrich humic acid by LeBoeuf and Weber [1997]. In the event of a glass transition, there is continuity of enthalpy and entropy, however, there is a discontinuity in the heat capacity $C_p$ (a
pseudo second-order transition). This can be studied by means of Differential Scanning Calorimetry (DSC). In the present study, DSC measurements have been carried out for two reasons: i) to test whether a glass transition as reported for purified humic acid would also occur in the natural soils and sediments employed in the present study, giving indications on the rigidity of the OM matrix and ii) to investigate whether a glass transition would happen between 20°C and 60°C (the two experimental temperatures), because the event of a glass transition between those temperatures would limit the calculation of enthalpies of slow desorption because these are calculated from the differences in desorption kinetics between 20°C and 60°C.

Methods

Chemicals. 1,2,3,4-tetrachlorobenzene (TeCB), pentachlorobenzene (QCB), hexachlorobenzene (HCB), 2,4,6-trichlorobiphenyl (PCB-30), 2,4,4'-trichlorobiphenyl (PCB-28), 2,2',4,5'-tetrachlorobiphenyl (PCB-49), 2,3,5,6-tetrachlorobiphenyl (PCB-65), and 2,3',4,4',5-pentachlorobiphenyl (PCB-118) were obtained from various commercial sources. Tenax TA (60-80 mesh; 177-250 mm), a porous polymer based on 2,6-diphenyl-p-phenylene oxide, was obtained from Chrompack. Before use, the Tenax TA beads were rinsed with hexane, acetone and water (all 3 times 10 mL/g Tenax) and dried overnight at 75°C.

Soils and sediments. Four sediments and four soils were sampled from several nonpolluted spots in the eastern parts of The Netherlands (sediments A1, B4, B8 and G1; soils E3, C1 and B2). Also the previously studied OVP sediment [Comelissen et al. 1997a,b] was considered in the characterizations and correlations. The soils and sediments were dried overnight at 70°C, ground in a mortar and sieved at 500 μm to remove coarse particles. The soils and sediments did not show very large variations in particle size distribution; all contained a significant amount of relatively coarse (> 100 μm) and relatively fine (< 16 μm) particles. Both OC and total N (in the organic matrix) were determined with a Carlo Elba Element Analyzer after removal of inorganic carbon with 0.1 M HCl and combustion at 1100°C. Total O and sorbent aromaticity could only be measured for the soils and sediments with a substantial OC content (>10%) as well as for the OVP sediment. Total O in the OM has been measured by removal of the mineral matrix by HF treatment, followed by elemental analysis. For the determination of aromaticity, the dry sorbents were subjected to CP-MAS 13C-NMR. The integrated area of the spectrum between 105 and 160 ppm
Sorbent and sorbate characteristics

represents aromatic carbon [Malcolm and MacCarthy 1984, Xing et al. 1994a, b, c]. Sorbent origin and characteristics are given in Table 1. No background concentrations of the studied compounds could be detected in the sediments, which means that less than about 0.1% of the lab-added amounts was present.

DSC analysis. To test whether glass transitions could be observed for the soils and sediments studied, samples were subjected to Differential Scanning Calorimetry (DSC) measurements. In DSC measurements, the heat flow is measured that is required to increase the sample temperature at a constant rate. Commercially available humic acid from Aldrich was tested, as well as sediments OVP, B8 and G1. Before DSC-analysis, the samples were wetted for 1 week at 1:1 sediment: water mass ratios. Aldrich humic acid was also measured in dry form. Two DSC calorimeters were employed: a Seiko 120 device which accommodates small samples (10-30 mg) in 60 µL hermetically closed aluminium pans, and a Hart Scientific Microcalorimeter, model 4207, in which 4 cells can simultaneously measure 1 reference pan and 3 samples of 300-400 mg of sample in inert stainless steel pans closed by screw caps. To prevent misinterpretations of the DSC signals due to relaxation of the (non-reusable) Seiko pans, these pans were stored at 150°C for 1 h prior to the measurements. Temperature scanning was performed from -20°C to 110°C at a rate of 1°C/min. The initial temperature was chosen to be so low because it took about 20 min (until 0°C) for the signal to stabilize. Both the sample pan and an empty reference pan were scanned; the obtained signal of the empty pan was subtracted from the signals of the filled pan. Mass losses during measurements were below 0.01%. All samples were run twice in order to find out whether any irreversible or slowly reversible changes occurred in the samples during scanning. On the Hart calorimeter, scanning was performed from 0-100°C at a rate of 0.5°C/min. A pan filled with 270 mg Al₂O₃ was used as a reference ("empty") pan. Again, the obtained signals of the empty pans were subtracted from the signals of the filled pans. Mass losses were below 0.1%. The difference in heat flow between sample and reference is registered as the DSC signal. In the event of a glass transition, the discontinuity in the Cₚ of the material causes a discontinuity in the observed heat flow signal.

Soil/sediment loading. Sediment (0.1 to 2 g dry weight, the amount dependent on OC-content) was loaded with the test compounds by suspending it in 250 mL of water spiked with 25 µL methanol containing the test compounds and 1.25 mg of HgCl₂ to prevent microbial degradation. Suspensions were shaken for 14 days or 63 days at 20°C. For the determination of sediment-sorbed solute concentrations,
Table 1: The soils and sediments used in the present study, with their OC contents and C/N ratios.

<table>
<thead>
<tr>
<th>Code</th>
<th>Type</th>
<th>Origin</th>
<th>OC-content (%)</th>
<th>N-content (%)</th>
<th>O-content (%)</th>
<th>C/(N+O) ratio</th>
<th>Aromaticity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OVP</td>
<td>sediment</td>
<td>shallow lake</td>
<td>3.2</td>
<td>0.29</td>
<td>1.48</td>
<td>1.80</td>
<td>37</td>
</tr>
<tr>
<td>A1</td>
<td>sediment</td>
<td>small river</td>
<td>0.7</td>
<td>0.053</td>
<td>n.d.</td>
<td>-</td>
<td>n.d.</td>
</tr>
<tr>
<td>B4</td>
<td>sediment</td>
<td>very young peat</td>
<td>48</td>
<td>2.44</td>
<td>35.12</td>
<td>1.28</td>
<td>13</td>
</tr>
<tr>
<td>B8</td>
<td>sediment</td>
<td>mature peat</td>
<td>46</td>
<td>1.08</td>
<td>30.7</td>
<td>1.45</td>
<td>18</td>
</tr>
<tr>
<td>G1</td>
<td>sediment</td>
<td>boggy lake</td>
<td>35</td>
<td>0.70</td>
<td>12</td>
<td>2.76</td>
<td>21</td>
</tr>
<tr>
<td>E3</td>
<td>soil</td>
<td>podzol horizon</td>
<td>0.5</td>
<td>0.014</td>
<td>n.d.</td>
<td>-</td>
<td>n.d.</td>
</tr>
<tr>
<td>C1</td>
<td>soil</td>
<td>forest topsoil</td>
<td>14.5</td>
<td>0.64</td>
<td>12.89</td>
<td>1.07</td>
<td>16</td>
</tr>
<tr>
<td>B2</td>
<td>soil</td>
<td>peat soil</td>
<td>38.5</td>
<td>0.80</td>
<td>36.54</td>
<td>1.03</td>
<td>7</td>
</tr>
</tbody>
</table>

n.d.: could not be determined due to detection limit problems.
Sorbent and sorbate characteristics

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 water and 60-70 ml hexane for 6 h. The sediment-sorbed concentrations ranged from 10 mg/kg OC (PCB-118) to 200 mg/kg OC (TeCB). The supernatant water was analyzed by extracting 20 ml of water with 2 ml hexane. The hexane was analyzed on GC-ECD for the chlorobenzenes and PCBs.

Desorption kinetics. The desorption kinetics of the soils and sediments loaded for either 14 days or 63 days were determined at both 20°C and 60°C by means of the Tenax solid-phase extraction method described in previous papers [Cornelissen et al. 1997a,b,c, 1998]. In the 60°C-desorption experiment, the sediments were first desorbed at 20°C for 24 h in order to remove the rapidly desorbing fraction. After this, desorption was continued at 60°C. 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 [Cornelissen et al. 1997b, Pignatello 1990] and the very fast solute absorption from water to Tenax [Cornelissen et al. 1997b]. Because of the rapid solute removal from the aqueous phase, backward re-adsorption during desorption is much slower than the slow desorption process [Cornelissen et al. 1997b]; this is required for the validity of eq. 1 (see below). During desorption, a mixture of Tenax TA (0.2-1 g), sediment (0.1-2 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 20 mL hexane; hexane was analyzed as described above. After termination of desorption the remaining sediment and supernatant water were refluxed with 60-70 ml hexane for 6 h to extract and analyze all chlorobenzenes and PCBs still present in the sediment.

The mass balances (ratios between (mass of solute desorbed plus mass not desorbed) and the initial mass of solute) were 80-120% for all soils and sediments.

Desorption data interpretation. Desorption from sediment can be described by the following first-order expression [Cornelissen et al. 1997a,b] on the assumption that

\[ k_{\text{slow}} \ll k_{\text{rap}} \]

\[
\frac{S_t}{S_0} = F_{\text{rap}} e^{-k_{\text{rap}}t} + F_{\text{slow}} e^{-k_{\text{slow}}t}
\]

(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\(^{-1}\)) are the rate constants of rapid and slow desorption, respectively.

Values of \( F_{\text{rap}} \), \( F_{\text{slow}} \), \( k_{\text{rap}} \) and \( k_{\text{slow}} \) were determined by minimizing the cumulative squared residuals between experimental and calculated values of \( \ln(S_r/S_0) \) in eq. 1. For the 60°C-experiments, a very slowly desorbing fraction and corresponding rate constant were needed for the description of the desorption kinetics after 24 h. An equation similar to eq. (1) was used in those cases, with \( F_{\text{slow}} \) and \( F_{\text{very slow}} \) and their rate constants instead of \( F_{\text{rap}} \) and \( F_{\text{slow}} \) [Cornelissen et al. 1997a].

**Calculation of activation enthalpies.** Assuming temperature-independent activation enthalpies and entropies, the following relationship between the activation enthalpy for slow desorption \( \Delta H^\#_{\text{des}} \) and the rate constant \( k_{\text{slow}} \) is valid [Atkins 1986]

\[
\Delta H^\#_{\text{des}} = - R \cdot \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \cdot \ln \left( \frac{k_{\text{slow}}^{T_1}}{k_{\text{slow}}^{T_2}} \right)
\]

in which \( k_{\text{slow},T} \) is the rate constant of slow desorption at temperature \( T \).

**Results and discussion**

**\( K_{\text{OC}} \)-values.** From the overall OC-water distribution ratios (\( K_{\text{OC}}^{\text{overall}} = c_w/(c_s f_{\text{OC}}) \), with \( c_w \) aqueous solute concentration, \( c_s \) solute concentration in the sediment and \( f_{\text{OC}} \) the sediment/soil OC fraction), we calculated \( K_{\text{OC}} \) values for the rapid fraction, with [Cornelissen et al., 1997c]

\[
K_{\text{OC}}^{\text{rap}} = K_{\text{OC}}^{\text{overall}} F_{\text{rap}}
\]

Generally, the measured \( K_{\text{OC}}^{\text{rap}} \) values range from roughly the \( K_{\text{ow}} \) values down to two orders of magnitude lower than \( K_{\text{ow}} \), dependent on sorbent and sorbate. The \( K_{\text{OC}}^{\text{rap}} \)-values have not been corrected for DOC sorption, because of the uncertainty in \( K_{\text{DOC}}\), the DOC-water partition coefficient. Reported \( K_{\text{DOC}} \) values range from 0.1-\( K_{\text{OC}} \) to 1-\( K_{\text{OC}} \) [Burgess et al. 1996, Koelmans 1995, Cornelissen et al. 1997b]. However, sorption to DOC was probably only slight because of the relatively low amounts of DOC released during incubation (3-8 mg/L): corrections for DOC sorption would only
be 0.002-0.02 log-unit (TeCB, with $K_{OC} = 0.1 \cdot K_{OC}$ and $1 \cdot K_{OC}$, respectively) to 0.04-0.4 log-unit (PCB-118).

Correlations between log $K_{OC}^{rap}$ and log $K_{ow}$ (Figure 1) were good, with PCB-28 as a slight outlier for all soils and sediments. We plot $K_{OC}^{rap}$ and not $K_{OC}^{overall}$ because linear partitioning behavior as assumed in the calculation of partition coefficients probably only occurs for the rapidly desorbing fraction [Huang et al. 1997a, Xing and Pignatello 1997, Cornelissen et al., chapter 8]. The correlation parameters are presented in Table 2. Intercepts were all significantly above 0 except for B4 sediment (t-test, 95%); all slopes were significantly below unity (t-test, 95%).

Figure 1: Relation between log $K_{OC}^{rap}$ (the OC-water partition coefficient for the rapidly desorbing fraction) and log $K_{ow}$ for all sorbents studied. Drawn lines are obtained by linear regression.

Table 2: Slopes and intercepts of the log $K_{ow}$ - log $K_{OC}^{rap}$ plots, along with standard deviations (std). The number of chemicals used in the correlation was 8.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>slope</th>
<th>intercept</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OVP</td>
<td>0.54 ± 0.05</td>
<td>2.12 ± 0.32</td>
<td>0.94</td>
</tr>
<tr>
<td>A1</td>
<td>0.65 ± 0.06</td>
<td>0.98 ± 0.36</td>
<td>0.95</td>
</tr>
<tr>
<td>B4</td>
<td>0.74 ± 0.07</td>
<td>0.19 ± 0.43</td>
<td>0.95</td>
</tr>
<tr>
<td>B8</td>
<td>0.59 ± 0.07</td>
<td>1.49 ± 0.42</td>
<td>0.92</td>
</tr>
<tr>
<td>G1</td>
<td>0.65 ± 0.05</td>
<td>0.90 ± 0.29</td>
<td>0.97</td>
</tr>
<tr>
<td>E3</td>
<td>0.58 ± 0.06</td>
<td>1.64 ± 0.35</td>
<td>0.94</td>
</tr>
<tr>
<td>C1</td>
<td>0.60 ± 0.05</td>
<td>1.46 ± 0.29</td>
<td>0.96</td>
</tr>
<tr>
<td>B2</td>
<td>0.68 ± 0.06</td>
<td>0.99 ± 0.32</td>
<td>0.96</td>
</tr>
</tbody>
</table>
It is observed that sediment B4 shows a relatively low y-intercept of 0.19. $K_{oc}^{rap}$-values are significantly lower for this sediment than for the other 7 sorbents (t-test, 95%). A reason is probably the low age of the sediment: it has only recently been formed from plant materials, as is also indicated by its relatively low content of aromatic carbon (only 13% of total OC). It has been observed before that strongly reduced, old sediments show higher $K_{oc}$-values than more recently formed ones [Weber et al. 1992, Young and Weber 1995, Grathwohl and Reinhard 1993, Grathwohl 1990]. Variations in $K_{oc}$ among various sorbents have been reported by Huang et al. [1997], who observed a standard deviation of 30-50% in their $K_{oc}$ values for different soils and sediments, the extent of deviation depending on solute concentration. In the present study, these standard deviations were 58-69% for all solutes studied. Rutherford observed a factor of 3 variation in $K_{oc}$ values among various soils [Rutherford et al. 1992]. Kile and Chiou [1995] observed that $K_{oc}$ values were relatively constant (within a factor of 3) among pristine soils and sediments, whereas sorbents with anthropogenic contamination exhibited significantly larger $K_{oc}$s.

In Table 4 (see further), correlation coefficients $r^2$ between the (a measure for rapid, linear sorption strength of the sorbent organic matter) vs. sorbent characteristics are presented. The $K_{oc}^{rap}$ vs. $K_{ow}$ intercepts showed weak correlations with OC, total-N, O, and aromaticity. For the polarity index $C/(N+O)$ a correlation was altogether absent. This is remarkable because Xing et al. [1994a,b,c] has reported good correlations between $K_{oc}$ and both polarity index and aromaticity, $K_{oc}$ increasing with decreasing polarity index and with increasing OC aromaticity. In addition, Chiou et al. [1998] speculated that the reason for the high $K_{oc}$ values they observed for PAHs (compared to those for chlorinated compounds) could be due to the more compatible cohesive energy densities of PAHs in aromatic parts of the OM. This also implies that OM aromaticity is important for sorption. Also Chen et al. [1996] observed that $K_{oc}$ increased with soil nonpolarity; this was especially clear for a shale sample in which no detectable N was present whereas the OC content was 65%: the subsequent C/N ratio was probably above 10,000. Also Rutherford et al. [1992] reported a relation of increasing $K_{oc}$ with increasing soil nonpolarity. Grathwohl [1990] reported that $K_{oc}$ increased with decreasing $H/C$ ratio. The reason why these authors did observe relationships with $K_{oc}$ whereas we did not may be that the variation in $K_{oc}^{rap}$ among our sorbents was less than one order of magnitude, whereas e.g. Xing et al. [1994a,b,c] used some widely different model sorbents (like chitin, cellulose, collagen, lignin, and carbon) to establish his relationships.
Desorption kinetics at 20°C and 60°C. Through measurements at elevated temperature (60°C), it has been shown that long-term desorption behavior can be measured in a relatively short time [Cornelissen et al. 1997a], because of the strong temperature dependence of slow desorption. Moreover, previous experiments have revealed that an additional very slow fraction was needed to describe the last phase of desorption after more than 500-800 h [Cornelissen et al. 1997a]. In Figure 2, the desorption of HCB from sediment B4 has been shown at 20°C (upper curve) and 60°C (lower). The first 20 h, desorption was measured at 20°C in both cases in order to desorb the rapidly desorbing fraction; after 20 h the desorption temperatures of 20°C and 60°C were imposed. In Table 3 the values of $F_{\text{slow}}$ (%) and $k_{\text{slow}}$ (h$^{-1}$; at 20°C and 60°C), $F_{\text{very slow}}$ (%) and $k_{\text{very slow}}$ (h$^{-1}$; at 20°C and 60°C) have been given, for HCB. The values for $k_{\text{very slow}}$ at 20°C are extrapolations from the 60°C values; this extrapolation has been carried out under the assumption that the temperature dependence of very slow desorption is equal to that of slow desorption. This assumption has been shown to be reasonable [Cornelissen et al. 1997a].

Figure 2: Desorption at 20°C (diamonds) and 60°C (triangles) of HCB from sediment B4 (adsorption time 14 d). During the first 24 h of the 60°C experiment desorption was carried out at 20°C to remove the rapidly desorbing fraction. The drawn lines are fits to eq. 1.

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HCB sediment B4; incubation time 14 d; desorption at 20°C and 60°C
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Table 3: $F_{\text{slow}}$ (%) and $k_{\text{slow}}$ (20°C and 60°C, $10^{-3}$ h$^{-1}$), as well as $F_{\text{very slow}}$ (%) and $k_{\text{very slow}}$ ($10^{-3}$ h$^{-1}$, 60°C and 20°C, the latter values obtained by extrapolation), for HCB. All $k$-values measured after 2 weeks of equilibration.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$F_{\text{slow}}$ 14 d (%)</th>
<th>$F_{\text{slow}}$ 63 d (%)</th>
<th>$k_{\text{slow}}$ 20°C ($10^{-3}$ h$^{-1}$)</th>
<th>$k_{\text{slow}}$ 60°C ($10^{-3}$ h$^{-1}$)</th>
<th>$F_{\text{very slow}}$ 14 d (%)</th>
<th>$F_{\text{very slow}}$ 63 d (%)</th>
<th>$k_{\text{very slow}}$ 20°C ($10^{-3}$ h$^{-1}$)</th>
<th>$k_{\text{very slow}}$ 60°C ($10^{-3}$ h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OVP</td>
<td>21.8*</td>
<td>-</td>
<td>3.03 ± 0.11*</td>
<td>122 ± 2 *</td>
<td>-</td>
<td>0.48 ± 0.03*</td>
<td>2.6 ± 1.3*</td>
<td></td>
</tr>
<tr>
<td>A1</td>
<td>21.7 ± 2.1***</td>
<td>-</td>
<td>6.50 ± 0.46</td>
<td>-</td>
<td>-</td>
<td>0.48 ± 0.03*</td>
<td>2.6 ± 1.3*</td>
<td></td>
</tr>
<tr>
<td>B4</td>
<td>15.8 ± 1</td>
<td>14.2 ± 1.0</td>
<td>4.30 ± 0.7</td>
<td>262 ± 37</td>
<td>7.0 ± 1.6</td>
<td>7.7 ± 1.2</td>
<td>0.04</td>
<td>2.72 ± 0.27</td>
</tr>
<tr>
<td>B8</td>
<td>24.0 ± 3</td>
<td>32.1 ± 4</td>
<td>3.0 ± 0.74</td>
<td>190 ± 44</td>
<td>10.2 ± 0.1</td>
<td>8.9 ± 2.2</td>
<td>0.06</td>
<td>3.5 ± 0.4</td>
</tr>
<tr>
<td>G1</td>
<td>45.0 ± 5.7</td>
<td>40.2 ± 1.1</td>
<td>2.67 ± 0.33</td>
<td>145 ± 23</td>
<td>12.0 ± 1.4</td>
<td>14.1 ± 3.1</td>
<td>0.09</td>
<td>4.94 ± 0.53</td>
</tr>
<tr>
<td>E3</td>
<td>18.0 ± 1.7</td>
<td>19.3 ± 7</td>
<td>3.28 ± 0.13</td>
<td>256 ± 4</td>
<td>5.0 ± 1.0</td>
<td>7.2 ± 1.1</td>
<td>0.12</td>
<td>9.2 ± 1.5</td>
</tr>
<tr>
<td>C1</td>
<td>41.3 ± 6.0</td>
<td>35.6 ± 2</td>
<td>6.20 ± 3.1</td>
<td>133 ± 20</td>
<td>10.9 ± 1.0</td>
<td>14.4 ± 0.7</td>
<td>0.23</td>
<td>4.95 ± 0.76</td>
</tr>
<tr>
<td>B2</td>
<td>37.4 ± 10.1</td>
<td>32.2 ± 1.5</td>
<td>3.51 ± 0.6</td>
<td>188 ± 51</td>
<td>10.8 ± 0.9</td>
<td>14.3 ± 2.2</td>
<td>0.05</td>
<td>2.8 ± 1.1</td>
</tr>
</tbody>
</table>

*: equilibration time 34 d.
**: directly measured at 20°C (no extrapolation from 60°C to 20°C).
***: value for $F_{\text{slow}} + F_{\text{very slow}}$. 
Sorbent and sorbate characteristics

From Table 3 it can be observed that for all soils and sediments slow and very slow fractions could be observed, with their rate constants of desorption at 20°C in the order of $10^{-3}$ and $10^{-4}$-10$^{-5}$ h$^{-1}$, respectively. This means that slow and very slow desorption, as introduced in one of our previous studies [Cornelissen et al. 1997a] occurs in soils and sediments of widely varying characteristics.

Desorption kinetics after 14 and 63 days. In Figure 3, desorption curves (plotted as $\ln S_t/S_0$ vs. time) are presented for the 2 incubation times (HCB in sediment B4 at 20°C). Also for the other compounds and sediments, differences in slow fractions and rate constants of slow desorption between 14 and 63 d of incubation were not significant when tested at the 95% confidence level. In Table 3, $F_{\text{slow}}$ (%) is given for HCB after the two contact times, for the different soils and sediments tested. For comparison, results obtained with the same method for a different lab-contaminated sediment (OVP [Cornelissen et al. 1997b]) are given. These values were measured after 34 days of incubation.

Figure 3: Desorption of PCB-30 from sediment B4 after 14 d (diamonds) and 63 d (triangles), respectively.

This reveals that there is only a slight difference in desorption behavior between 14 and 63 days: obviously the "aging" process is proceeding very slowly between the 14 and 63 days. Previous results revealed stronger differences in $F_{\text{slow}}$ between 2 and 34 days of incubation (about a factor of 2 [Cornelissen et al. 1997b]). These results (a stronger effect of aging between 2 and 34 d than between 14 and 63 d) is consistent with recent findings from Cousins et al. [1998] who reported than PCB soil-air
partition coefficients generally increased between 3 and 83 d of incubation, after which they remain unchanged during 309 d of subsequent incubation. Another experiment in the same publication reveals that there is a difference in extent of sorption between lab-added and aged PCBs during the first 14 d of incubation of the lab-added ones, after which the distinction vanishes. These results indicate that most of the slow sorption process occurs in the first days or weeks of sorbent-contaminant contact time. We have previously found [Cornelissen et al., chapter 8] that adsorption to the slow compartment reaches more than 99% of equilibrium after 2 to 4 weeks, even at low solute concentrations (such as employed presently). Adsorption to the very slow compartment, however, may take far longer to complete (up to months), especially at low solute concentrations. This all indicates that loading of the slow and very slow compartments is still happening between a few days and a few weeks. After that, mainly the very slow compartment is filled. This is only partly supported by the present results that show only a very slight increase in $F_{very\ slow}$ between 14 and 63 d of adsorption. (Slow+very slow) fractions of over 90% have been reported for aged sediments [Ten Hulscher et al. accepted, Cornelissen et al. 1997a] which indicates that the aging process, although slowly, could continue for extended periods of time. In other studies, significant slow desorption after only a few days of incubation has been reported [Kan et al. 1994].

**Activation enthalpies of slow desorption.** Values for $\Delta H^\ast_{des}$ are presented in Figure 4, for the different soils and sediments. We show the averages for the different test compounds with their standard deviations, because the individual compounds did not show much variation and no trend with hydrophobicity and/or molecular volume (correlation coefficients, $r^2$, below 0.2). From Figure 4 it can be observed that $\Delta H^\ast_{des}$ is in the same order of magnitude for all soils and sediments (about 60-100 kJ/mol), and that values were comparable to previously determined values for OVP (lab-contaminated) and KM (field-contaminated) sediments [Cornelissen et al.1997a](only significant differences between OVP/KM and B4/B8 sediments, Student t-test, 95%). Only in the cases of soils E3 and C1 there was a difference in $\Delta H^\ast_{des}$ between 14 and 63 days of incubation (Student t-test, 95%). The value of 60-100 kJ/mol is in the same order of magnitude as a previously observed value of 66 kJ/mol by Steinberg et al. [1987], slightly higher than a value of 46 kJ/mol reported by Uzgiris [1995], and much higher than the -28 to +29 kJ/mol range reported by Piatt et al. [1996]. The activation enthalpy of slow desorption may reflect an enthalpy of activated diffusion through the organic matter (in the case of OM diffusion as the mechanism of slow
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sorption), or, alternatively, the enthalpy of release from "high-energy" sorption sites in the OM (in the case of a site sorption mechanism).

Figure 4: Activation enthalpies of slow desorption, $\Delta H_{\text{des}}^\#$, for all sorbents studied, after 14 d (open bars) and 63 d (closed bars) of adsorption, respectively. For comparison, the previously studied OVP (equilibration time 34 d) and KM (field-aged) sediments are also included [Cornelissen et al., 1997a]. Error bars represent standard deviations.

Soils vs. sediments. In none of the parameters measured ($F_{\text{slow}}$, $k_{\text{slow}}$, $\Delta H_{\text{des}}^\#$) there were significant differences between soils and sediments; the averages were tested by means of a Student t-test with 95% confidence interval. This indicates that knowledge obtained from slow sorption research performed with soil can probably be extended to sediment and vice versa, as is often implicitly assumed. Also Huang et al [1997], who studied 27 different soils and sediments and Chen et al [1996] (9 soils/sediments) reported no significant sorption differences between soils and sediments. On the other hand, Kile and Chiou [1995], who studied about 70 soils and sediments from China and the USA, report that $K_{\text{oc}}$ values for sediments are about twice those for soils. All these authors studied adsorption and no desorption.
DSC measurements. In Figure 5a, the two sequential measurements for the dry humic acid (9 mg) are given; in the case of a Seiko apparatus exothermic effects are plotted in the upward y-direction. Therefore, a glass transition would involve a shift in heat flow in a downward direction because the rubbery state has a larger heat capacity than the glassy one. No clear glass transition is observed in Figure 5a; the only hint towards an endothermic effect is the slight bend in the curve of the first measurement at 45-50°C. However, this effect is much less pronounced than the effect reported by LeBoeuf and Weber [1997]. We did not observe any glass transition in the wet humic acid (results not shown). This is remarkable because LeBoeuf and Weber did observe a glass transition for Aldrich humic acid, and the Seiko 120 apparatus is about 10 times more sensitive to small signals than the Perkin Elmer 7 DSC they employed [Seiko manual 1992]. LeBoeuf and Weber did not report their scanning rate, but our scanning rate of 1°C/min should be low enough even to measure very small heat effects (about 0.005 mW), and certainly effects of the size reported by LeBoeuf and Weber (about 0.1 mW shift in heat flow). The reason for the fact that we do not observe a glass transition for the Aldrich humic acid whereas LeBoeuf and Weber do may be that the Aldrich humic acid stems from various batches. However, there are some other noteworthy features that can be observed from the DSC curves. During the first run, there are some exothermic processes occurring at temperatures above 55°C. This could be explained by some oxidation process of the organic matter because scanning is performed in the presence of oxygen. During the second run of the same sample, this exothermic effect is not observed anymore, indicating that some irreversible or slowly reversible changes in the humic acid sample occur when it is heated to temperatures above 55-60°C. During the second run, there are some very small ripples in the curve at 70-90°C; however, these cannot be glass transition temperatures because the effects are exothermic, and lie at a higher temperature than the glass transition temperature observed by LeBoeuf for dry Aldrich humic acid (62°C). In addition, their magnitude is only 5 μW for 9 mg of sample, instead of 100 μW for the measurements by LeBoeuf and Weber; unfortunately, they did not denote the amount of sample used.

The scans for the samples OVP (scanned once; 87 mg), B8 and G1 (both scanned twice; 18 and 46 mg, respectively) are also given in Figure 5. For none of the samples a glass transition could be observed. Again the exothermic effect was observed for the organic-matter rich sediments B8 and G1 (90 and 70% OM, respectively) but not or much less for the organic-matter poor OVP sediment (6% OM), indicating that this effect probably occurs in the organic matter regions. During the second run,
Figure 5: DSC scans obtained with the Seiko 120, for (a) dry Aldrich humic acid, (b) OVP sediment, (c) B8 sediment. Plotted is the heat flow vs. temperature, with exothermic effects in the upward y direction.
Chapter 6

Figure 6: DSC scans obtained with the Hart microcalorimeter, for Aldrich humic acid (lower), G1 sediment (middle), and OVP sediment (upper). Plotted is the heat flow vs. temperature, with exothermic effects in the downward y direction.

**Figure 6:** DSC scans obtained with the Hart microcalorimeter, for Aldrich humic acid (lower), G1 sediment (middle), and OVP sediment (upper). Plotted is the heat flow vs. temperature, with exothermic effects in the downward y direction.
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the effect was much less for G1 and almost absent for B8.
The scans obtained for 300-400 mg of sample in the Hart calorimeter are presented in Figure 6. Here exothermic effects are plotted in a downward y-direction; on the y-axis are mV-units which are directly proportional to the DSC signal (μW). Again, the exothermic effects are observed at 55-90°C for the G1 and humic acid, but not for the OVP sediment. Only for the humic acid, there is a small hint of a glass transition at about 45-50°C (like in the Seiko measurements), after which the exothermic effects start. This glass transition would be consistent with the earlier observations by LeBoeuf and Weber. However, the presently observed effect was much less clear than the effect that they observed. There is no sign of a glass transition for the sediment samples OVP and G1.

In summary, there are hardly any or no thermodynamic effects occurring in the samples between 20°C and 60°C. This means that probably no structural changes in the sediment occur between the two temperatures at which desorption kinetics have been determined. It could also be that there is a shift between glassy and rubbery structures in the sediments, but that this shift occurs over such a broad temperature range (because of sediment heterogeneity) that it is not measurable. So, the fact that we could not observe a glass transition temperature does not mean that there are no "glassy", relatively rigid parts in sediment organic matter.

Correlations with sorbate characteristics. Because sorbate polarity is an important parameter in sorption, we test whether sorbate polarity also influences slow/rapid distribution ratios. The logarithm of the distribution coefficient between \((F_{\text{slow}} + F_{\text{very slow}})\) and \(F_{\text{rap}}\), \(\log\left(\frac{F_{\text{slow}} + F_{\text{very slow}}}{F_{\text{rap}}}\right)\), is plotted against \(\log K_{OC}\), for soil B2 and sediment B4 (Figure 7). This figure shows that there is a correlation between \(\log\left(\frac{F_{\text{slow}} + F_{\text{very slow}}}{F_{\text{rap}}}\right)\) and \(\log K_{OC}\). Such a correlation could be observed for all soils and sediments, which indicates that there may be a hydrophobicity difference between the rapid and slow sorbing sediment compartment, as argued in a previous paper [Cornelissen et al. 1997b]. An interpretation of these results is that the rapid sorbing compartment consists of organic matter-water or mineral-water interfaces, while the slowly and very slowly desorbing compounds reside in relatively well-sheltered interior parts of the organic matter.
Correlations with soil/sediment characteristics. In Table 4, the correlations coefficients ($r^2$) are given between (de)sorption parameters ($\log K_{OC}$, $\log[(F_{slow} + F_{very slow})/F_{rap}]$, $k_{slow}$, $k_{very slow}$) and sediment characteristics (OC, total-N, O, C/(O+N), and OC aromaticity). Neither of the sediment parameters correlated well with desorption parameters, indicating that the studied sediment characteristics do not influence the slow desorption process, at least for relatively freshly contaminated soils and sediments. This means that no simple relationships between desorption behavior and macroscopic sorbent characteristics can be established from the present data. A reason for this may be that "lumped" macroscopic parameters such as employed in the correlations (apart from OC aromaticity) do not reflect variations in molecular structure, while it is structural characteristics that probably determine slow desorption behavior.

Values for $k_{slow}$ and $k_{very slow}$ lie within close boundaries for solutes varying a factor of 1000 in $K_{ow}$ and sorbed in widely different lab-contaminated soils and sediments: $k_{slow}$ varies only by a factor of 5, ranging from $1.5 \cdot 10^{-3}$ h$^{-1}$ to $6 \cdot 10^{-3}$ h$^{-1}$ at 20°C, and $k_{very slow}$ varies within a factor of 4, ranging from $2 \cdot 10^{-3}$ h$^{-1}$ to $8 \cdot 10^{-3}$ h$^{-1}$ at 60°C, the latter values being about 2 orders of magnitude lower at 20°C. Previous results showed that $k_{slow}$ and $k_{very slow}$ lie in this order of magnitude ($1-5 \times 10^{-3}$ h$^{-1}$) for a number of
Table 4: Correlation coefficients ($r^2$) between sorption (intercept of log $K_{OC}^{lin}$-log $K_{ow}$ relationship) / desorption parameters ($\log([F_{slow}+F_{very slow}]/F_{rap})$, $k_{slow}$, and $k_{very slow}$) and sorbent descriptors (OC, total-N, O, C/(N+O), and aromaticity). Values averaged for all compounds are given, as well as standard deviations, minimum and maximum values. The number of sorbents for the correlations was 8 (OC and N) or 6 (O, C/(N+O), and aromaticity). The number of solutes for the standard deviations in the $r^2$-values was 8.

<table>
<thead>
<tr>
<th>Correlations of sorption and desorption parameters vs. sorbent characteristics</th>
<th>$r^2$</th>
<th>min</th>
<th>max</th>
</tr>
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<tr>
<td><strong>intercept log $K_{OC}^{lin}$-log $K_{ow}$ vs. sediment characteristics</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Descriptor</td>
<td></td>
<td></td>
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<tr>
<td>OC</td>
<td>0.36</td>
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<td>N</td>
<td>0.49</td>
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</tr>
<tr>
<td>O</td>
<td>0.45</td>
<td></td>
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</tr>
<tr>
<td>C/N+O</td>
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</tr>
<tr>
<td>aromaticity (%)</td>
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<td></td>
</tr>
<tr>
<td><strong>$\log([F_{slow}+F_{very slow}]/F_{rap})$ vs. sediment characteristics</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Descriptor</td>
<td>$r^2$</td>
<td>min</td>
<td>max</td>
</tr>
<tr>
<td>OC</td>
<td>0.03 ± 0.03</td>
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<td>0.11</td>
</tr>
<tr>
<td>N</td>
<td>0.16 ± 0.07</td>
<td>0.00</td>
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</tr>
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<td>C/N+O</td>
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<td>aromaticity (%)</td>
<td>0.04 ± 0.03</td>
<td>0.00</td>
<td>0.09</td>
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<td><strong>$k_{slow}$ vs. sediment characteristics</strong></td>
<td></td>
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</tr>
<tr>
<td>Descriptor</td>
<td>$r^2$</td>
<td>min</td>
<td>max</td>
</tr>
<tr>
<td>OC</td>
<td>0.15 ± 0.13</td>
<td>0.00</td>
<td>0.37</td>
</tr>
<tr>
<td>N</td>
<td>0.09 ± 0.16</td>
<td>0.00</td>
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</tr>
<tr>
<td>O</td>
<td>0.48 ± 0.31</td>
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<tr>
<td>C/N+O</td>
<td>0.41 ± 0.26</td>
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<td>aromaticity (%)</td>
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<tr>
<td>Descriptor</td>
<td>$r^2$</td>
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<td>max</td>
</tr>
<tr>
<td>OC</td>
<td>0.11 ± 0.14</td>
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</tr>
<tr>
<td>N</td>
<td>0.21 ± 0.22</td>
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<tr>
<td>O</td>
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<td>0.04</td>
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<td>aromaticity (%)</td>
<td>0.35 ± 0.20</td>
<td>0.00</td>
<td>0.61</td>
</tr>
</tbody>
</table>
field-contaminated sediments (HCB/DCB in Delfzijl sediment [Cornelissen et al. 1997c], 15 PAHs in Petroleum Harbor sediment [Cornelissen et al. 1998] and PCBs in Lake Ketelmeer sediment [Cornelissen et al. 1997a]). This shows that, with respect to slow and very slow desorption rate constants, there is no need to establish relationships with sorbent and sorbate characteristics: for most compounds and most soils and sediments values are approximately constant. This constancy may also partly explain why no correlations could be observed.

For $F_{slow}$ and $F_{very slow}$, it is also observed that they are reasonably constant among the various presently studied lab-contaminated sorbents (factor of 5 variation in both $F_{slow}$ and $F_{very slow}$). $F_{slow}$ and $F_{very slow}$ are sometimes high for field-contaminated sediments ($F_{slow} + F_{very slow}$ as high as 90-99% [Cornelissen et al. 1997b,c]); on the other hand $F_{slow} + F_{very slow}$ has been found to be as low as 20% in other aged sediments [Cornelissen et al. 1998a].

If diffusion through OM were an important process in slow desorption, it would be expected that OM-rich sorbents (possessing relatively large continuous OM parts and thus requiring longer diffusional pathways) would exhibit relatively small values for $k_{slow}$. Especially for the soils and sediments that almost entirely consist of OM (B2, B4, B8, and G1) large continuous parts of OM are expected. So, the absence of a correlation between $k_{slow}$ and OC content implies that intra-organic matter diffusion is probably not an important process in slow desorption. We have previously shown that OM is probably the most important factor in slow desorption (because hardly any slowly desorbing compound was present in a sediment whose OM had been removed), so it must be another OM process which causes slow desorption. Another mechanism proposed in the literature is that the amorphous part of the organic matter showing rapid, linear sorption and the (voids in) microcrystalline part shows slow, nonlinear Langmuir-like sorption behavior. Diagenesis of humic materials is expected to increase the fraction of microcrystalline, glassy-polymer humic material and therefore slow fractions are expected to increase with increasing soil/sediment age, and slow desorption rate constants are expected to decrease. In fact, it has been shown by Huang and Weber [1997b] that the extent of hysteresis and sorption isotherm nonlinearity (both indicative of slow sorption) increase with increasing soil diagenesis. Still the present results are not in complete accordance with the hypothesis of increasing slow sorption with increasing diagenesis. The reason is that the very young sediments used (B4, which was sampled from a pond in which the plant materials probably had only just been converted into humic material, with 13% aromatic OC, and the peat soil B2 which contained only 7% aromatic OC) showed
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\( F_{\text{slow}} \) values of 5-37\% and \( F_{\text{very slow}} \) values of 4-15\% (Table 3). These values are in the same order of magnitude as the values for the other more mature soils and sediments. This indicates that also newly formed organic matter could show slow sorption.

Acknowledgment

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Literature


