SORBATE SIZE–DEPENDENT MAXIMUM CAPACITIES FOR ADSORPTION OF ORGANIC COMPOUNDS IN THE SLOWLY AND VERY SLOWLY DESORBING DOMAINS OF A SEDIMENT

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Abstract—Maximum capacities were determined for adsorption of six polycyclic aromatic hydrocarbons, seven polychlorinated biphenyls, and five chlorobenzenes in both the slowly desorbing domain and the very slowly desorbing domain of a sediment. For separate compound classes in the two desorption domains, log-transformed maximum adsorption capacities were linearly related to the relative magnitude of the shadow of the sorbate on an imaginary planar surface. For planar compounds, the ratio of maximum adsorption capacities for the slowly desorbing domain and the very slowly desorbing domain was approximately two. This ratio was eightfold higher for strongly nonplanar polychlorinated biphenyls, which suggests that adsorption depends on sorbate thickness in the very slow desorption domain but not in the slow desorption domain. The rates of decrease of the log-transformed sum of maximum capacities for adsorption in the slow desorption domain and the very slow desorption domain with increasing relative magnitude of the shadow of the sorbate on a planar surface were similar to those derived from literature data regarding maximum capacities for adsorption onto a soil and a sediment. It is proposed that the rates of decrease for both the slow desorption domain and the very slow desorption domain may have general applicability to soils and sediments.

Keywords—Black carbon Desorption Polycyclic aromatic hydrocarbons Polychlorinated biphenyls Chlorobenzenes

INTRODUCTION

Adsorption of organic compounds onto black carbon, kerogen, and coal in sediments and soils in addition to absorption is a well-accepted phenomenon. Many studies have demonstrated that adsorption may dominate over absorption at the low contaminant concentrations commonly found today. Therefore, a quantitative and mechanistic understanding of these adsorption processes is needed to assess the environmental risks of organic contaminants in sediments and soils.

Adsorption sites are finite in number. Studies concerning the variation of the number of adsorption sites among either different soils and sediments or different adsorbates are scarce. Langmuir capacities for adsorption of phenanthrene onto 27 different soils and sediments ranged from 1 to 364 µg/g organic carbon (OC) [1]. This range can be reduced to 330 to 7,540 µg/g OC by normalization to the soil or sediment OC content. Recently, from desorption studies of phenanthrene added to 19 sediments and soils, maximum adsorption capacities ($Q_{\text{max}}$) for the slowly desorbing domain ($Q_{\text{max, slow}}$) as well as for the very slowly desorbing domain ($Q_{\text{max, very slow}}$) varied substantially and correlated with OC content [2]. Normalization of the $Q_{\text{max}}$ to OC content resulted in a reduction of the ranges to 260 to 2,170 and 61 to 1,060 µg/g OC for $Q_{\text{max, slow}}$ and $Q_{\text{max, very slow}}$, respectively. The sum of these ranges compares well with the range in the study by Huang et al. [1]. For three geosorbents of the 19 sediments and soils studied, literature values for $Q_{\text{max}}$ derived from isotherms could be found. These values were fairly close to the sum of $Q_{\text{max, slow}}$ and $Q_{\text{max, very slow}}$ [2].

Kan et al. [3] determined the $Q_{\text{max}}$ of toluene, naphthalene, 1,2-dichlorobenzene, phenanthrene, 4,4’-dichlorobiphenyl, 2,2,5,5’-tetrachlorobiphenyl, and $p,p’$-DDT onto Lula sediment. These capacities decreased from 125 to 0.36 µg/g on increasing the n-octanol–water partition coefficient ($K_{\text{ow}}$) [3]. For a dark-gray silt loam from Dover Air Force Base (Dover, DE, USA), the $Q_{\text{max}}$ of benzene, chlorobenzene, 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, 1,2,4,5-tetrachlorobenzene, naphthalene, fluorene, phenanthrene, and pyrene ranged from 113 to 25 µg/g [4]. These capacities did not decrease on increasing $K_{\text{ow}}$ but, instead, were higher for liquid sorbates than for solid sorbates [4]. For adsorption onto 10 different soot and soot-like materials, maximum capacities for adsorption for a range of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) were calculated from experimental soot–water distribution coefficients at low concentrations in water and theoretical values for the Langmuir affinity for adsorption [5]. These $Q_{\text{max}}$ values were related to sorbent-specific surface area, OC content as an approximate measure for surface oxidation, and two-dimensional area occupied by a sorbate molecule [5]. Maximum capacities for adsorption of nonplanar compounds onto the soot and soot-like materials were smaller than for planar compounds [5].

In the present study, maximum capacities for adsorption will be presented for 18 different planar and nonplanar compounds on a sediment from which native organic compounds were removed. The 18 compounds comprise seven PAHs, five chlorobenzenes, three mono-ortho-substituted PCBs, and three PCBs with two or more chlorine atoms at ortho positions. The $Q_{\text{max}}$ values were determined from desorption to Tenax beads (Chrompack, Bergen op Zoom, The Netherlands) as an infinite sink in water. Desorption from sediment to Tenax can be described to proceed in three kinetically distinct stages: A rapidly desorbing fraction is followed by a slowly desorbing fraction...
Materials and Methods

Materials

Sediment from Lake Ketelmeer (The Netherlands; settled river Rhine sediment; OC content, 0.112 g/g, before removal of native organic compounds) was collected from a depth of 40 to 120 cm on November 27, 1996. After homogenization, the sediment was sieved over 125 μm and stored in plastic containers in the dark at 6°C. Before use in sorption experiments, the sediment was dried overnight at 105°C and further heated at 300°C for 24 h to remove native organic compounds [7]. After heating, the sediment was stored in an exsiccator at room temperature.

Naphthalene and chrysene were from Sigma (Zwijndrecht, The Netherlands). Biphenyl, phenanthrene, 1,3-dichlorobenzene, and pentachlorobenzene were from Merck (Amsterdam, The Netherlands). Fluoranthene, benzo[a]fluoranthene, dibenzo[a,h]anthracene, and 1,2,4-trichlorobenzene were from Aldrich (Zwijndrecht, The Netherlands). The 1,2,3,4-tetrachlorobenzene was from Janssen Chimica (Geel, Belgium). Hexachlorobenzene was from LGC (Teddington, United Kingdom). The PCB 1 (2-chlorobiphenyl), PCB 4 (2,2’-dichlorobiphenyl), and PCB 9 (2,5-dichlorobiphenyl) were from Brunschwig (Amsterdam, The Netherlands). The PCB 19 (2,2’,6-trichlorobiphenyl) and PCB 54 (2,2’,6,6’-tetrachlorobiphenyl) were from Ultra Scientific (North Kingstown, RI, USA). The PCB 28 (2,4,4’-trichlorobiphenyl) was from Promochem (Wesel, Germany). Tenax TA® (60–80 mesh) was from Chrompack. Before use, Tenax beads were rinsed with Milli-Q® water (Millipore, Bedford, MA, USA), acetone (Mallinckrodt Nanograde, Phillipsburg, NJ, USA), and hexane (Mallinckrodt Nanograde); each step was repeated three times with 10 ml of solvent per 1 g of Tenax. After rinsing, Tenax was dried at 75°C.

Incubation of sediment with organic compounds

For each organic compound, individual solutions in methanol (Baker high-performance liquid chromatography [HPLC] analyzed; Mallinckrodt Baker) were made. A Milli-Q water solution was made with HgCl₂ (Baker grade) at a final concentration of 24 mg/L and NaN₃ (Baker grade) at a final concentration of 153.6 mg/L. Dry sediment (1–2 g) was weighed into 300-ml conical flasks, and the Milli-Q water solution was added, leaving a headspace of approximately 20 ml. For each sorbate, incubation was carried out in triplicate. Sorbate solutions in methanol were added to the sediment suspension, keeping methanol content less than 0.1%. Final sorbate concentrations in the water phase were at least 30% of the aqueous solubility. The addition of sorbates depended on their aqueous solubility. For instance, phenanthrene was added in a single step, with a total incubation time of 4 d. Benzo[a]fluoranthene, however, was added in 43 steps, with short time intervals, over 3 d, after which the mixture was equilibrated for another 3 d. Earlier, we found that equilibrium was reached within 10 h [7]. After equilibration, aqueous concentrations were measured to check if concentrations remained close to aqueous solubilities. For equilibration, flasks were closed with a glass stopper, and the suspension was shaken at 250 rpm in a Sanyo Gallenkamp 103400 XX2.3 incubator (Loughborough, UK) at 20°C.

The sorbate concentration in the water phase was checked to ensure it exceeded 30% of the aqueous solubility after equilibration. To that end, 5 to 10 g of suspension were centrifuged in closed glass tubes for 20 min in a Sanyo Gallenkamp MSE type Falcon 6/300 centrifuge at 1,300 g. After centrifugation, the unfiltered supernatant was analyzed for PAHs by HPLC (see below) directly or was extracted with n-hexane and analyzed for chlorobenzenes and PCBs by gas chromatography (see below). After at least 4 d of incubation, the suspensions were centrifuged in stainless-steel tubes at 1,300 g for 20 min. The supernatant was removed, and the sediment was slurried with 70 ml of Milli-Q water and put into a 100-ml separation funnel for desorption studies.

Desorption experiments

The desorption of organic compounds from the sediments to Tenax was carried out as described previously [8]. Briefly, a mixture of Tenax TA (0.6 g), sediment (1 g dry wt), and Milli-Q water (70 ml) was constantly shaken in a 100-ml separation funnel. At each extraction step, the Tenax was refreshed and extracted with n-hexane (20 ml). Tenax is easily separated from the sediment and water, because the Tenax beads stick to the wall of the separation funnel. The desorption was determined by 17 consecutive extraction steps over a total desorption time of 20 d. For PAHs, n-hexane extracts were evaporated under a gentle nitrogen flow to 1 ml. After that, acetanilide (Mallinckrodt ChromAr) was added and evaporated again until 1 ml. The n-hexane extracts with chlorobenzenes and PCB were analyzed directly.

At the end of the desorption, the remnant amount of sorbate in sediment was analyzed by refluxing the sediment for 6 h with 20 ml of acetone and 50 ml of n-hexane. After refluxing, a part of the solvent mixture was evaporated under nitrogen and, at the end, was taken up in acetonitrile for PAH analysis. For chlorobenzenes and PCBs, the n-hexane extract was analyzed directly.

Acetonitrile extracts (20 μl) were injected on a Hewlett-Packard 1100 HPLC (Hewlett-Packard, Amstelveen, The Netherlands) equipped with fluorescence detection and a Vydac 201TP54 reversed-phase C₁₈ column (Grace Vydac, Hesperia, CA, USA). The elution was done with a gradient of Milli-Q water and acetonitrile. The PAH quantification was based on an external PAH standard.

Hexane extracts (1 ml) were injected on an Agilent 6890 gas chromatography system (Agilent Technologies, Palo Alto, CA, USA) equipped with a 63Ni electron-capture detector. Temperature programmed separation was carried out on a CP sil 8 CB capillary column (length, 50 m; inner diameter, 0.25 mm; film thickness, 0.25 μm; helium as a carrier gas; Chrompack). Tenax beads and extraction solvents were regularly checked for blank levels.

Desorption data analysis

Desorption from sediment has been found to be triphasic: Rapidly, slowly, and very slowly desorbing fractions \( F_{\text{rapid}} \), \( F_{\text{slow}} \), and \( F_{\text{very slow}} \), respectively) can be discerned [8]. It is described by
Table 1: Maximum capacities for adsorption of polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and chlorobenzenes in both the slowly desorbing domain and the very slowly desorbing domain (Q_{max, slow} and Q_{max, very slow}, respectively; nmol/g sediment) of Ketelmeer sediment and sorbate relative contact areas. Ranges are mean ± standard deviation

<table>
<thead>
<tr>
<th>Compound</th>
<th>Relative contact area</th>
<th>Q_{max, slow}</th>
<th>Q_{max, very slow}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>1</td>
<td>240 ± 20</td>
<td>138 ± 7</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>1.34</td>
<td>200 ± 57</td>
<td>94 ± 10</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>1.51</td>
<td>63 ± 3</td>
<td>28 ± 1</td>
</tr>
<tr>
<td>Chrysene</td>
<td>1.69</td>
<td>56 ± 1</td>
<td>17 ± 1</td>
</tr>
<tr>
<td>Benzo[a]fluoranthene</td>
<td>1.86</td>
<td>30 ± 2</td>
<td>20 ± 1</td>
</tr>
<tr>
<td>Dibenz[a, h]anthracene</td>
<td>2.08</td>
<td>10.4 ± 0.4</td>
<td>11.0 ± 0.6</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>1.22</td>
<td>118 ± 10</td>
<td>145 ± 8</td>
</tr>
<tr>
<td>2-Chlorobiphenyl</td>
<td>1.26</td>
<td>100 ± 16</td>
<td>77 ± 5</td>
</tr>
<tr>
<td>2,5-Dichlorobiphenyl</td>
<td>1.36</td>
<td>—</td>
<td>66 ± 4</td>
</tr>
<tr>
<td>2,4,4’-Trichlorobiphenyl</td>
<td>1.46</td>
<td>15.4 ± 1.2</td>
<td>36 ± 3</td>
</tr>
<tr>
<td>2,2’Dichlorobiphenyl</td>
<td>1.26</td>
<td>—</td>
<td>20 ± 1</td>
</tr>
<tr>
<td>2,2’,6-Trichlorobiphenyl</td>
<td>1.33</td>
<td>129 ± 12</td>
<td>10.5 ± 0.8</td>
</tr>
<tr>
<td>2,2’,6,6’-Tetrachlorobiphenyl</td>
<td>1.40</td>
<td>38 ± 5.0</td>
<td>1.8 ± 0.2</td>
</tr>
<tr>
<td>1,3-Dichlorobenzene</td>
<td>0.92</td>
<td>1010 ± 200</td>
<td>719 ± 67</td>
</tr>
<tr>
<td>1,2,4-Trichlorobenzene</td>
<td>1.05</td>
<td>460 ± 110</td>
<td>317.4 ± 20.5</td>
</tr>
<tr>
<td>1,2,3,4-Tetrachlorobenzene</td>
<td>1.18</td>
<td>185 ± 3</td>
<td>144 ± 9</td>
</tr>
<tr>
<td>Pentachlorobenzene</td>
<td>1.32</td>
<td>32 ± 2</td>
<td>38 ± 3.5</td>
</tr>
<tr>
<td>Hexachlorobenzene</td>
<td>1.45</td>
<td>23 ± 4.6</td>
<td>4.6 ± 0.5</td>
</tr>
</tbody>
</table>

* Not determined because of substantial data scatter for initial stages of desorption.

\[
\frac{dF_{\text{rapid}}}{dt} = -k_{\text{rapid}}F_{\text{rapid}} \tag{1}
\]

\[
\frac{dF_{\text{slow}}}{dt} = -k_{\text{slow}}F_{\text{slow}} \tag{2}
\]

\[
\frac{dF_{\text{very slow}}}{dt} = -k_{\text{very slow}}F_{\text{very slow}} \tag{3}
\]

at \( t = 0 \):

\[
F_{\text{initial rapid}} + F_{\text{initial slow}} + F_{\text{initial very slow}} = 1 \tag{4}
\]

at \( t = t \):

\[
F_{\text{rapid}} + F_{\text{slow}} + F_{\text{very slow}} + F_{\text{des}} = 1 \tag{5}
\]

where \( F_{\text{des}} \) (g/g) is the fraction cumulatively desorbed and is calculated by dividing the mass cumulatively desorbed at time \( t \) by the sum of the mass cumulatively desorbed at the end of the desorption and the mass still in the sediment. The rate constants for desorption of the linearly sorbed fraction and for slow and very slow desorption are designated \( k_{\text{rapid}} \), \( k_{\text{slow}} \), and \( k_{\text{very slow}} \) (1/h), respectively.

Values of \( k_{\text{rapid}} \), \( k_{\text{slow}} \), and \( k_{\text{very slow}} \) and initial values for \( F_{\text{rapid}} \), \( F_{\text{slow}} \), and \( F_{\text{very slow}} \) were determined by fitting data for \( F_{\text{des}} \) to Equations 1 to 5 using the EPISODE package (in stiff mode) of the Scientist® software (Micro Math Research, Saint Louis, MO, USA). The sum of squared deviations ranged from 1.1 \( \times 10^{-3} \) to 3.5 \( \times 10^{-2} \). Fitted values for \( F_{\text{rapid}} \) were substantially larger than those for \( F_{\text{slow}} \) and \( F_{\text{very slow}} \) because of the high sorbate loadings. Fitted values for, especially, \( k_{\text{slow}} \) and \( k_{\text{very slow}} \) were almost constant, at approximately \( 1 \times 10^{-2} \) and \( 5 \times 10^{-4} \) 1/h, respectively, as found in our earlier studies (see, e.g., [9]).

The \( Q_{\text{max, slow}} \) and \( Q_{\text{max, very slow}} \) values were calculated by multiplying the total starting sorbate concentration in sediment by \( F_{\text{slow}} \) and \( F_{\text{very slow}} \), respectively. As a result, \( Q_{\text{max}} \) values based on bulk soil mass were obtained.

Estimation of sorbate–sorbent relative contact areas

The carbonaceous surface of soil and soot-like materials may be envisaged as being built from planar PAH-like moieties [10]. Therefore, sorbate–sorbent contact areas were taken to be equal to the maximum value of the area of the hypothetical shadow produced by the sorbate on a planar surface. The areas were determined as described previously [5]. Briefly, prints of three-dimensional representations of molecular structures made in ACD/ChemSketch (Advanced Chemistry Development, Toronto, ON, Canada) were cut out and weighed. For PCBs, the software was allowed to rotate molecular structures to maximize the visualization of the planar surface area displayed on-screen. The PCB dihedral angles were set to 40, 60, and 90° for non-, mono-, and di-ortho-PCBs, respectively, based on data from De Bruin et al. [11]. Contact areas relative to arbitrarily chosen naphthalene are given in Table 1.

RESULTS AND DISCUSSION

The \( Q_{\text{max, slow}} \) and \( Q_{\text{max, very slow}} \) values are listed in Table 1. For 2,5-dichlorobiphenyl and 2,2’-dichlorobiphenyl, data scatter for the early stages of desorption prevented an accurate distinction between the rapidly desorbing fraction and the slowly desorbing fraction. As a result, for these two compounds, only the magnitude of the very slowly desorbing fraction could be obtained from the analysis of the desorption data.

Qualitatively, \( Q_{\text{max}} \) values in Table 1 decrease with increasing sorbate size. Earlier, in a theoretical study of PAHs and PCBs on the soot and soot-like materials, different linear characterizations of the non-planar di-ortho-chlorinated PCBs, mono-ortho-chlorinated PCBs, and di-ortho-chlorinated PCBs on the soot and soot-like materials [5], a similar decrease was found. In that study, it was determined that log-transformed \( Q_{\text{max}} \) values decreased linearly with increasing sorbate relative contact area. These sorbate relative contact areas were taken as equal to the relative area of the shadow of the sorbate on a planar surface. For PAHs, non-ortho-chlorinated PCBs, mono-ortho-chlorinated PCBs, and di-ortho-chlorinated PCBs on the soot and soot-like materials, different linear regression parameters were obtained. Furthermore, \( Q_{\text{max}} \) values for highly nonplanar di-ortho-chlorinated PCBs were less than those for relatively more planar compounds. The data in Table 1 qualitatively show that \( Q_{\text{max}} \) values decrease with increasing relative contact area. The linear relation between log-transformed \( Q_{\text{max}} \) values and relative contact area is illustrated in
Fig. 1. Maximum capacities for adsorption in the very slowly desorbing domain of Ketelmeer sediment (A) for polycyclic aromatic hydrocarbons (PAHs; open circles) and (B) for chlorobenzenes (filled squares), biphenyl and mono-ortho-polychlorinated biphenyls (PCBs; filled diamonds), and PCBs with two or more chlorine atoms at ortho positions (open diamonds). The dashed line is the linear regression line for PAHs. The drawn line is the linear regression line for the chlorobenzenes, biphenyl, and the mono-ortho-PCBs. The dotted line is the linear regression line for the PCBs with two or more chlorine atoms at ortho positions.

Figures 1 and 2 for the very slowly desorbing domain and the slowly desorbing domain, respectively.

Figure 1B illustrates that $Q_{\text{max, very slow}}$ values for PCBs with two or more chlorine atoms at ortho positions are smaller than those for PAHs, similar to the findings by van Noort et al. [5] for soot and soot-like materials. Data points in Figure 1B for mono-ortho-chlorinated PCBs are close to the PAH regression line, in contrast to the findings of van Noort et al. [5], who found that for soot and soot-like materials, mono-ortho-chlorinated PCB $Q_{\text{max}}$ values were smaller than those for PAHs. It should be noted, however, that in the present study, the range of PCB relative contact areas was 1.22 to 1.46, whereas it was 1.33 to 1.81 for the study of soot- and soot-like materials. Therefore, it cannot be ruled out that Ketelmeer $Q_{\text{max}}$ values for PCBs with four or more chlorine atoms would have been smaller than those for PAHs. Figure 1B also illustrates that $Q_{\text{max, very slow}}$ values for mono-ortho-chlorinated PCBs are higher than those for PCBs with two or more chlorine atoms at ortho positions. For soot and soot-like materials, such a difference was not observed [5], for which we have no explanation in the present study.

For $Q_{\text{max, slow}}$, Figure 2 illustrates that the data points for the two PCBs with two or more chlorine atoms at ortho positions are very close to the linear regression line for the chlorobenzenes, biphenyl, and mono-ortho-chlorinated PCBs. This is in contrast to Figure 1 for the $Q_{\text{max, very slow}}$ values, in which data points for the PCBs with two or more chlorine atoms at ortho positions were substantially below the regression line for the chlorobenzenes, biphenyl, and mono-ortho-chlorinated PCBs. That suggests that in the slow desorption domain, the number of adsorption sites does not depend on sorbate thickness, whereas in the very slow desorption domain, it does.

This dependence on sorbate thickness also appears from a consideration of values for the ratio of $Q_{\text{max, slow}}$ and $Q_{\text{max, very slow}}$ (given in Table 2). The $Q_{\text{max, slow}}:Q_{\text{max, very slow}}$ data for PAHs, for chlorobenzenes, and for biphenyl and mono-ortho-chlorinated PCBs in Table 2 show that within these three groups, this ratio is virtually constant, and this ratio equals approximately two for the three groups. Recently, from a study of $Q_{\text{max, slow}}$ and $Q_{\text{max, very slow}}$ values for phenanthrene added to 19 different soils and sediments [2], it was deduced that $Q_{\text{max, slow}}:Q_{\text{max, very slow}}$ was fairly constant, at approximately two. That rather constant ratio for phenanthrene in various soils and sediments, combined with our present findings for different sor-

![Graph](image)

![Graph](image)

Table 2. Ratio ($Q_{\text{max, slow}}:Q_{\text{max, very slow}}$) of maximum adsorption capacities for the slowly desorbing domain and the very slowly desorbing domain. Ranges are mean ± standard deviation

<table>
<thead>
<tr>
<th>Compound</th>
<th>$Q_{\text{max, slow}}:Q_{\text{max, very slow}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAHs</td>
<td>2.0 ± 0.8</td>
</tr>
<tr>
<td>Chlorobenzenes</td>
<td>2.0 ± 1.6</td>
</tr>
<tr>
<td>Biphenyl and mono-ortho-chlorinated PCBs</td>
<td>0.8 ± 0.4</td>
</tr>
<tr>
<td>PAHs, chlorobenzenes, biphenyl, and mono-ortho-chlorinated PCBs</td>
<td>1.7 ± 1.2</td>
</tr>
<tr>
<td>Di-ortho-chlorinated PCBs</td>
<td>15.7 ± 4.7</td>
</tr>
</tbody>
</table>

$^a$ PAHs = polycyclic aromatic hydrocarbons; PCBs = polychlorinated biphenyls.
chlorobenzenes and PCBs with less than two chlorine atoms.

Table 3. Regression parameters, with standard errors, for the data in Figure 1 and Figure 2

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Slowly desorbing domain</th>
<th>Very slowly desorbing domain</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Slope</td>
<td>Intercept</td>
</tr>
<tr>
<td>Polycyclic aromatic hydrocarbons</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorobenzenes and polychlorinated</td>
<td>$-1.25 \pm 0.09$</td>
<td>$3.74 \pm 0.15$</td>
</tr>
<tr>
<td>biphenyls*</td>
<td>$-3.20 \pm 0.20$</td>
<td>$6.00 \pm 0.26$</td>
</tr>
<tr>
<td>2,2'-Dichlorobiphenyl, 2,2',6'-trichlorobiphenyl</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>and 2,2',6,6'-tetrachlorobiphenyl</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

*For the very slowly desorbing domain not including polychlorinated biphenyls with two or more chlorine atoms at ortho positions.

bates on a single sediment, suggests that for planar compounds in various soils and sediment, $Q_{\text{max, slow}}:Q_{\text{max, very slow}}$ can be expected to be approximately two.

For the strongly nonplanar PCBs with two or more chlorine atoms at ortho positions, this ratio is higher by a factor of approximately eight. We reported previously [9] for in situ contaminants in two sediments that the ratio of $F_{\text{slow}}$ to $F_{\text{very slow}}$ for some planar compounds was higher, by a factor of three to seven, than for di-ortho-chlorinated PCBs. That suggests that differences in $F_{\text{slow}}:F_{\text{very slow}}$ values between planar and nonplanar compounds may be explained, at least in part, by differences in $Q_{\text{max, slow}}$ to $Q_{\text{max, very slow}}$ ratios.

The regression parameters for the linear regressions shown in Figures 1 and 2 are given in Table 3. For PAHs, chlorobenzenes, and PCBs with less than two chlorine atoms at ortho positions, the values for the slopes and intercepts in Table 3 indicate hardly any differences between the slowly desorbing domain and the very slowly desorbing domain. Slopes for the linear regressions were almost equal within compound class and the very slowly desorbing domain. Slopes for the slowly desorbing domain and the very slowly desorbing domain. Therefore, the log-transformed sum of $Q_{\text{max, slow}}$ to $Q_{\text{max, very slow}}$ for a PCB with two or more chlorine atoms at ortho positions could be expected to be approximately 0.2 log units lower than that for a comparable planar chlorinated compound. We have no explanation for this relatively low $Q_{\text{max, very slow}}$ value for 2,2',5,5'-tetrachlorobiphenyl in Lula sediment.

For Lula sediment, maximum capacities for adsorption were determined for toluene, naphthalene, 1,2-dichlorobenzene, phenanthrene, 4,4′-dichlorobiphenyl, 2,2',5,5'-tetrachlorobiphenyl, and $p,p'$-DDT [3]. In Figure 3, log-transformed $Q_{\text{max}}$ values from Kan et al. [3] are plotted versus the sorbate relative contact area. For the linear regressions in Figure 3, toluene was put in the chlorinated compounds group because of the relatively bulky methyl group, which would be more similar to a chlorine atom than to a hydrogen atom. The chlorinated compounds group did not include 2,2',5,5'-tetrachlorobiphenyl, because this PCB has two chlorine atoms at ortho positions.

Qualitatively, the regression lines in Figure 3 are comparable to those in Figures 1 and 2 for the PAHs and for the chlorobenzenes and PCBs with less than two chlorine atoms at ortho positions. The regressions parameters are listed in Table 4, along with those for the sum of $Q_{\text{max, slow}}$ and $Q_{\text{max, very slow}}$ for Ketelmeer sediment. The slopes of the regression lines for Lula sediment are similar to those for Ketelmeer sediment. The intercepts for Lula sediment were 0.4 to 0.8 log units lower than those for Ketelmeer sediment. This may be explained, in part, by differences in OC content. One could speculate that differences in black carbon content may play a role as well. The OC content of Lula sediment is 0.0027 g/g [3], whereas Ketelmeer sediment OC content is 40-fold higher (0.112 g/g).

In Figure 3, the data point for 2,2',5,5'-tetrachlorobiphenyl is more than one log unit below the regression line for the chlorinated compounds. Such a relatively low value could not be expected on the basis of the present findings for Ketelmeer sediment for the following reason: For the Ketelmeer slow desorption domain, data points for PCBs with two chlorine atoms at ortho positions were close to the chlorinated compounds regression line (Fig. 2). The $Q_{\text{max, slow}}$ to $Q_{\text{max, very slow}}$ ratios were approximately two (Table 2) for planar compounds.

For adsorption onto a dark-gray silt loam, maximum capacities were reported for benzene, some PAHs, and chlorobenzenes [4]. The PAHs were naphthalene, fluorene, phenanthrene, and pyrene. The chlorobenzenes comprised chlorobenzene, 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, and 1,2,4,5-tetrachlorobenzene. From the data in Xia and Ball [4],
$Q_{\text{max}}$ values for the four PAHs can be derived to be almost constant, at 229 to 263 nmol/g, and not to decrease with increasing relative contact area. For benzene, $Q_{\text{max}}$ was slightly higher at 1,450 nmol/g. A linear regression of the log-transformed $Q_{\text{max}}$ data for benzene and the four PAHs versus relative contact area suggests a slope of $-0.9$ ($r^2 = 0.7$), which is in between the corresponding values for Ketelmeer sediment and Lula sediment. For chlorobenzene, 1,2-dichlorobenzene, and 1,2,4-trichlorobenzene, $Q_{\text{max}}$ values were almost constant, at 675 to 755 nmol/g, and did not decrease with increasing relative contact area. For 1,2,4,5-tetrachlorobenzene, $Q_{\text{max}}$ was lower at 115 nmol/g. A linear regression of log-transformed chlorobenzene $Q_{\text{max}}$ values versus relative contact area suggested a slope of $-1.7$ ($r^2 = 0.5$). This slope is lower than the corresponding values for Ketelmeer sediment and Lula sediment but higher than the slope for benzene and PAHs in this soil.

The slopes of log $Q_{\text{max}}$ values versus relative contact area regressions for the Ketelmeer sediment also can be compared to the slopes obtained from a theoretical study [5] of $Q_{\text{max}}$ values for PAHs and PCBs on 10 different soot and soot-like materials. For the PAHs, the slope was $-2.89$, which was similar to the value of $-2.52$ derived by van Noort et al. [5] from experimental values for PAHs on an activated carbon presented in Walters et al. [12]. These values of $-2.89$ and $-2.52$ are substantially higher than the value of $-1.02$ for the Ketelmeer sediment. A similar difference is present for non-ortho-chlorinated PCBs. For the soot and soot-like materials, the slope was $-7.35$, whereas for Ketelmeer sediment, it was $-3.03$. That could suggest that the carbonaceous material in Ketelmeer sediment onto which adsorption takes place does not morphologically resemble soot, coal, charcoal, active carbon, or graphite on a molecular scale.

The close similarities between slopes for regressions of log $Q_{\text{max}}$ versus relative contact area for Ketelmeer sediment, for Lula sediment, and for the dark-gray silt loam, although less certain for the latter, suggest that the values for the slopes in the present study may, perhaps, apply to sediments and soils in general. Furthermore, work in this area is needed to more firmly substantiate this generality.

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