Supporting Information for the Manuscript

“Effects of Native Organic Material and Water on Sorption Properties of Reference Diesel Soot”

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SI-1. Methods and results of PAH concentration analysis.
SI-3. Extended descriptions for batch sorption experiments
SI-4. Comparison of sorption isotherms determined after two equilibration time periods.
SI-5. An indication of specific interactions in the EOM phase.

This material consists of 10 pages with 2 tables and 3 figures.
SI-1. Methods and results of PAH concentration analysis.

An aliquot (5.3%) of the composite methanol extract from the soot sample was reserved for PAH analysis. This extract was transferred to a 250 mL glass bottle and was spiked with methanol stock solution of internal standards (naphthalene-$d_8$, acenaphthene-$d_{10}$, phenanthrene-$d_{10}$, chrysene-$d_{12}$, and perylene-$d_{12}$). The extract was then mixed with 200 mL water, and the aqueous mixture was back-extracted with 20 mL of cyclohexane. After phase separation, ca. 15 mL of the cyclohexane layer were taken, concentrated under an N$_2$ stream, and injected into GC/MS (HP 6890GC/HP 5973MSD). A DB-5MS (30 m $\times$ 0.25 mm i.d., 0.25 $\mu$m film thickness, Agilent) capillary column was used for peak separation. Helium was used as carrier gas with a flow rate of 0.8 mL/min. The injector and transfer line temperatures were 250 and 315 °C, respectively. The oven temperature was 65 °C for 4 min, ramped up to 270 °C at a rate of 10 °C/min, held for 10 min, ramped further up to 310 °C at 10 °C/min, and held for 6.5 min. The detector was operated in the SIM mode for 16 EPA priority PAHs and two methylnaphthalenes. The PAHs thereof that were quantifiable are presented in Table S1 with their concentrations.

<table>
<thead>
<tr>
<th>PAH</th>
<th>this study</th>
<th>ref 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>naphthalene</td>
<td>1.2</td>
<td>n.a.</td>
</tr>
<tr>
<td>2-methylnaphthalene</td>
<td>1.2</td>
<td>n.a.</td>
</tr>
<tr>
<td>1-methylnaphthalene</td>
<td>0.71</td>
<td>n.a.</td>
</tr>
<tr>
<td>phenanthrene</td>
<td>10.2</td>
<td>17.0</td>
</tr>
<tr>
<td>fluoranthene</td>
<td>7.6</td>
<td>26.6</td>
</tr>
<tr>
<td>pyrene</td>
<td>0.21</td>
<td>0.9</td>
</tr>
<tr>
<td>chrysene</td>
<td>0.67</td>
<td>4.56</td>
</tr>
</tbody>
</table>

n.a., no data available.

Table S2. Properties of the probe sorbates used.

<table>
<thead>
<tr>
<th>sorbate</th>
<th>Abb.</th>
<th>$E^a$</th>
<th>$S^a$</th>
<th>$A^a$</th>
<th>$B^a$</th>
<th>$L^a$ (25 °C)</th>
<th>log $S_w$ (25 °C)</th>
<th>log $K_{ow}$ (25 °C)</th>
<th>log $K_{aw}$ (20 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-octane</td>
<td>nOCT</td>
<td>0.000</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>3.677</td>
<td>−0.13</td>
<td>5.18</td>
<td>1.95</td>
</tr>
<tr>
<td>cyclooctane</td>
<td>cOCT</td>
<td>0.413</td>
<td>0.10</td>
<td>0.00</td>
<td>0.00</td>
<td>4.329</td>
<td>0.90</td>
<td>4.45</td>
<td>0.51</td>
</tr>
<tr>
<td>n-propylbenzene</td>
<td>PrBZ</td>
<td>0.604</td>
<td>0.50</td>
<td>0.00</td>
<td>0.15</td>
<td>4.230</td>
<td>1.72</td>
<td>3.69</td>
<td>−0.49</td>
</tr>
<tr>
<td>naphthalene</td>
<td>NAPH</td>
<td>1.340</td>
<td>0.92</td>
<td>0.00</td>
<td>0.20</td>
<td>5.161</td>
<td>1.49</td>
<td>3.30</td>
<td>−1.90</td>
</tr>
<tr>
<td>tetrachloroethylene</td>
<td>PCE</td>
<td>0.639</td>
<td>0.44</td>
<td>0.00</td>
<td>0.00</td>
<td>3.584</td>
<td>2.31</td>
<td>3.40</td>
<td>−0.27</td>
</tr>
<tr>
<td>1,2,4-trichlorobenzene</td>
<td>TCB</td>
<td>0.980</td>
<td>0.81</td>
<td>0.00</td>
<td>0.00</td>
<td>1.084</td>
<td>1.69</td>
<td>4.02</td>
<td>−1.15</td>
</tr>
</tbody>
</table>

*Linear solvation energy relationship parameters: $E$, excess molar refraction; $S$, dipolarity/polarizability parameter; $A$, solute hydrogen-bond acidity; $B$, solute hydrogen-bond basicity; $V$, molar volume. Data are from Abraham et al. (2-5). $S_w$, aqueous solubility; $K_{ow}$, octanol–water partitioning coefficients; from ref 6. Calculated by LSERs. See Supporting Information of ref 7.

Solid solubilities. From ref 8. From ref 9.
SI-3. Extended descriptions for batch sorption experiments.

The suppliers and the purities of the probe chemicals were as following: \textit{n}-octane (Fluka, 99.7%); cyclooctane (Fluka, 99.5%); \textit{n}-propylbenzene (Aldrich, 98%); \textit{d}_8\text{-}naphthalene (Aldrich, 98 atom%); tetrachloroethene (Aldrich, 99.9%).

Sorption isotherms were determined by the method used in ref 10 with minor modifications. Thus, 5–50 mg of the untreated or the extracted soot were weighed into glass vials and were mixed with 15 or 17 mL of water containing 200 mg/L (3.08 mM) NaN\textsubscript{3} and 5 mM CaCl\textsubscript{2}. These vials were closed with polyethylene caps and silicon-PTFE septa lined inside with aluminum foil and were horizontally shaken for one day to wet the soot. The caps, septa, and foil were then removed. Aluminum foil has a smooth surface and does not remove a significant amount of sorbent from the batch, as tested previously (10). The soot suspensions were spiked with methanol stock solutions of a sorbate and immediately sealed with aluminum crimp caps and silicon-aluminum septa (Fischer Scientific). The methanol content did not exceed 0.2 vol\% in the aqueous phase so that cosolvent effects on the sorption are unlikely. For each sorbate, five concentrations were prepared in duplicates. No replicate was prepared for tetrachloroethene to the untreated soot, nor was a sorption isotherm of tetrachloroethene to the extracted soot determined, because of the limited availability of the soot sample and the relatively weak sorption of tetrachloroethene which requires a large amount of sorbent. The vials were then horizontally shaken at 20 °C for 28 days. The results were not significantly different from those of preliminary experiments with an equilibration time of 10 days (Figure S2). The highest equilibrium aqueous phase concentrations in the measured isotherms were 11–57\% of the solubilities of the sorbates. An except was tetrachloroethene (0.5%), for which the data at the highest concentration was not available. Background concentrations of the probe compounds were examined by preparing soot-water suspensions without sorbate spiking and were found to be below the detection levels.
Equilibrium aqueous phase concentrations were determined by a headspace sampling method, where 250–1000 µL of the gas phase in the batch reactor was withdrawn by a gas-tight syringe and analyzed by GC/MS (TraceGC 2000/TraceDSQ, ThermoFinnigan) equipped with a RTX-VMS column (60 m × 0.32 mm i.d., 1.8 µm film thickness, Restek Corp.). Sampling and injection were fully automated using a Combi PAL autosampler system (CTC Analytics). The sample tray was temperature-controlled at 20 °C during the measurement sequence using a Peltier tray cooler. Calibration standards were prepared in the same volume of water as in the sorption batches, but without sorbent. Two days were given for dissolution and air–water equilibrium distribution of the analytes in the standard solutions. Since the headspace concentration of the sorbate is proportional to the freely dissolved aqueous phase concentration, the headspace method does not require a separation of the aqueous phase from the sorbent and is thus free of artifacts due to suspended colloidal particles. Sorbed concentrations were determined by mass balance calculations, assuming no loss of the sorbate during the sorption period as proven in preliminary experiments (Figure S1). The fraction of the sorbate in the gas phase was taken into account using air–water partitioning coefficients ($K_{aw}$) at 20 °C (see Table S2 for values of $K_{aw}$). Note that the $K_d$ values of the octanes determined this way are influenced by the accuracy of the $K_{aw}$ values. The values used in this study were carefully selected as reported previously (10).
Figure S1. GC/MS peak areas for samples prepared 33 days before and just before analysis. Sample vials (20 mL) contained water (15 mL) and analytes and were sealed with aluminum-lined septa. Headspace was sampled and injected into the GC/MS, as described in the text. The values shown are the mean of 4 replicates. The error bars indicate standard deviations.
SI-4. Comparison of sorption isotherms determined after two equilibration time periods.

Figure S2. Comparison of sorption isotherms determined after two equilibration time periods. Abbreviations denote: nOCT, n-octane; cOCT, cyclooctane; PrBZ, n-propylbenzene; NAPH, naphthalene; PCE, tetrachloroethene. Data for n-octane and cyclooctane to the untreated soot are from ref 10. Solid lines indicate the fitted Freundlich isotherms to the data points from the longer-term experiments.
To investigate molecular interactions in/on a sorbent, it is useful to convert sorbent–water partitioning coefficients to sorbent–air partitioning coefficients through a thermodynamic cycle using air–water partitioning coefficients ($K_{aw}$). Here we calculate the EOM–air partitioning coefficients ($K_{EOM/air}$) as,

$$K_{EOM/air} = K_{EOM/W} \cdot K_{aw}^{-1}$$

In Figure S3 below, the log of the $K_{EOM/air}$ values obtained are compared to the log of the hexadecane–air partitioning coefficients ($K_{HD/air}$). $K_{HD/air}$ serves as the descriptor for nonspecific interactions. Figure S3 indicates that there is a 0.5–1 log-unit deviation in $K_{EOM/air}$ between $n$-propylbenzene and $n$-octane, although the log $K_{HD/air}$ values of the two sorbates are nearly identical. Since $n$-octane does not undergo any specific interaction but $n$-propylbenzene does to some extent, the observed difference in log $K_{EOM/air}$ indicates the presence of specific interactions with $n$-propylbenzene in the EOM phase. However, the type of specific interactions (i.e., permanent dipole–dipole interactions, hydrogen bonding interactions) cannot be identified with the current data set.

**Figure S3.** Log EOM–air partitioning coefficients ($K_{EOM/air}$) plotted against log hexadecane–air partitioning coefficients ($K_{HD/air}$).
Literature Cited in the Supporting Information


