Supporting Information

to

Sorption-induced effects of humic substances on mass transfer of organic pollutants through aqueous diffusion boundary layers: the example of water/air exchange

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A) Figure S1



Figure S1. First-order plot of normalized gas-phase concentration of n-octane, showing the depletion of n-octane during dynamic purging experiments with aqueous solutions in the absence (\blacksquare) and presence(\blacktriangle) of CHA (reduced-activity system).

B) Derivation of eq. 4

In order to derive quantitative data about the mass-transfer rates across the aqueous boundary layer, we applied the boundary layer model as described already in the main text. The mass flux of any compound through the boundary layer is described by eq. 3 of the main text ($j = k_L \times A \times (c_{bulk} - c_{surface})$, which in case of $c_{surface} \approx 0$ can be simplified to eq. S1.

$$j = k_{\rm L} \times A \times C_{\rm bulk} \tag{S1}$$

In addition, the flux of the model compound in the effluent can be described by

$$j = Q \times c_{\rm g} \tag{S2}$$

where *Q* is the volumetric gas flow rate.

Combining eqs. S1, and S2 results in eq. S3:

$$c_{\text{bulk}} = \frac{Q}{k_{\text{L}} \times A} \times c_{\text{g}}$$
(S3)

The depletion of the model compound in the system due to the purging can be described by eq. S4:

$$c_{\text{tot}} = c_{\text{tot},0} - \frac{Q}{V_{\text{w}}} \times \int_{0}^{t} c_{\text{g}} \, \mathrm{d}t \tag{S4}$$

with c_{tot} and $c_{tot,0}$ as total concentrations of the analyte in the liquid phase at *t* and *t* = 0, respectively. If the system consists only of headspace volume and a homogeneous aqueous phase than it holds $c_{tot} = c_{bulk}$ and $c_{tot,0} = c_{bulk,0}$ so that eq. S3 can be used to introduce gas phase concentrations into eq. S4 in order to give eq. S5:

$$c_{\rm g} = c_{\rm g,0} - \frac{k_{\rm L} \times A}{V_{\rm w}} \times \int_{0}^{t} c_{\rm g} \,\mathrm{d}t \tag{S5}$$

By means of derivation by d*t*, it is possible to describe the change of the gas phase concentration as a function of time:

$$\frac{\mathrm{d}C_{\mathrm{g}}}{\mathrm{d}t} = -\frac{k_{\mathrm{L}} \times A}{V_{\mathrm{w}}} \times C_{\mathrm{g}}$$
(S6)

Integration of eq. S6 yields eq. S7 which is identical with eq. 4 in the main text:

$$\ln\left(\frac{c}{c_0}\right)_g = -\frac{k_L \times A}{V_w} \times t = -m \times t$$
(S7)

Thus, a plot of $\ln\left(\frac{c}{c_0}\right)_g$ versus time should be linear. The effective mass-transfer

coefficient $k_{\rm L} \ge A$ is calculated from the slope *m*. For this purpose, any time period of a running purging experiment can be considered. The initial concentration c_0 is the gas phase concentration of the model compound at the start of the observation period and *t* is the time elapsed after this start time.

The derivation of an equation for interpretation of contaminant depletion in terms of effective mass-transfer coefficients for the case of $c_{surface} \neq 0$ is described in the Supplementary material of (Ramus et al. 2011). There we also showed that the approximation $c_{surface} \approx 0$ is justified if the gas phase concentration of the compound measured during purging (c_g) is much smaller than the value measured at equilibrium ($c_{g,eq}$, after closing the system), i.e. if it holds that $c_g/c_{g,eq} << 1$.

C) Figure S2



Figure S2. Effective mass-transfer coefficients of benzene at various concentrations of a) CHA, b) SRHA, c) SRFA and d) SDS (below and above $CMC_{SDS} = 2300 \text{ mg L}^{-1}$) determined for the reduced-activity system. Solid lines were drawn as guides to the eye. Error bars represent 2 σ .

D) Equation S8 for calculation of predicted values for the ratio of effective mass-transfer coefficients in the presence of CHA (Figure 3 in the main text)

$$\left(\frac{(k_{\rm L} \times A)_{\rm n-octane}}{(k_{\rm L} \times A)_{\rm benzene}}\right)^{\rm CHA} = \left(\frac{(k_{\rm L} \times A)_{\rm n-octane}}{(k_{\rm L} \times A)_{\rm benzene}}\right)^{\rm water} \times \frac{(k_{\rm L} \times A)_{\rm n-octane}^{\rm sorp}}{(k_{\rm L} \times A)_{\rm n-octane}^{\rm no \ sorp}}$$
(S8)

The effective mass-transfer coefficient of benzene was assumed not to be affected by sorption-induced effects, due to its insignificant sorbed fraction for CHA concentrations \leq 1 g L⁻¹. Therefore, this term does not need to appear in eq. S8.

 $\frac{(k_{\rm L} \times A)_{n-\rm octane}^{\rm sorp}}{(k_{\rm L} \times A)_{n-\rm octane}^{\rm no \ sorp}}$ was calculated according to eq. 10, using log $K_{\rm DOC}$ = 4.05, ξ = 1 and

 $D_{\rm u}/D_{\rm b} = 50$ and 5, respectively.



E) Figure S3 and discussion of conditions in the constant-activity system

Figure S3. Normalized concentrations of n-octane and benzene in the gas phase during the purging experiment with passive dosing (constant-activity system). Concentrations measured at the first sampling point (15 min after starting purging + mixing of the aqueous phase) were used for normalization (c_0). Line for benzene was obtained by fitting to first-order kinetics, line for n-octane illustrates hypothetical case of $c/c_0 = 1$. Error bars represent 2 σ .

Partitioning of the model compounds between PDMS and water phase

The partition coefficients of the PDMS sheets K_{PDMS} for benzene and n-octane can be approximately predicted from the PDMS/water partition coefficients reported in the literature for the PDMS phase of SPME fibers. For n-octane log $K_{PDMS-fiber,n-octane} =$ 4.42 (Kopinke et al. 1999) was determined and for benzene values between log $K_{PDMS-fiber,benzene} =$ 1.94 (Paschke and Popp 1999) and 2.10 (Nardi et al. 2003) were reported.

Based on log $K_{\text{PDMS,n-octane}} = 4.42$ for system containing water and 2 g L⁻¹ of the PDMS sheets the ratio between the PDMS-sorbed amount ($n_{\text{PDMS,n-octane}}$) and the freely dissolved amount of n-octane ($n_{\text{free,n-octane}}$) is predicted as

 $n_{\text{PDMS,n-octane}}/n_{\text{free,n-octane}} = K_{\text{PDMS,n-octane}} \times c_{\text{PDMS}} = 53$. Due to this high ratio, it is reasonable to expect that the PDMS sheets act as a non-depleting source for n-octane during the considered time scales ($t \le 150$ min). This assumption was confirmed experimentally by the results shown in Fig. S3, where constant n-octane concentrations were observed over about 150 min of purging in the passive dosing system.

For benzene, enrichment in PDMS is not high enough in order to provide a significant source effect. Adding 2 g L⁻¹ PDMS sheets into an aqueous solution of benzene results in a benzene depletion by a factor of $f_{\text{PDMS}} = c_{\text{bulk}}/c_{\text{total}} = 0.44 \pm 0.03$. The partition coefficient log $K_{\text{PDMS,benzene}} = 2.20$ which is calculated from the experimentally determined f_{PDMS} value is in accordance with the above mentioned values for $K_{\text{PDMS-fiber,benzene}}$.

The sorption effect caused by the PDMS sheets reduces the rate constant for removal of benzene by purging by a factor of f_{PDMS} according to

$$\ln\left(\frac{c}{c_0}\right)_g = -\frac{k_L \times A}{V_w} \times f_{PDMS} \times t$$
(S9)

Eq. S9 which is different from eq. S7 only by the factor f_{PDMS} , can be derived analogously to the procedure described in part B of this Supporting information, with the exception that the bulk water phase concentration is related to the total concentration of benzene in the system by $c_{bulk} = f_{PDMS} \times c_{tot}$.

The presence of the various DHS in a concentration of 1 g L⁻¹ did not significantly affect f_{PDMS} , which is reasonable taking into account the insignificant sorption of benzene by DHS at this concentration (Table 1). Only in the presence of 5 g L⁻¹ SDS, f_{PDMS} was increased to 0.56 ± 0.02, which is due to the solubility enhancement effect of the micelles for benzene ($x_{sorb,benzene} = 0.29$ at 5 g L⁻¹ SDS, Table 1).

Even after taking into account the buffering effect of the sheets (by applying eq. S9) there is still a difference in the $k_{\rm L} \times A$ values determined for benzene in the constant activity system in comparison to the system without PDMS sheets (a factor of about 4). This is clearly due to the reduced agitation intensity of the water phase in the presence of the PDMS sheets (at the same stirring rate) which was also observed visually.

Rate of compound redelivery from the PDMS sheets

In order to interprete the passive dosing experiments with respect to mass transfer in the aqueous boundary layer at the water/gas interface, it is necessary to assure that compound delivery by the PDMS sheets into the water phase is instantaneous compared to depletion from the water by purging. Fig. S3 illustrates that this assumption is indeed justified. From the start of measurement of n-octane headspace concentrations (15 min after starting purging + mixing of the water phase) this concentration was constant within the experimental error range. This observation disproves the objection that delivery of n-octane from the sheets has any influence on mass transfer of n-octane into the gas phase. Otherwise, the approach to a steady state concentration (determined by both, water/gas and PDMS/water mass transfer) different from the start concentration should have been observable during the experiment shown in Fig. S3.

In order to explain this in more detail: the aqueous phase is initially in equilibrium with the PDMS sheets. After starting the mixing in addition to purging, n-octane is continuously removed from the aqueous phase. If the re-delivery from the PDMS sheets was too slow in order to compensate this loss, then there should be a decline in the measured headspace concentration until a steady state concentration is reached. This steady state concentration cannot be reached in less than 15 min, considering the low rate of water/gas mass transfer (as illustrated by the slow decline of c/c_0 for benzene in Figure S3).

F) Derivation of eq. 12 for calculation of predicted values in Fig. 4

In order to predict the sorption-induced effect on the n-octane flux, we make again use of eqs. 3 and 10 of the main text, which are presented as eqs. S10 and S11 here again:

$$j = k_{\rm L} \times A \times \left(c_{\rm bulk} - c_{\rm surface} \right)$$
(S10)

$$\frac{(k_{\rm L} \times A)^{\rm sorp}}{(k_{\rm L} \times A)^{\rm no \, sorp}} = \left(\frac{1 + K_{\rm DOC} \times c_{\rm DOC} \times \xi \times D_{\rm b} / D_{\rm u}}{1 + K_{\rm DOC} \times c_{\rm DOC}}\right)^{2/3}$$
(S11)

In case of the constant activity system, the concentration of the freely dissolved sorbate fraction is expected to be identical in the presence and absence of dissolved sorbents, whereas the bulk water phase concentration is increased by the sorbed fraction:

$$(C_{\text{bulk}})^{\text{no sorp}} = C_{\text{free}}$$
(S12)

$$(c_{\text{bulk}})^{\text{sorp}} = c_{\text{free}} + K_{\text{DOC}} \times c_{\text{DOC}} \times c_{\text{free}} = c_{\text{free}} \times (1 + K_{\text{DOC}} \times c_{\text{DOC}})$$
(S13)

The ratio of compound flux in the presence and absence of partitioning to a sorbent depends thus on the ratio of the mass-transfer coefficients and the different bulk-phase concentrations of the compound (provided that the boundary conditions of $c_{surface} = 0$ holds, which is given in our experiments):

$$\frac{j^{\text{sorp}}}{j^{\text{no sorp}}} = \frac{(k_{\text{L}} \times A)^{\text{sorp}}}{(k_{\text{L}} \times A)^{\text{no sorp}}} \times \frac{(c_{\text{bulk}})^{\text{sorp}}}{(c_{\text{bulk}})^{\text{no sorp}}}$$
(S14)

Introducing eqs. S11 - S13 into eq. S14 results in eq. S15:

$$\frac{j^{\text{sorp}}}{j^{\text{no sorp}}} = \left(1 + K_{\text{DOC}} \times c_{\text{DOC}} \times \xi \times D_{\text{b}} / D_{\text{u}}\right)^{2/3} \times \left(1 + K_{\text{DOC}} \times c_{\text{DOC}}\right)^{1/3}$$
(S15)

We can now calculate the expected ratio of the normalized gas phase concentrations of n-octane in the presence and absence of CHA according to eq. S16:

$$R_{n-\text{octane}}^{\text{sorp,calc}} = \frac{(c_{\text{N},n-\text{octane}})^{\text{CHA}}}{(c_{\text{N},n-\text{octane}})^{\text{water}}} = \frac{(j_{n-\text{octane}})^{\text{sorp}}}{(j_{n-\text{octane}})^{\text{water}}}$$
(S16)

The effective mass-transfer coefficient of benzene was assumed not to be affected by sorption-induced effects, due to its insignificant sorbed fraction for CHA concentrations $\leq 1 \text{ g L}^{-1}$. Therefore, the terms ($k_{\text{L}} \times A$)_{benzene} from eq. 5 (main text) do not need to appear in eq. S16.

Substituting the flux ratio in eq. S15 by eq. S16 results in eq. S17 which is identical with eq. 12 in the main text.

$$R_{n-\text{octane}}^{\text{sorp,calc}} = \frac{(j_{n-\text{octane}})^{\text{sorp}}}{(j_{n-\text{octane}})^{\text{no sorp}}} = \left(1 + K_{\text{DOC}} \times c_{\text{DOC}} \times \xi \times \frac{D_{\text{b}}}{D_{\text{u}}}\right)^{\frac{2}{3}} \times \left(1 + K_{\text{DOC}} \times c_{\text{DOC}}\right)^{\frac{1}{3}}$$
(S17)

Literature cited

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