

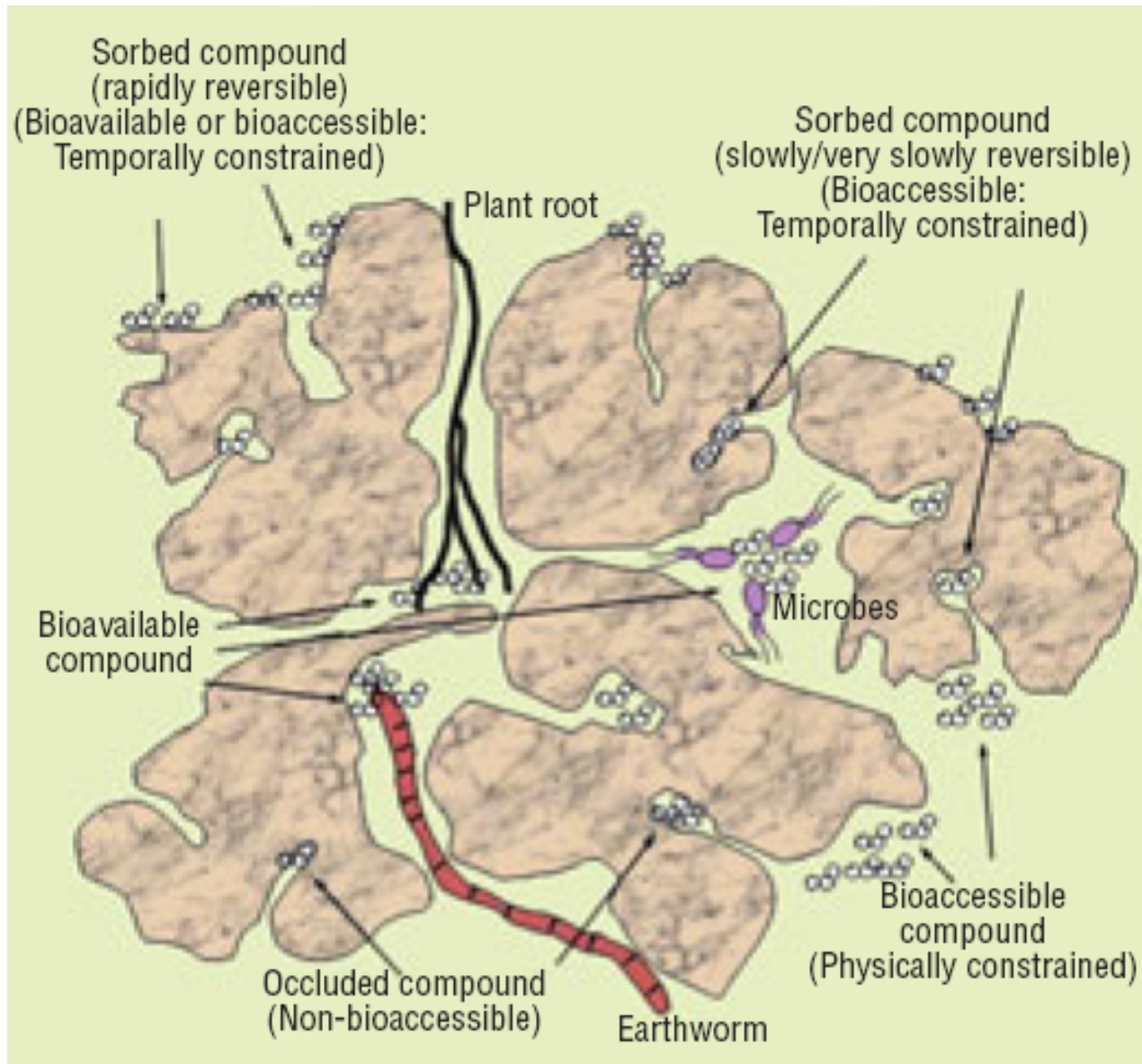
**BIOAVAILABILITY OF ORGANIC
CONTAMINANTS IN SEDIMENT AND SOIL
– EMERGING INSIGHTS**

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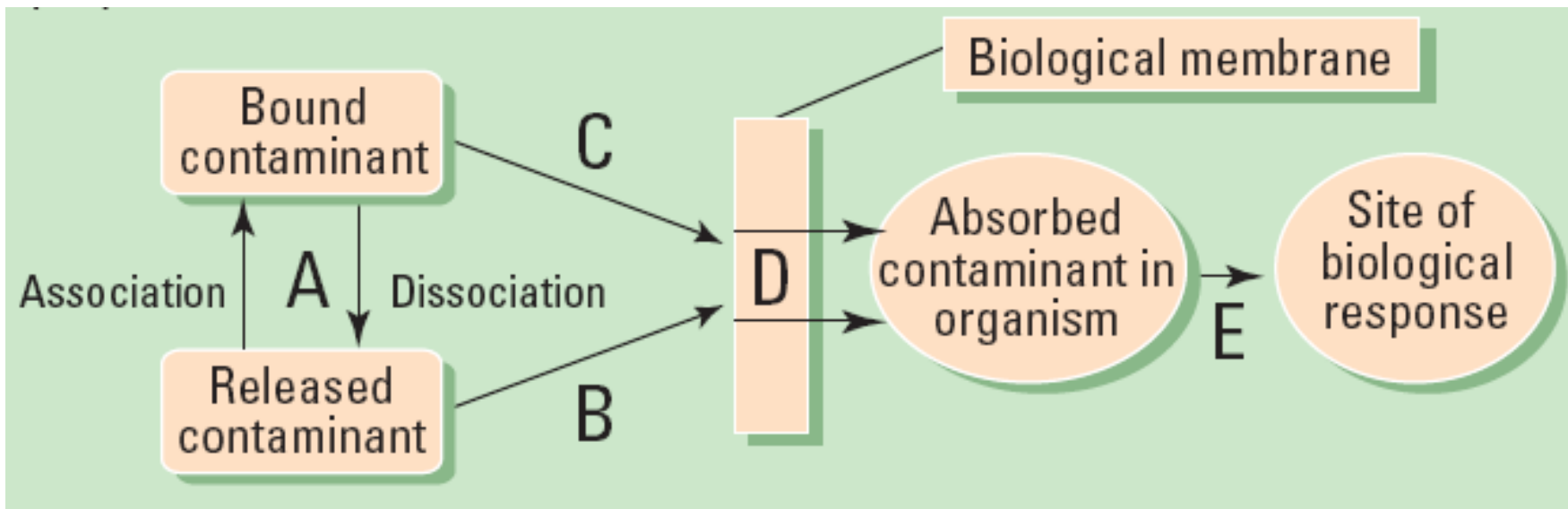
University of Amsterdam





K.T. Semple et al. 2004, Environ. Sci. Technol., 38:228A-231A.

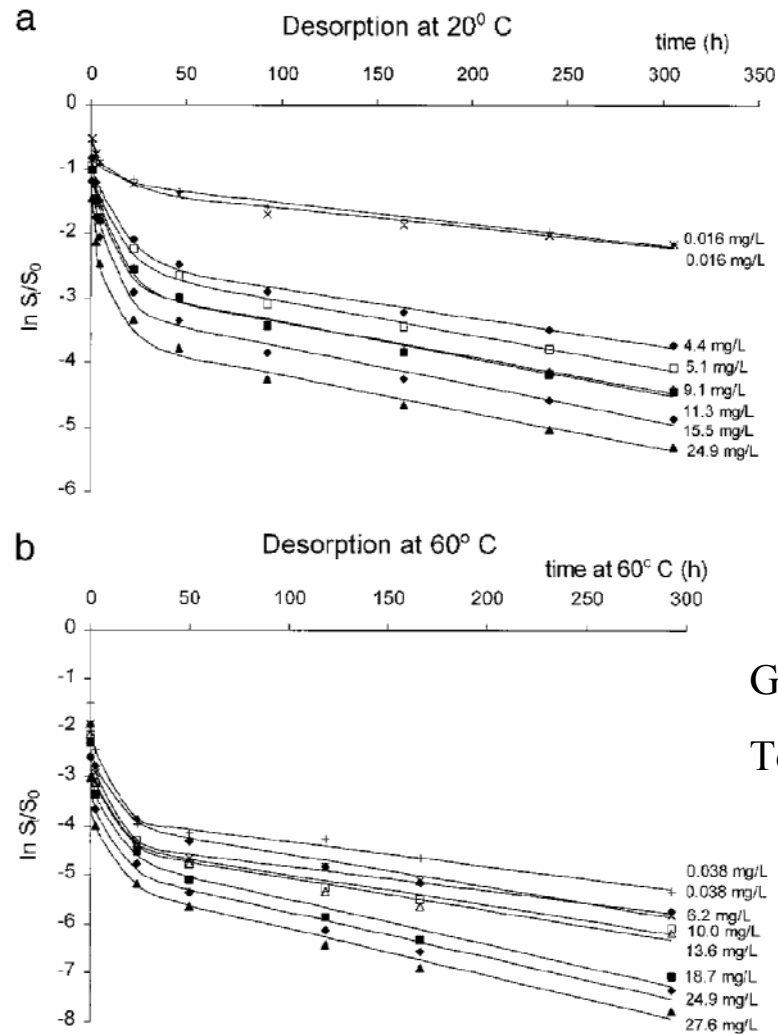




National Research Council. Bioavailability of Contaminants in Soils and Sediments: Processes, Tools, and Applications; National Academies Press: Washington, DC, 2002.



Desorption kinetics of HOCs



G. Cornelissen et al., 2000, Environ.
Toxicol. Chem., 19:1532-1539.

Fig. 1. Desorption curves of 1,2,4-trichlorobenzene (TCB) from spiked Oostvaardersplassen sediment at different TCB concentrations; plotted in $\ln(S_t/S_0)$ versus time. The solid line is obtained by exponential curve fitting to Equation 1. (a) Experiment at 20°C. (b) Experiment at 60°C (time at 60°C is time after the initial 24 h of desorption at 20°C, see text).

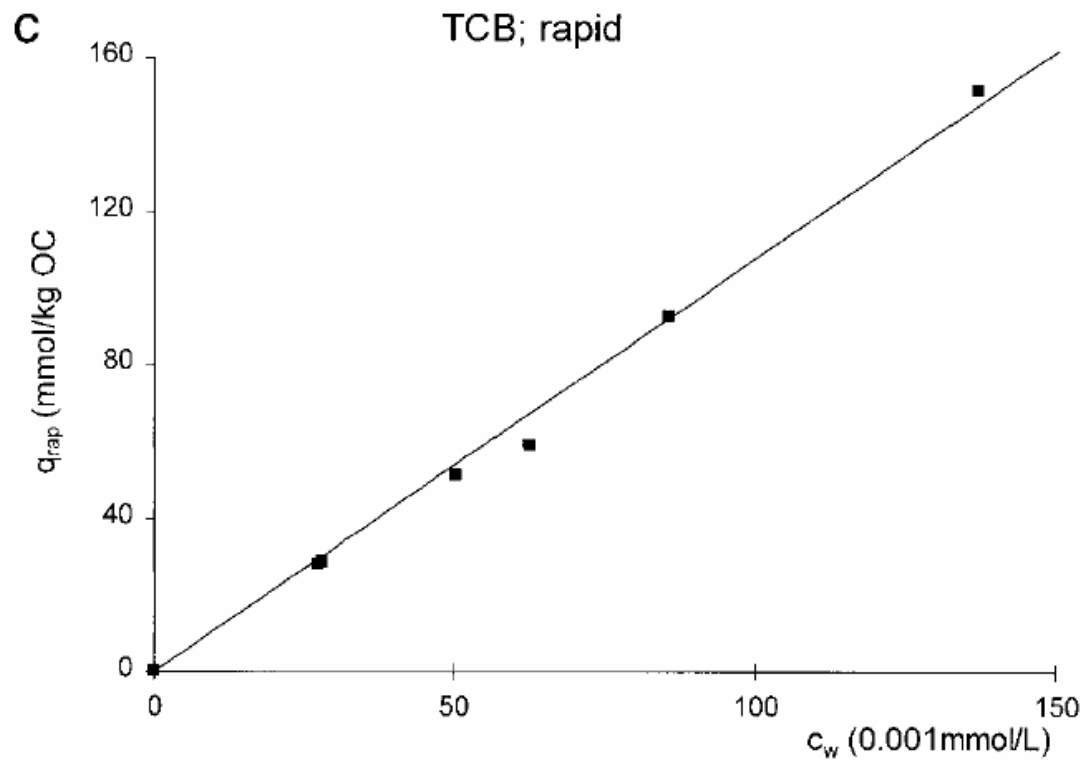
Table 1. Rate constants of rapid ($k_{d,rap}$), slow ($k_{d,slow}$) and very slow ($k_{d,vs}$) desorption. Average values for all concentrations are given, with standard deviations

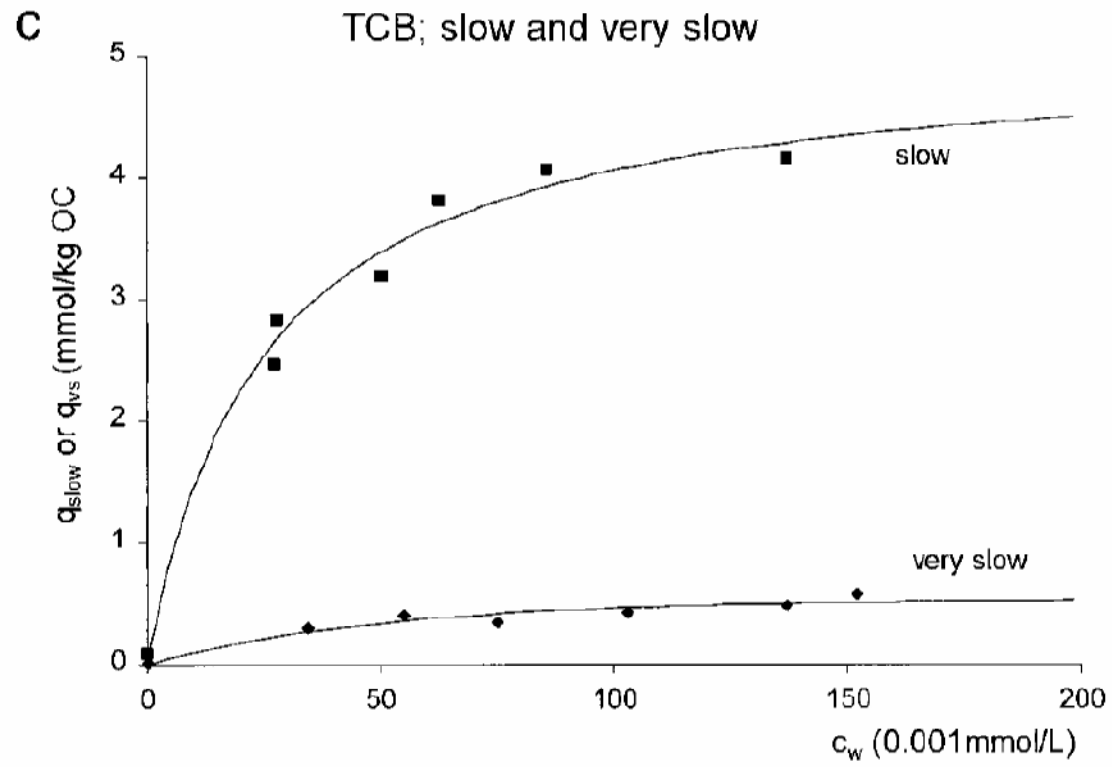
	$k_{d,rap}$ (per hour)	$k_{d,slow}$ ($10^{-3}/h$)	$k_{d,vs}$ 20°C ($10^{-4}/h$) ^a	$k_{d,vs}$ 60°C ($10^{-3}/h$)
TCE ^b	0.67 ± 0.18	5.4 ± 1.0	2.2	8.5 ± 1.9
DCB	0.46 ± 0.18	8.1 ± 2.6	2.8	6.4 ± 2.0
TCB	0.18 ± 0.09	5.4 ± 0.5	0.93	7.6 ± 0.6

^a Extrapolated from the values at 60°C by assuming that $k_{d,vs}$ has the same temperature dependence as $k_{d,slow}$.

^b TCE = trichloroethylene; DCB = 1,3-dichlorobenzene; TCB = 1,2,4-trichlorobenzene.







Bioavailability of sorbed fractions

Table 4. Rapidly desorbing fractions (F_{rap}) in laboratory-contaminated sediment at different contact times. Contact time reduction factor for F_{rap} calculated as the ratio of the average F_{rap} at contact time = 5, 14, and 91 d and the F_{rap} at contact time = 959 d. For $\log K_{\text{ow}}$ and molecular weight (M), see Table 3^a

	F_{rap}				Contact time reduction factor
	5 d ^b	14 d ^b	91 d ^b	959 d	
PAHs					
PHE	0.68 (0.68; 0.69)	0.63 (0.54; 0.72)	0.74 (0.74; 0.74)	0.55	1.2
FLU	0.61 (0.59; 0.62)	0.76 (0.75; 0.77)	0.70 (0.69; 0.70)	0.56	1.2
BaA	0.36 (0.29; 0.42)	0.66 (0.66; 0.66)	0.50 (0.49; 0.51)	0.41	1.2
CHR	0.35 (0.29; 0.40)	0.69 (0.68; 0.69)	0.50 (0.50; 0.50)	0.43	1.2
BbF	0.20 (0.07; 0.33)	0.32 (0.37; 0.28)	0.22 (0.21; 0.22)	0.28	0.9
BkF	0.14 (0.06; 0.21)	0.30 (0.37; 0.24)	0.23 (0.15; 0.30)	0.32	0.7
BaP	0.07 (0.05; 0.08)	0.29 (0.33; 0.25)	0.19 (0.18; 0.20)	0.28	0.6
Chlorobenzenes					
Penta	0.67 (0.71; 0.63)	0.72 (0.80; 0.63)	0.59 (0.58; 0.61)		
Hexa	0.56 (0.59; 0.54)	0.80 (0.84; 0.77)	0.67 (0.66; 0.68)	0.35	1.9

^a For abbreviations, see footnote of Table 2.

^b Measurements in duplicate; in parentheses are individual measurements.

R.H. Kraaij et al., 2002, Environ. Toxicol. Chem., 21:752-759.



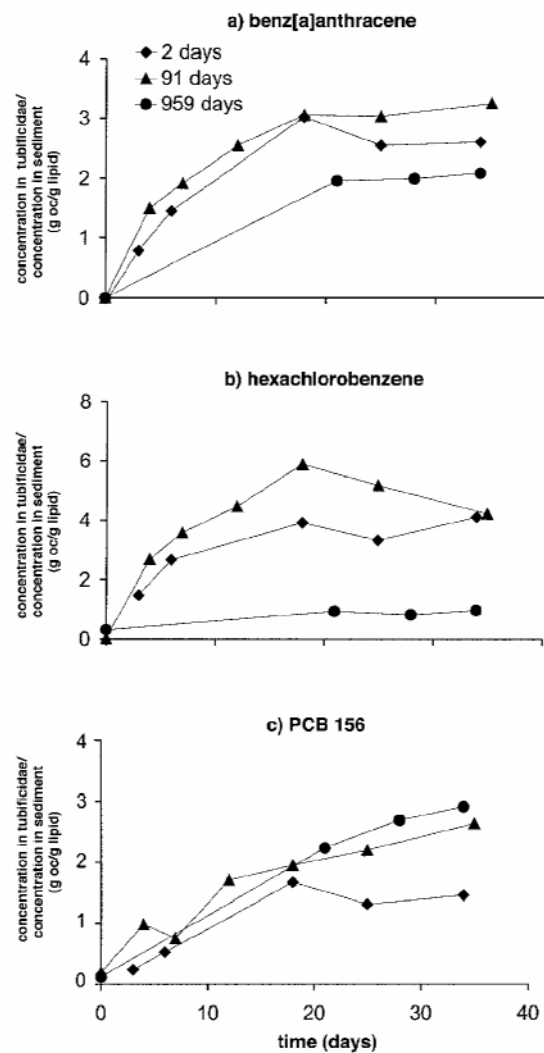


Fig. 1. Typical accumulation curves of (a) the polycyclic aromatic hydrocarbon benzo[a]anthracene, (b) the chlorobenzene hexachlorobenzene, and (c) the polychlorinated biphenyl 2,3,3',4,4',5-hexachlorobiphenyl in oligochaetes (Tubificidae) in lab-contaminated sediment at different contact times of the contaminant in the sediment. Accumulation expressed as lipid normalized concentration in biota divided by organic carbon-normalized concentration in the sediment ($\mu\text{g organic carbon}/\mu\text{g lipid}$).



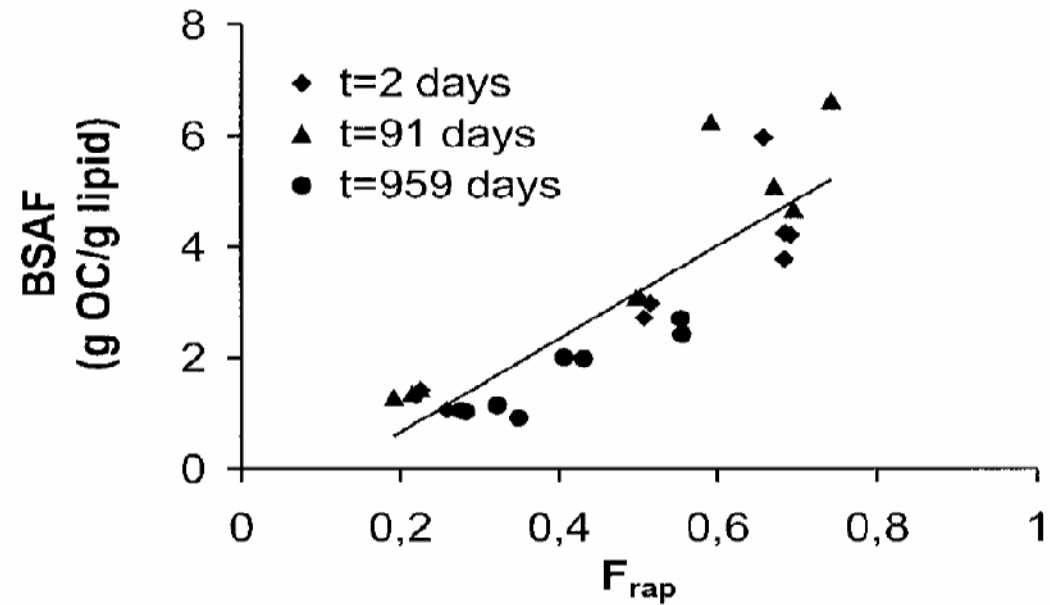


Fig. 4. Average biota-to-sediment accumulation factor (BSAF) (g organic carbon/g lipid) of chlorobenzenes and polycyclic aromatic hydrocarbons for oligochaetes (Tubificidae) in lab-contaminated sediment versus average rapidly desorbing fraction F_{rap} at the first, second, and third exposure, starting at a contact time of 2, 91, and 959 d, respectively. Regression line for all compounds included. R^2 of regression = 0.77.

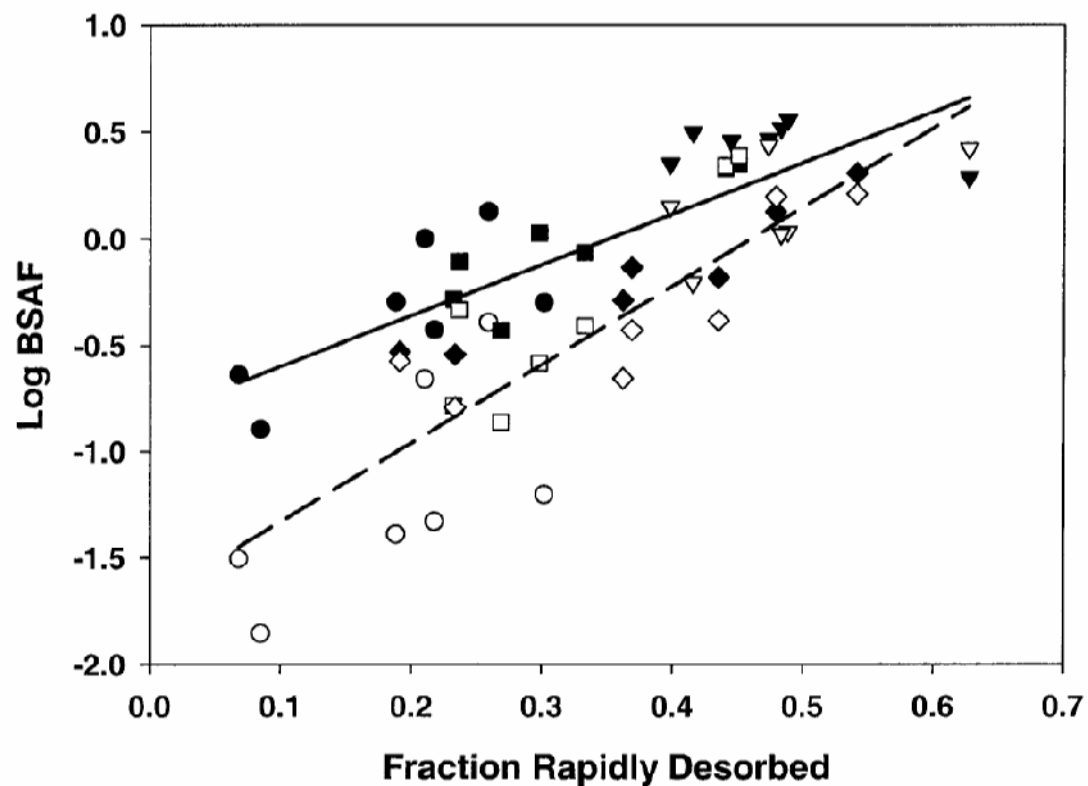


Fig. 2. Log biota-sediment accumulation factor (log BSAF) as a function of the rapidly desorbed compound for the four compounds across seven sediments. The solid symbols and line are for *L. variegatus* ($\log \text{BSAF} = 2.38 [0.32] - 0.84 [0.11]$, $r^2 = 0.67$) and the open symbols and dotted line are for *Diporeia* ($\log \text{BSAF} = 3.69 [0.50] - 1.69 [0.18]$, $r^2 = 0.66$) with ● = Benzo[*a*]pyrene, ▼ = Hexachlorobiphenyl, ■ = Tetrachlorobiphenyl, ◆ = Pyrene.

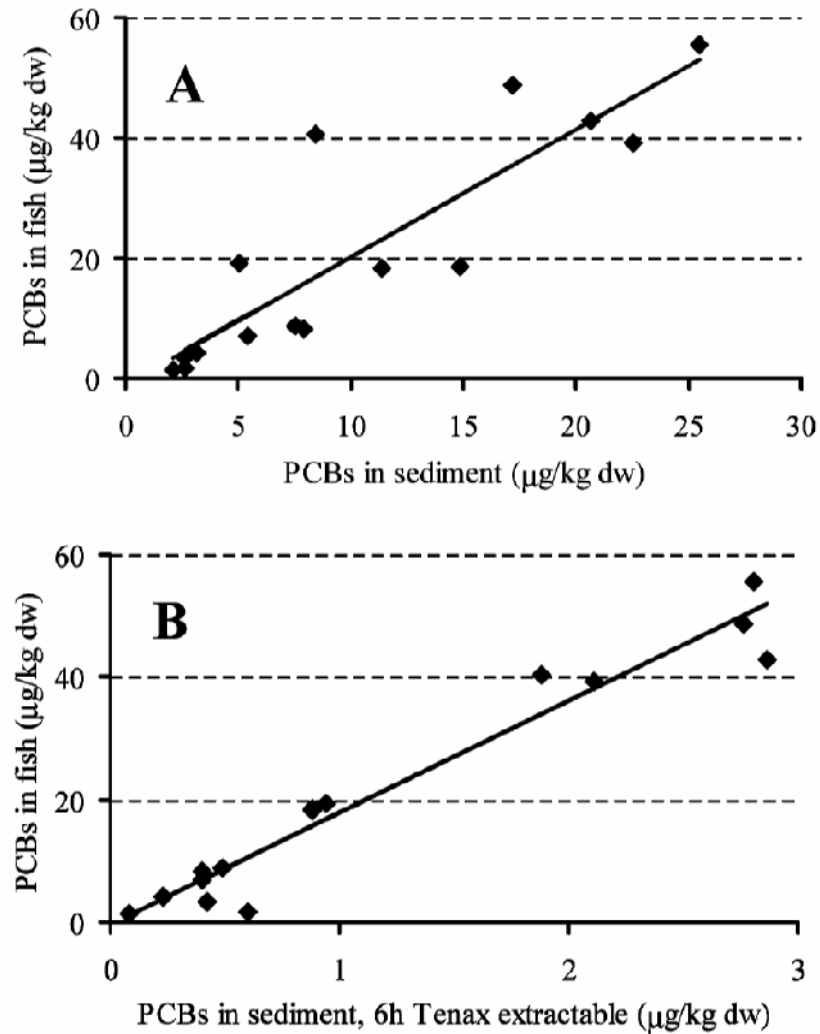


FIGURE 1. Levels of individual PCB congeners in carp against total- (A) and 6-h Tenax- (B) extractable sediment concentrations for enclosure 1b (low nutrient additions).

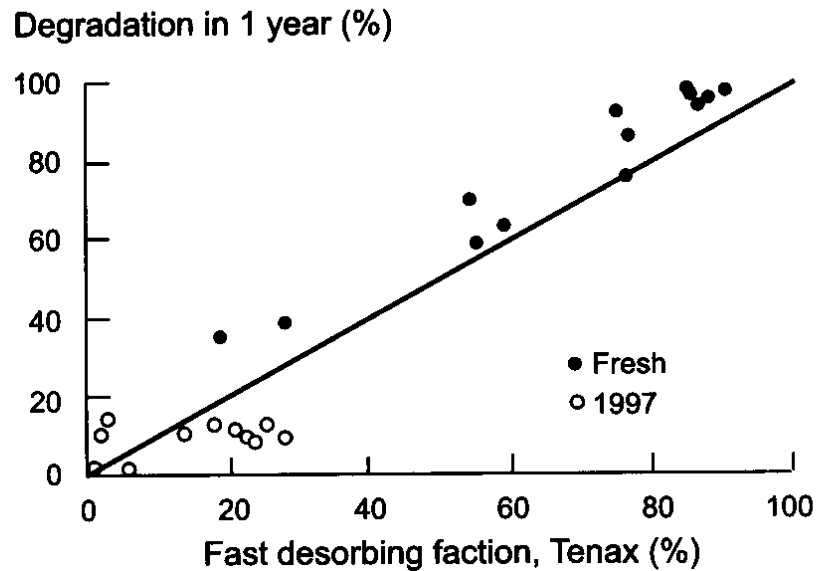


Figure 4.12 PAHs, percentage degraded on the landfarm Kreekraksluizen in one year versus percentage fast desorbing fraction (Tenax-measurement). The solid line is the line with slope =1.

J. Harmsen, 2004, PhD thesis.



Sorption to organic matter fractions: role of “black carbon”

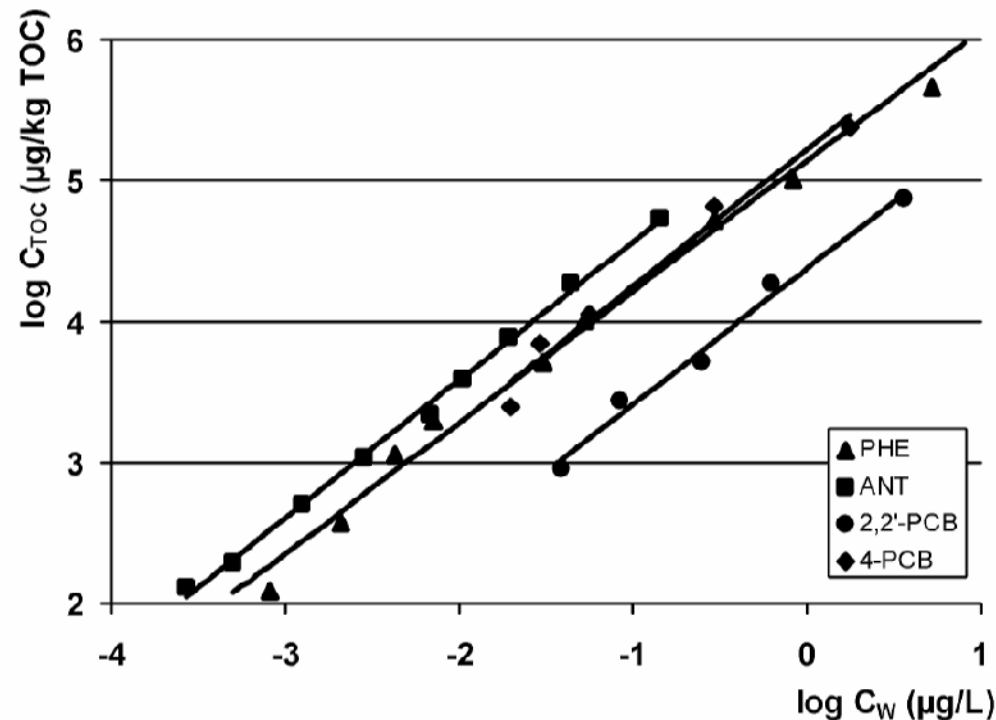


FIGURE 3. TOC-normalized Freundlich isotherms for PHE-*d*₁₀ (triangles), ANT-*d*₁₀ (squares), 4-PCB (diamonds), and 2,2'-PCB (circles) in original KET sediment. Lines obtained by linear regression.



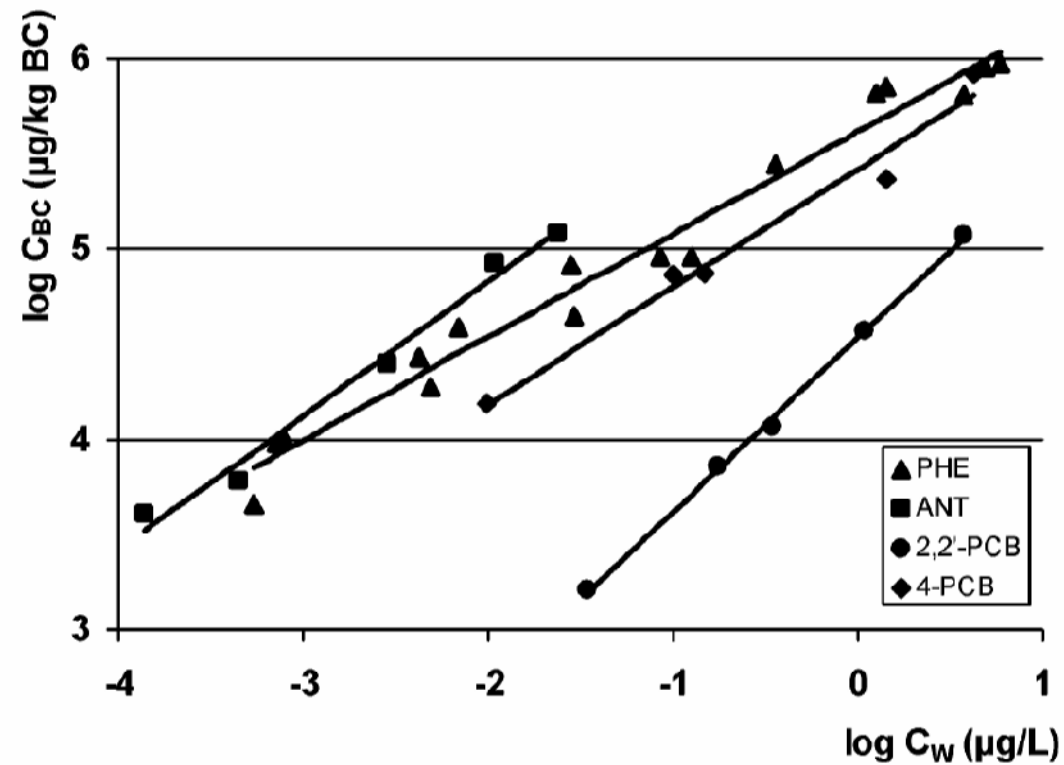


FIGURE 4. BC-normalized Freundlich isotherms for PHE-*d*₁₀ (triangles), ANT-*d*₁₀ (squares), 4-PCB (diamonds), and 2,2'-PCB (circles) in combusted KET sediment (OM and all native sorbates removed by 375 °C combustion). Lines obtained by linear regression.



$$C_S = f_{OC}K_{OC}C_W + f_{BC}K_{F,BC}C_W^{n,BC}$$

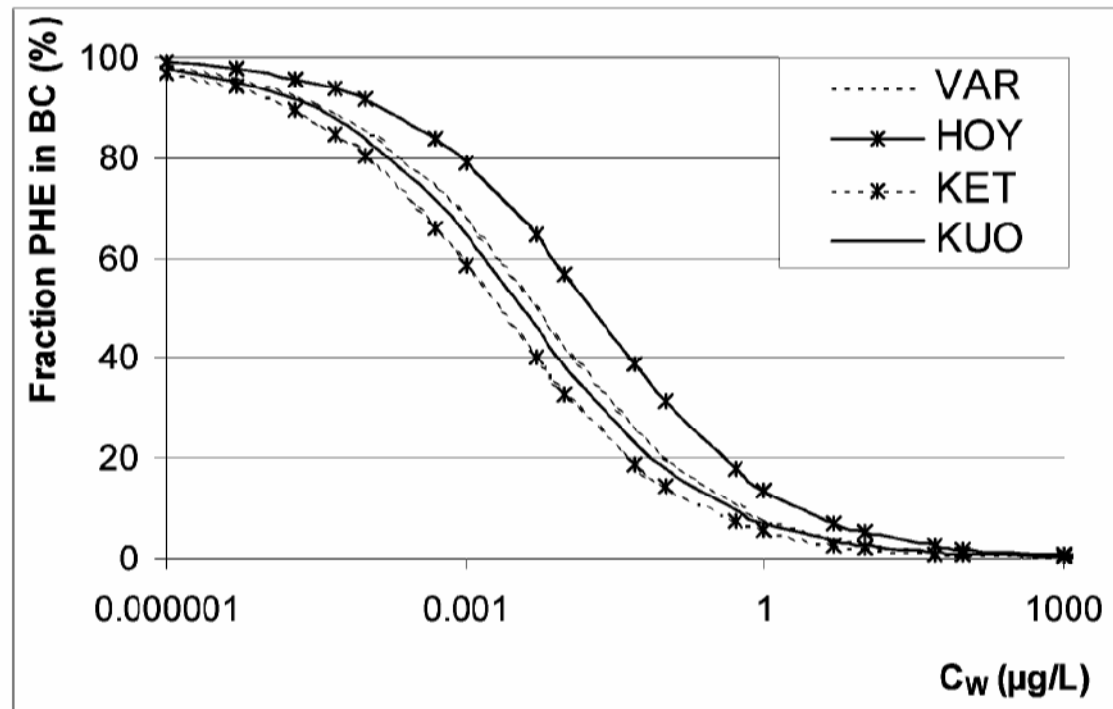


FIGURE 4. Importance of BC for the d_{10} -PHE sorption process (plotted as the percentage of total sorbed d_{10} -PHE that is in the BC) as a function of aqueous concentration C_W . The asterisks are added for clarity and do not represent actually measured data points.



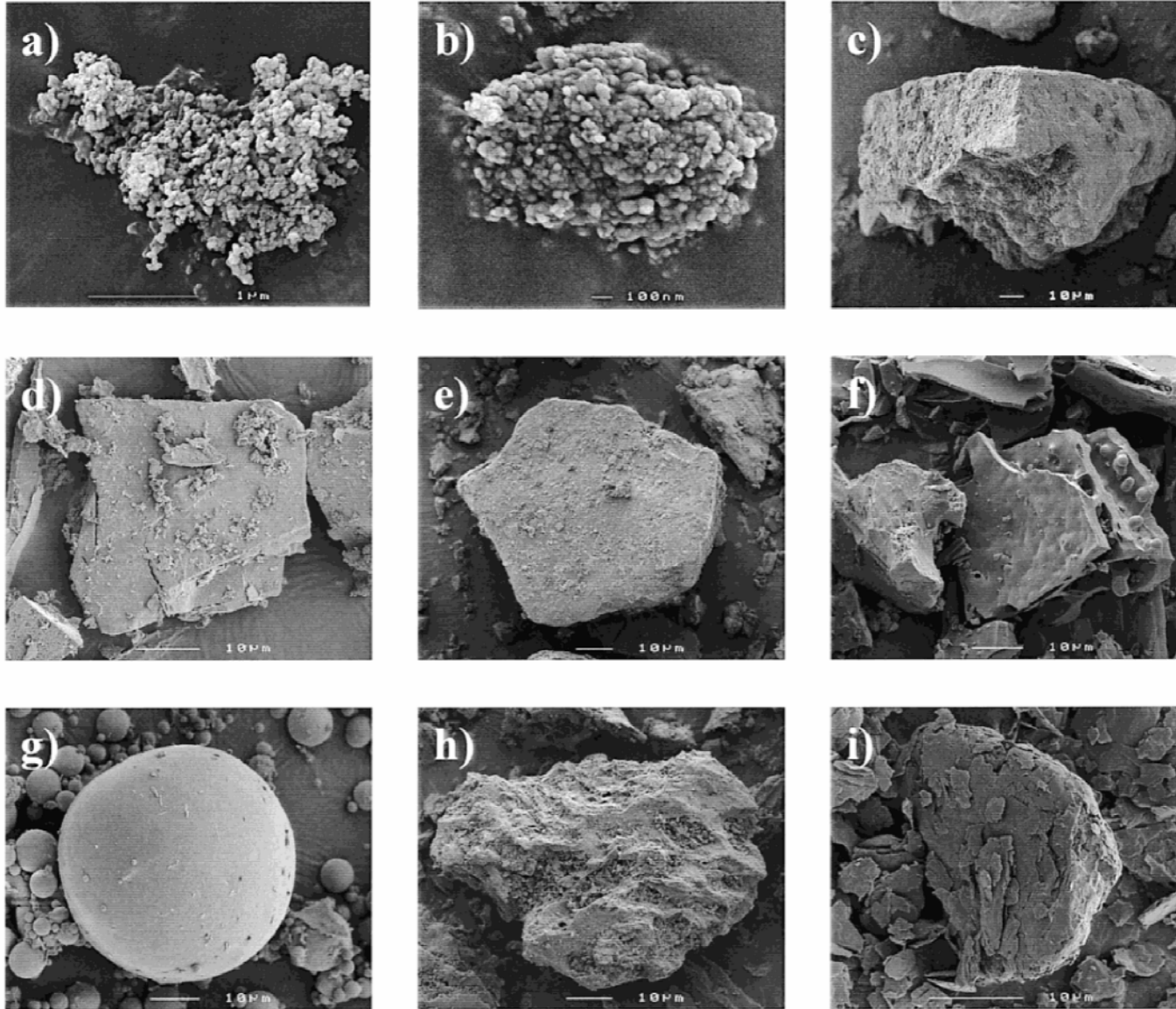


FIGURE 1. Scanning electron microscopy images of different types of soot and soot-like materials: (a) traffic soot, (b) oil soot, (c) wood soot, (d) coal soot, (e) coal, (f) charcoal, (g) fly ash, (h) activated carbon, and (i) graphite.

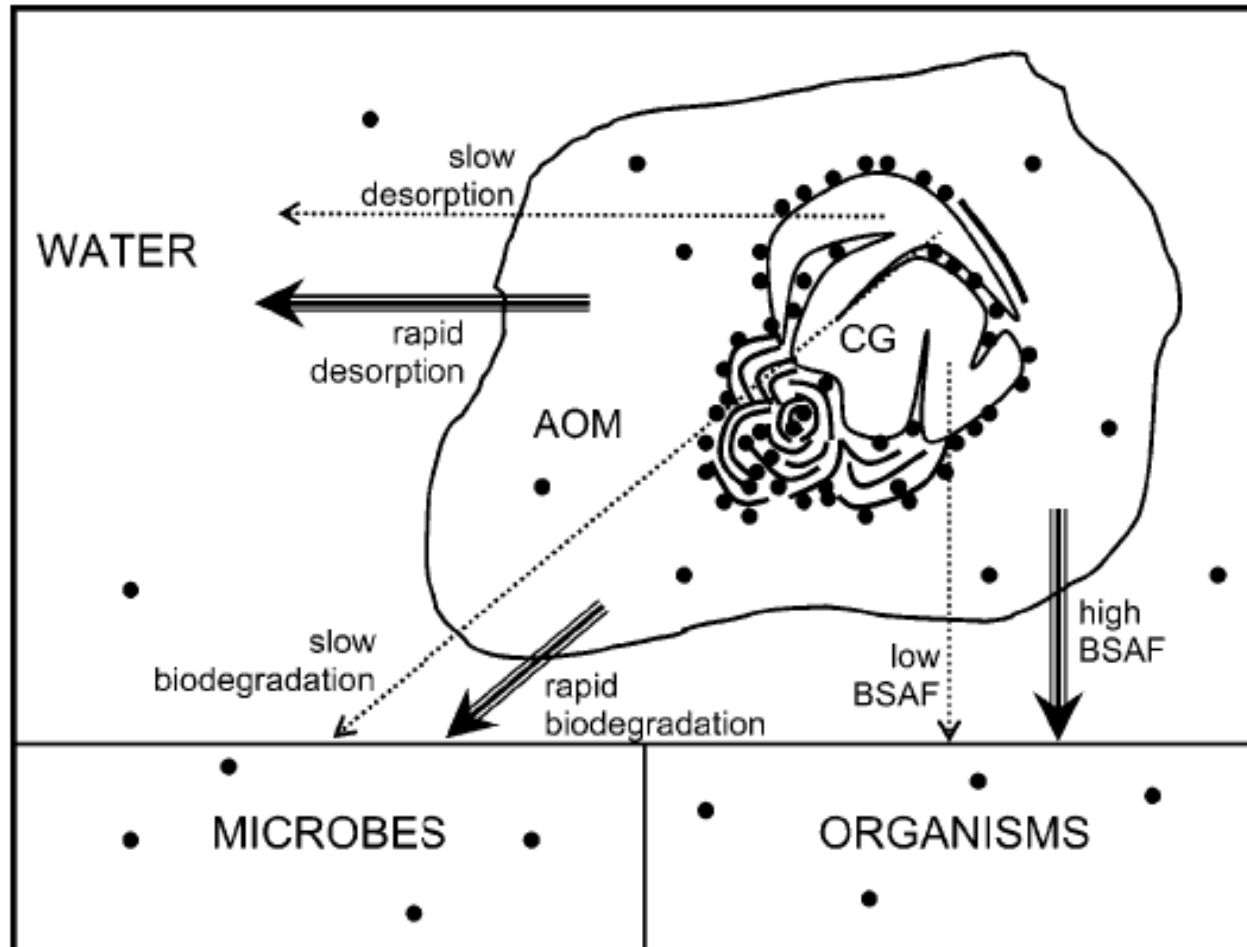
M.T.O. Jonker and A.A. Koelmans, 2002, *Environ. Sci. Technol.*, 36:3725-3734.

TABLE 3. Fractions of Native PAHs That Are Unavailable for Equilibrium Distribution

compd ^a	traffic soot	oil soot	wood soot	coal soot	coal	char coal	diesel soot (SRM 1650)
Phen	0.50	0.46	0.60	0.94	0.52	<0 ^b	0.46
Ant	0.79	0.52	0.73	0.95	<0	<0	0.73
Flu	0.73	0.63	0.84	0.86	0.57	<0	0.35
BaA	0.85	0.78	0.90	0.90	0.80	<0	0.42
BkF	0.86	0.88	0.94	0.88	0.79	<0	0.31
BghiPe	0.85	0.66	0.97	0.87	0.82	<0	<0

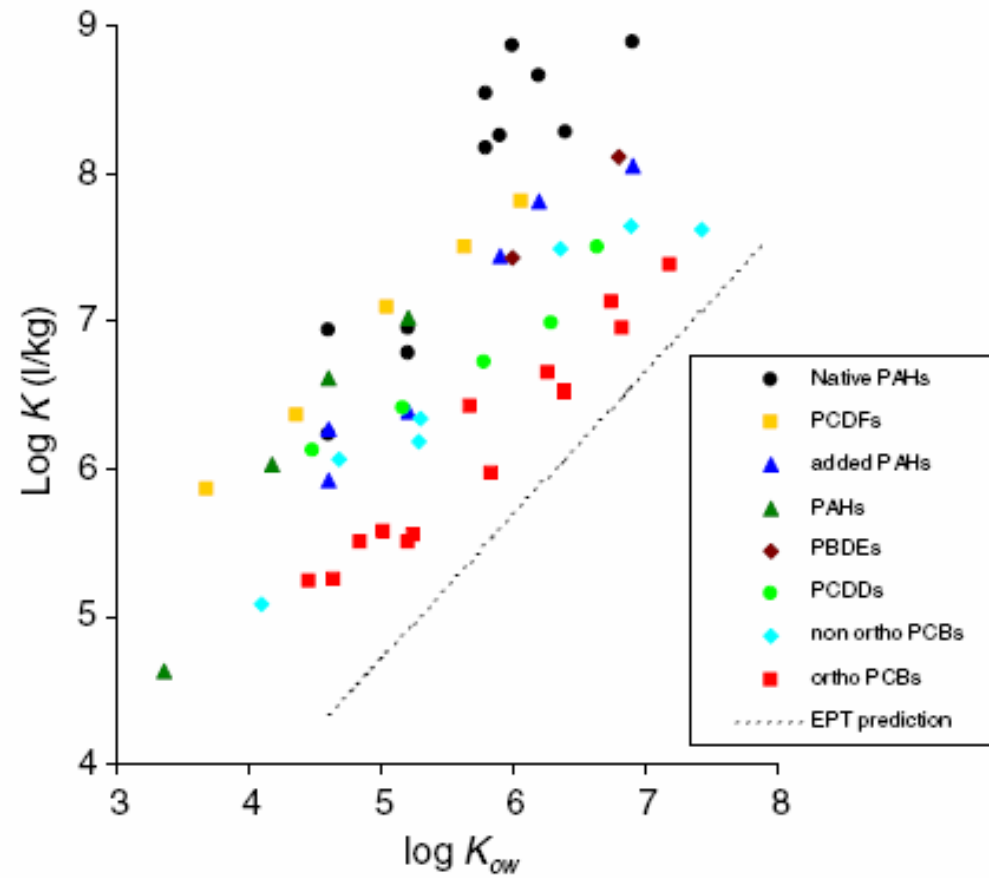
^a For explanation of abbreviations, see Table 2. ^b Value <0 represents sorbate–sorbent combinations for which $K_S^{D-PAH} > K_S^{PAH}$.





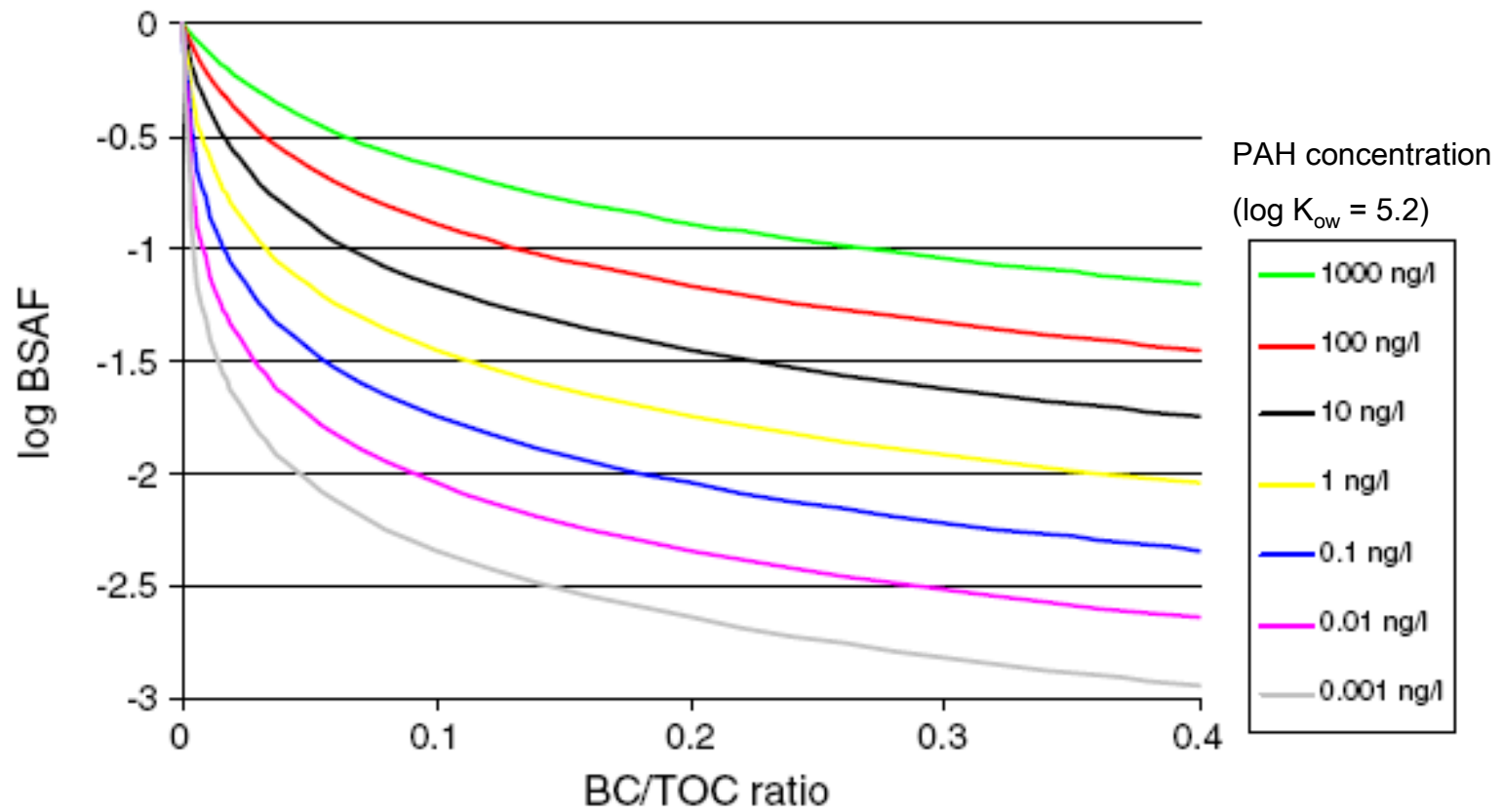
G. Cornelissen et al., 2005, Environ. Sci. Technol., 39:6881-6895.





A.A. Koelmans et al., 2006, Chemosphere, 63:365-377.





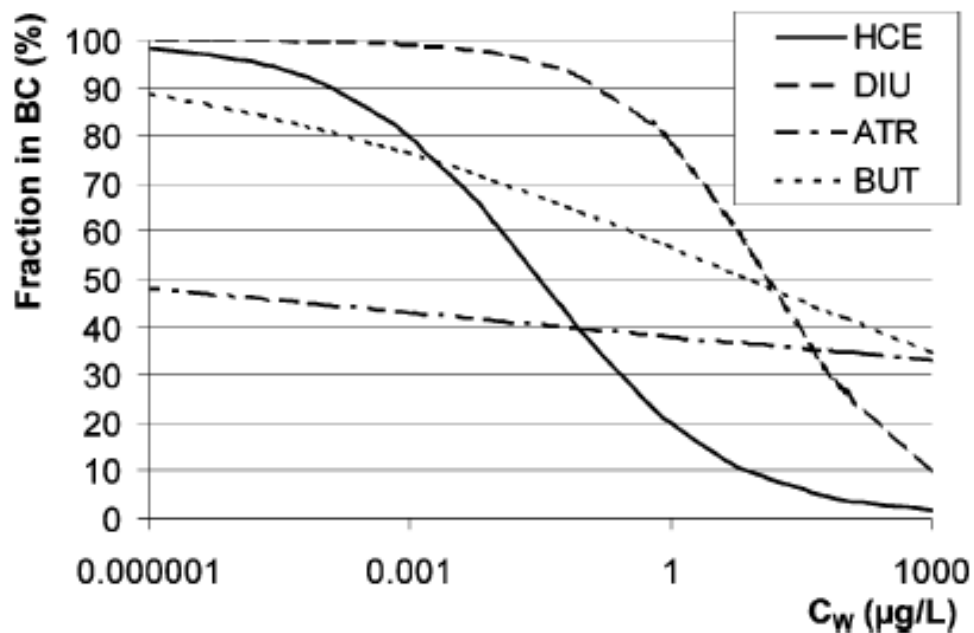
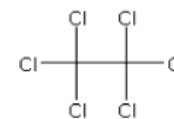
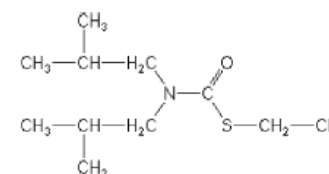


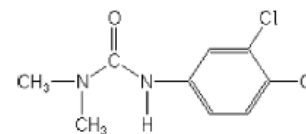
FIGURE 6. Importance of BC for the sorption of HCE, BUT, DIU, and ATR to Ketelmeer (KET) sediment, plotted as the percentage of total sorbate associated with BC, as a function of aqueous concentration C_w .



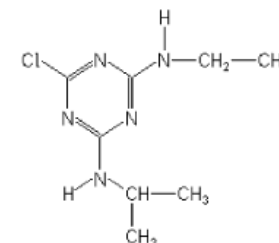
(1a) HCE



(1b) BUT



(1c) DIU



(1d) ATR

G. Cornelissen et al., 2006, Environ. Sci. Technol., 39:3688-3694.

Effect of DOM on bioavailability of HOCs

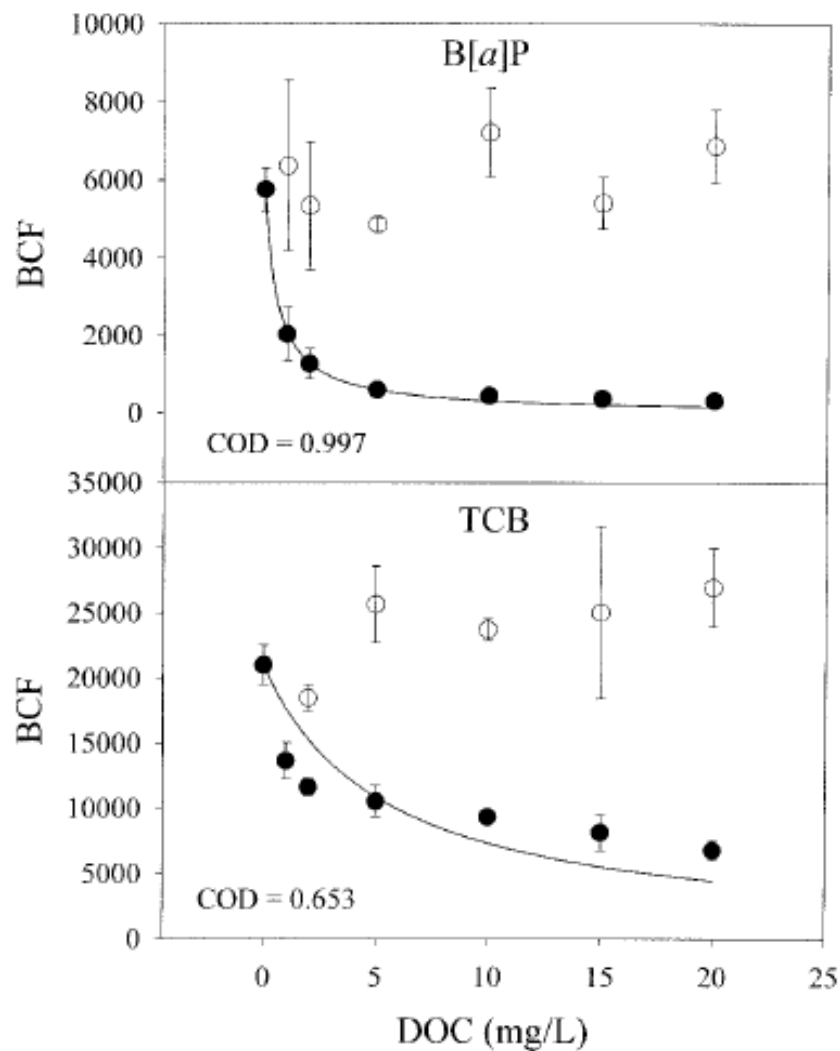


Fig. 4. Effect of dissolved organic matter concentration on bioconcentration of benzo[a]pyrene (BaP) and 3,3',4,4'-tetrachlorobiphenyl (TCB). ● = bioconcentration factor (BCF) based on total water concentration; ○ = BCF based on freely dissolved water concentration estimated by equilibrium dialysis. Equation 1 was used to fit the curves to the BCFs based on total water concentration. COD = coefficient of determination; DOC = dissolved organic carbon.

J. Arkkonen and J.V.K. Kukkonen,
2003, Environ. Toxicol. Chem, 22:518-
522.

Bioavailability of emerging compounds

- Surfactants (alcohol and alkylphenol ethoxylates)
- Pesticides
- Pharmaceuticals
- Brominated flame retardants (PBDEs, HBCD, TBBPA)
- Perfluorinated compounds (PFOS, PFOA, PFTOH)



Sorption of surfactants

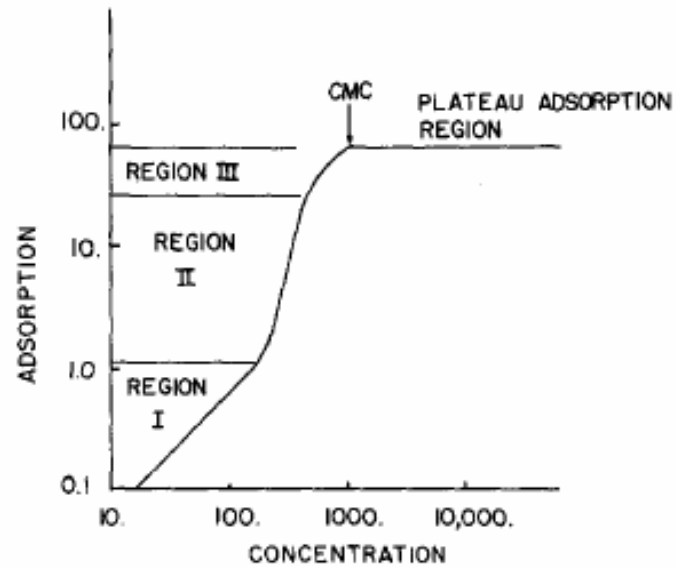


Fig. 1a-1 Illustration of adsorption regions for surfactant adsorption on mineral oxide surfaces.

L.K. Koopal et al., 1995, J Colloid Inter Science, 170:85-97

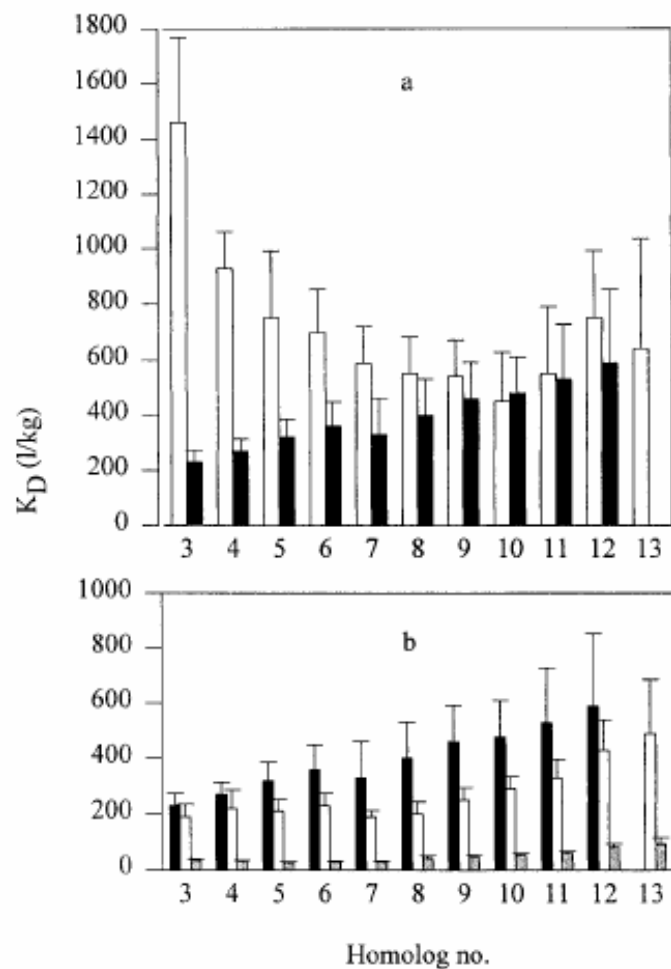


Substance	oc%	K L/kg	Koc
14C12-LAS	2.3	77	3348
14C12-LAS	3.04	288	9474
14C12-LAS	2.33	129	5536
14C12-LAS	1.2	91	7583
14C12-LAS	0.76	65	8553
C12-LAS	0.17	211	124117
C12-mixed LAS	40	1416	3540

Table IV-A.4 Reported sorption constants of C12-LAS from different references (from Annex IIC)



Sorption of APEs



D.M. John et al., 2000, Environ. Toxicol. Chem., 19:293-300.

Fig. 6. Adsorption partition coefficients (K_D) for each homolog component of nonylphenol ethoxylate₉, adsorbing onto (a) native sediment (open bars) and organic free sediment (dark bars), and (b) organic free sediment (dark bars), kaolinite (open bars), and silica (shaded bars). Error bars represent 95% confidence intervals.

Conclusions

- Hydrophobic organic compounds
 - Sorption process reasonably well understood
 - Black carbon important sorbent
 - Also for moderately hydrophobic chemicals?
 - Effects on bioavailability require complete clarification
- Polar organic compounds
 - Sorption process complex and not characterised
 - Effects on bioavailability unknown

