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The role of black carbon (BC) for the fate and behavior of organic pollutants in the environment

Thomas D. Bucheli

Pacific Basin Conference, November 20-22, Perth, AU

Content

- Introduction to BC
  - Environmental relevance
  - What is it & how do we measure it?
  - Global emission estimates?
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- BC: “the reverse of its dark side"
  - Traditional organic matter partition (OMP) model overestimates dissolved concentrations
  - Enhanced, BC inclusive, dual mode distribution model is closer to reality
  - Consequences for risk assessment
  - Application: Activated carbon (AC) amendment

Environmental relevance of BC

Jan O. Skjemstad
CSIRO

Influences:

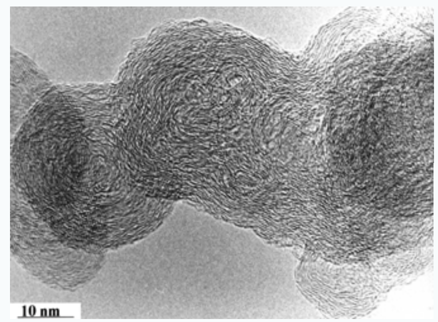
C-Availability

C-Turnover

Soil fertility

Sequestration of:

Carbon



Org. pollutants

Carbon dioxide

Mobility

Soil & sediment risk-assessment

Bioavailability

Global warming

Climate Change

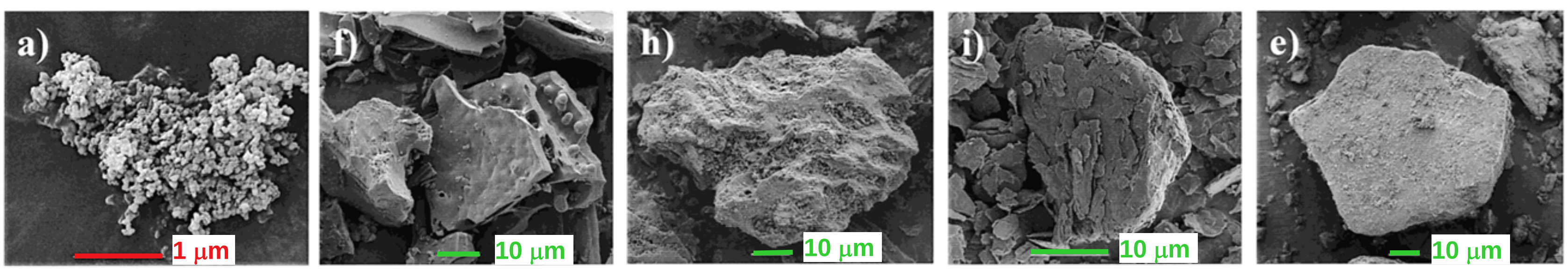
US HoR: Hearing examines BC and global warming (www.oversight.house.gov)

BC terminology

Carbonaceous geosorbents

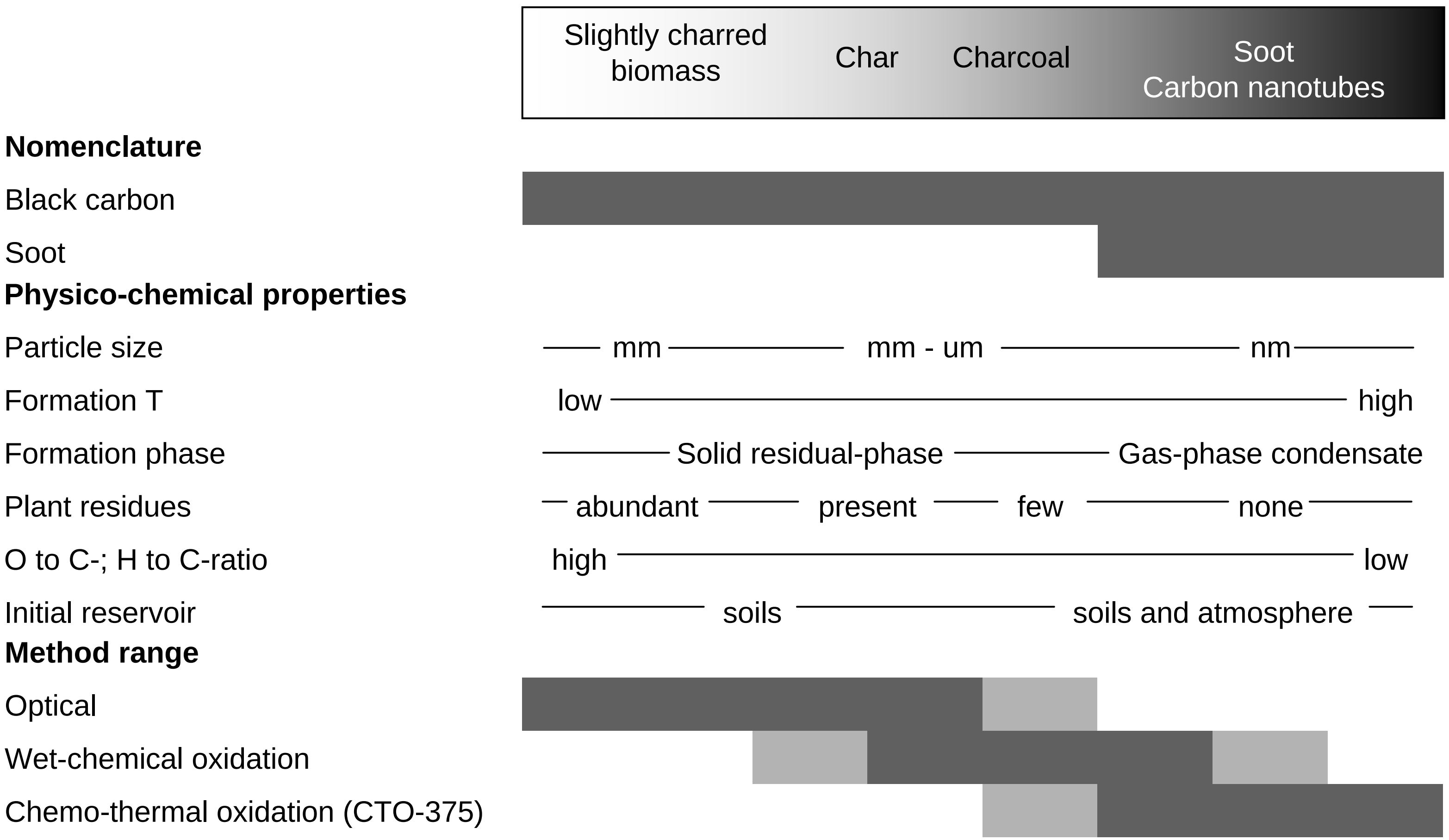
Black carbon | Geogenic origin

- Black carbon
  - Residues of incomplete combustion
    - Atmospheric recondensates
      - Soots
      - Carbon Nanotubes
    - Residuals
      - Chars
      - Charcoal
    - Activated Carbon
  - (By-)products of industrial fuel production
    - Cenospheres
    - Coke
    - Lampblack
- Geogenic origin
  - Diagenesis & catagenesis
    - Graphite
    - Coals
      - Peat
      - Brown coal
      - Bituminous coal
      - Anthracite
    - Kerogens
      - Type I-III



Pictures from Jonker & Koelmans 2002

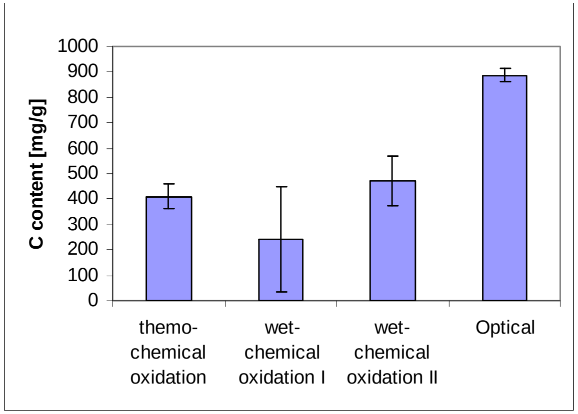
BC continuum and available methods of quantification



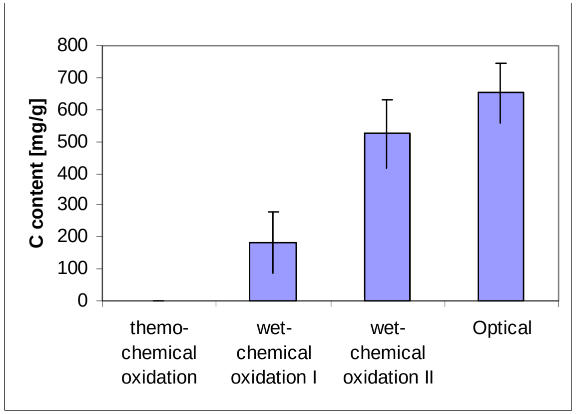
adapted from Elmquist *et al.*, 2006; Masiello, 2004

Different method measure different BC (the BC-ring trial)

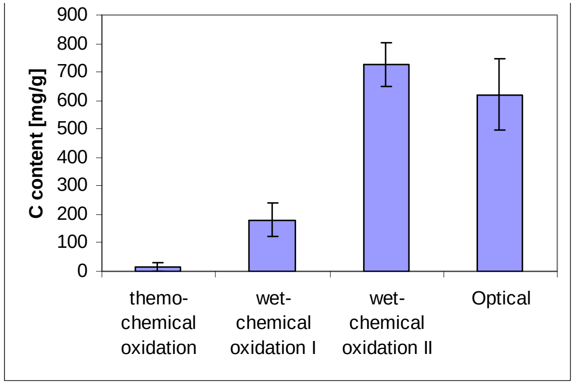
Hexane soot: positive control 1



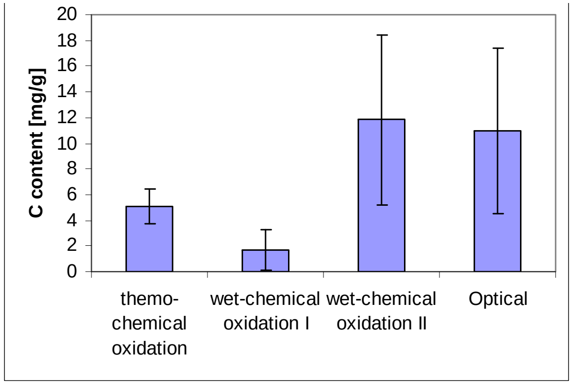
Wood char: positive control 2



Bituminous coal: negative control



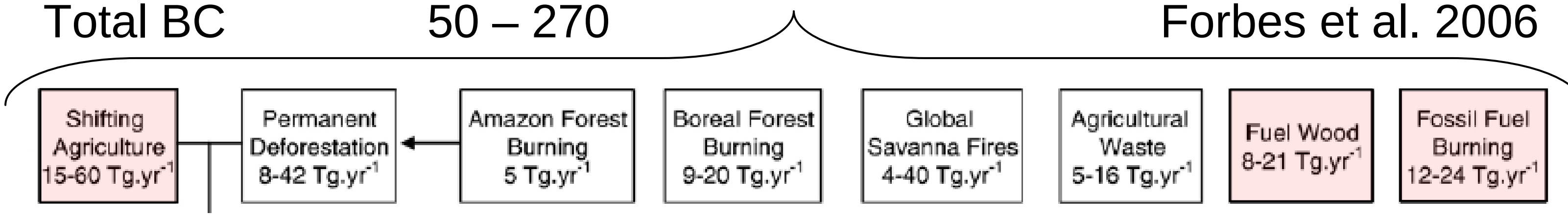
Marine sediment: real sample



Hammes et al. 2007

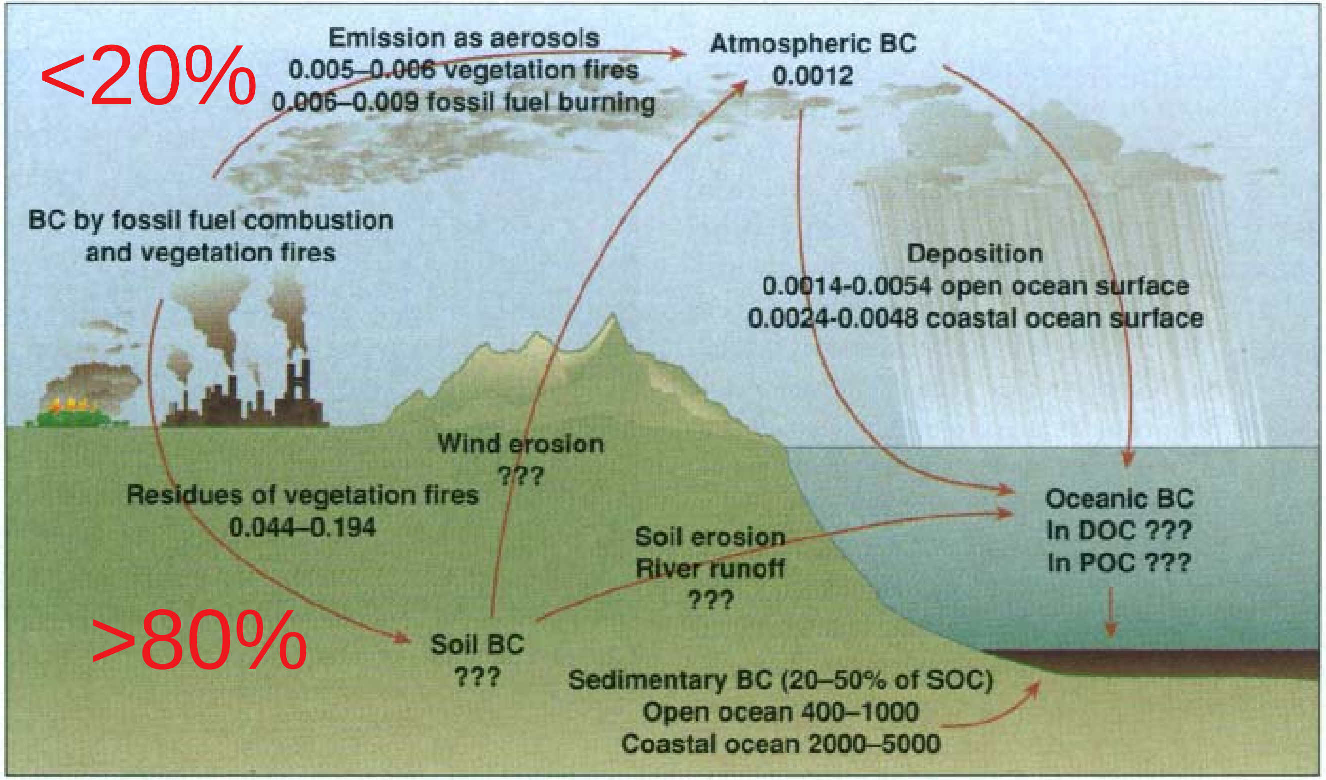
Global annual BC production

BC-type	Amount [Tg/y]	Source: Biomass [%]	Source: Fossil fuel [%]	Reference
Total BC	50 - 200	80	-	Kuhlbusch 1998
Total BC	50 – 270			Forbes et al. 2006



BC-type	Amount [Tg/y]	Source: Biomass [%]	Source: Fossil fuel [%]	Reference
Aerosol BC	11 - 15	33 - 45	55 - 67	Kuhlbusch 1998
Aerosol BC	8	60	40	Bond et al. 2004

Global distribution of BC

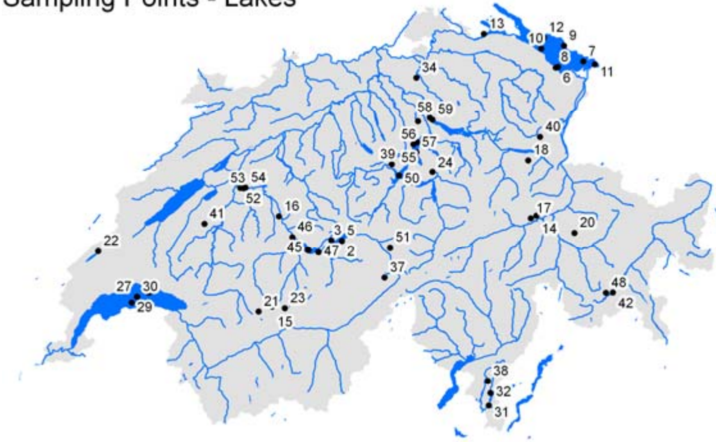


In the black. Masiello and Druffel (*1*) determined age differences of 2400 to 13,900 years between sedimentary organic carbon (SOC) and black carbon (BC). Thus, they conclude that sedimentary black carbon must have spent considerable time in an intermediate pool. Candidates are terrestrial soils and the oceanic dissolved organic carbon (DOC) pool [data from (*5*, *7*, *10*)]. All values are in petagrams (1 Pg = 10^{15} g) per year.

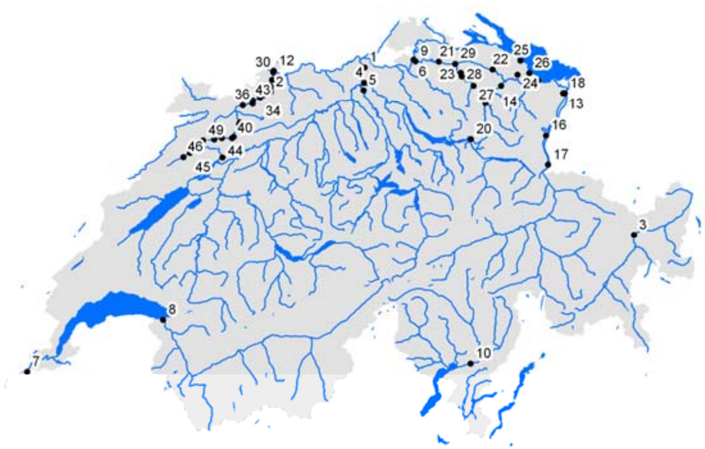
Kuhlbusch 1998

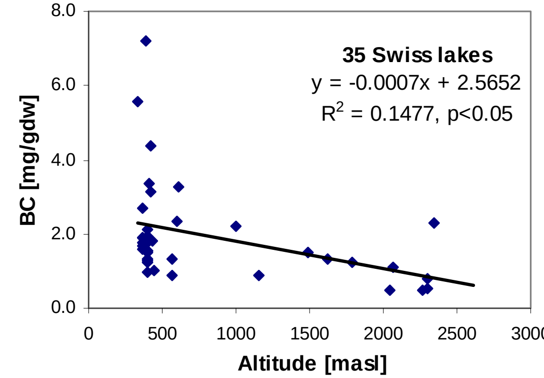
BC in Swiss lake sediment

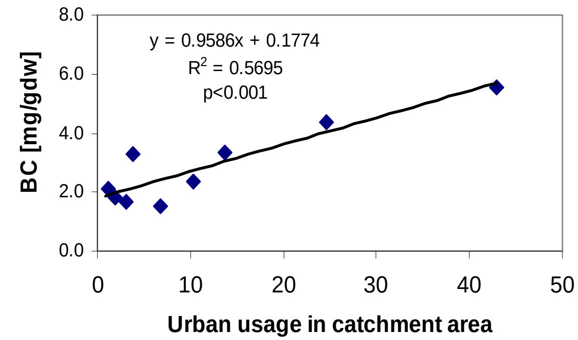
Sampling Points - Lakes

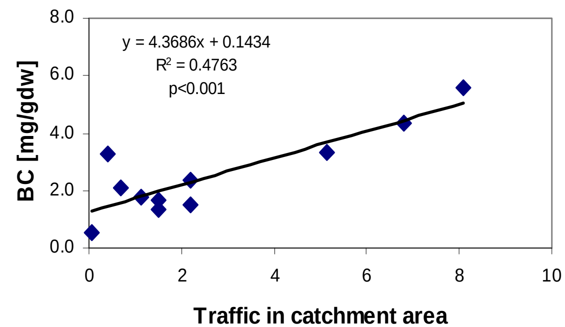


Sampling Points - Flowing Water









Sobek et al. in prep

BC/TOC ratios in sediments and soils

TABLE 2. BC/TOC Ratios (%) in Sediments and Soils

sample description	BC quantification method	median	quartile range	number of sites	ref
		Sediments			
Suwannee River DOM	CTO-375	0.34	n.a.[e]	1	122
Mexican Margin and several lakes	Chemical + CTO-375	1.0[c]	0.2–2.0[c]	12	118
Boston Harbor, Gulf of Maine	CTO-375	4	3–7	17	130
Swedish fjord	CTO-375	6	5–9	25	121[a]
Slovenian Lakes	CTO-375	6[b]	5–6[b]	12	133
French lakes, Mediterranean Sea	chemical	7	5–15	11	123
Boston Harbor and EPA sediments	CTO-375	8	6–16	32	93
Dutch flood plain lakes	CTO-375	9	8.7–9.6	3	55
Norwegian rivers and fjords	CTO-375	9	7–11	4	85
Eurasian Arctic river mouths	CTO-375	10	4–12	13	184
Finnish and Dutch lakes	CTO-375	11	3–13	5	88
Dutch and Finnish sediments	CTO-375	15	7–24	11	131
Pacific Ocean	chemical	17	14–25	26	185
Mississippi river, Gulf of Mexico	CTO-375	17	7–23	5	186
bay near New York	CTO-375	18	n.a.[e]	1	134
bay near New York	CTO-375	19	n.a.[e]	1	108
USA Great Lakes	CTO-375	20[b]	15–25[b]	>100	132
six seas around Europe	CTO-375	24	18–35	33	117
Chinese lacustrine sediments	chemical	33	26–37	3	107
median weighted per data point[g]		9	4–18	~300[f]	
median weighted per reference[h]		9	6–14	19[f]	
		Soils			
loam soil	CTO-375	0	n.a.[e]	1	108
Australian Soils	chemical + CTO-375	0.11[d]	0.07–0.15[d]	5	118
Swiss soils	CTO-375	2.3	1.7–4.9	23	106
EPA soils	CTO-375	5	n.a.[e]	2	93
Tenerife soils	CTO-375	6[b]	3–13[b]	38	102
German chernozemic soils	microscopy + ^{13}C NMR	9	3–15	9	140
Danish and American soils	CTO-375	12	6–15	7	131
Australian soils	UV photooxidation + coulometry	~20	~10–30	4	141
Chinese sandy soil	chemical	36	n.a.[e]	1	107
median weighted per data point[g]		4	2–13	90[f]	
median weighted per reference[h]		6	2–12	9[f]	

[a] Partly unpublished data. [b] Values approximated from graphical data representation. [c] Higher values (median 8%) before extensive chemical pretreatment. [d] Higher values (median 5%) before extensive chemical pretreatment. [e] Not applicable. [f] Number of data on which median and quartile range are based. [g] Median where each soil/sediment sampling site has a weight of one. [h] Median where each reference has a weight of one.

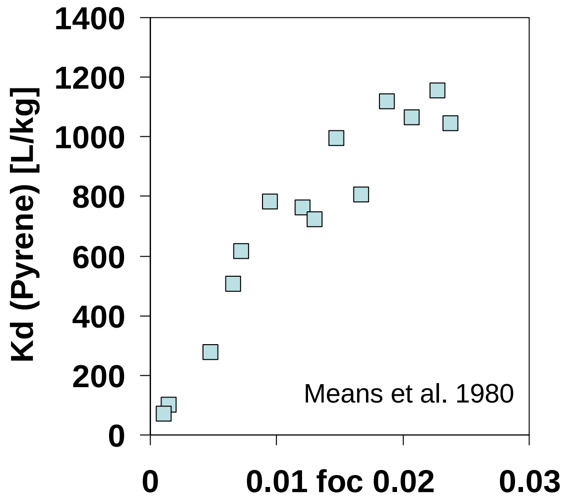
Cornelissen et al. 2005

BC: „the reverse of its dark side“…

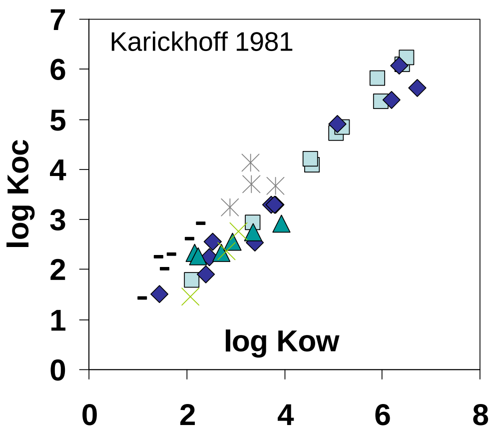
Traditional organic matter partition (OMP) model overestimates dissolved concentrations

Traditional organic matter partition (OMP) model for organic pollutants

$$K_d = \frac{c_{solid}}{c_{water}} = f_{oc} \cdot K_{oc}$$

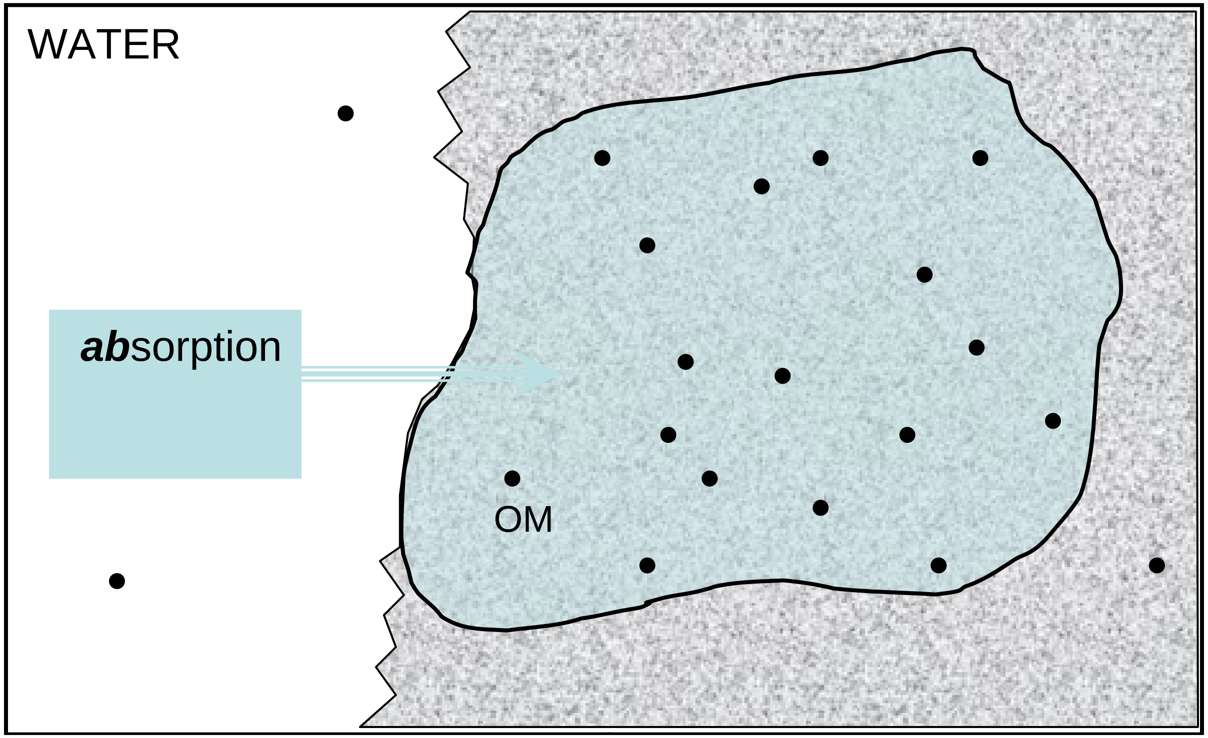


$$\log K_{oc} = a \cdot \log K_{ow} + b$$



K_d: solid-water partition coefficient [L_{water}/kg_{solid}]
f_{oc}: fraction of organic carbon [$g_{oc}/g_{total\ solid}$]
K_{oc}: organic carbon normalized partition coefficient [L_{water}/kg_{oc}]
K_{ow}: octanol-water partition coefficient [$L_{water}/L_{octanol}$]

Visualization of OMP model

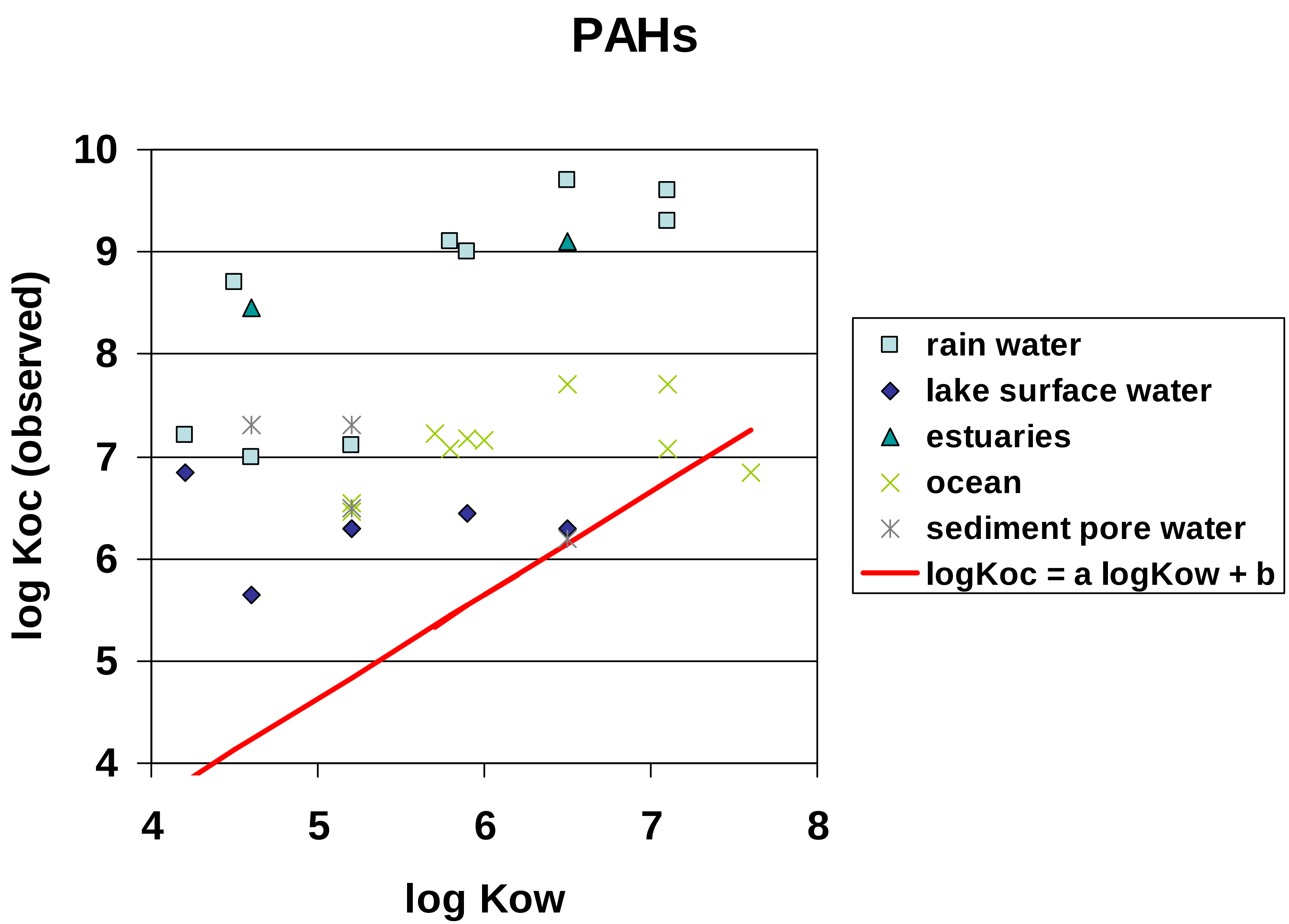


Modified after Cornelissen et al. 2005

Frequent (field) observations in conflict with OMP model

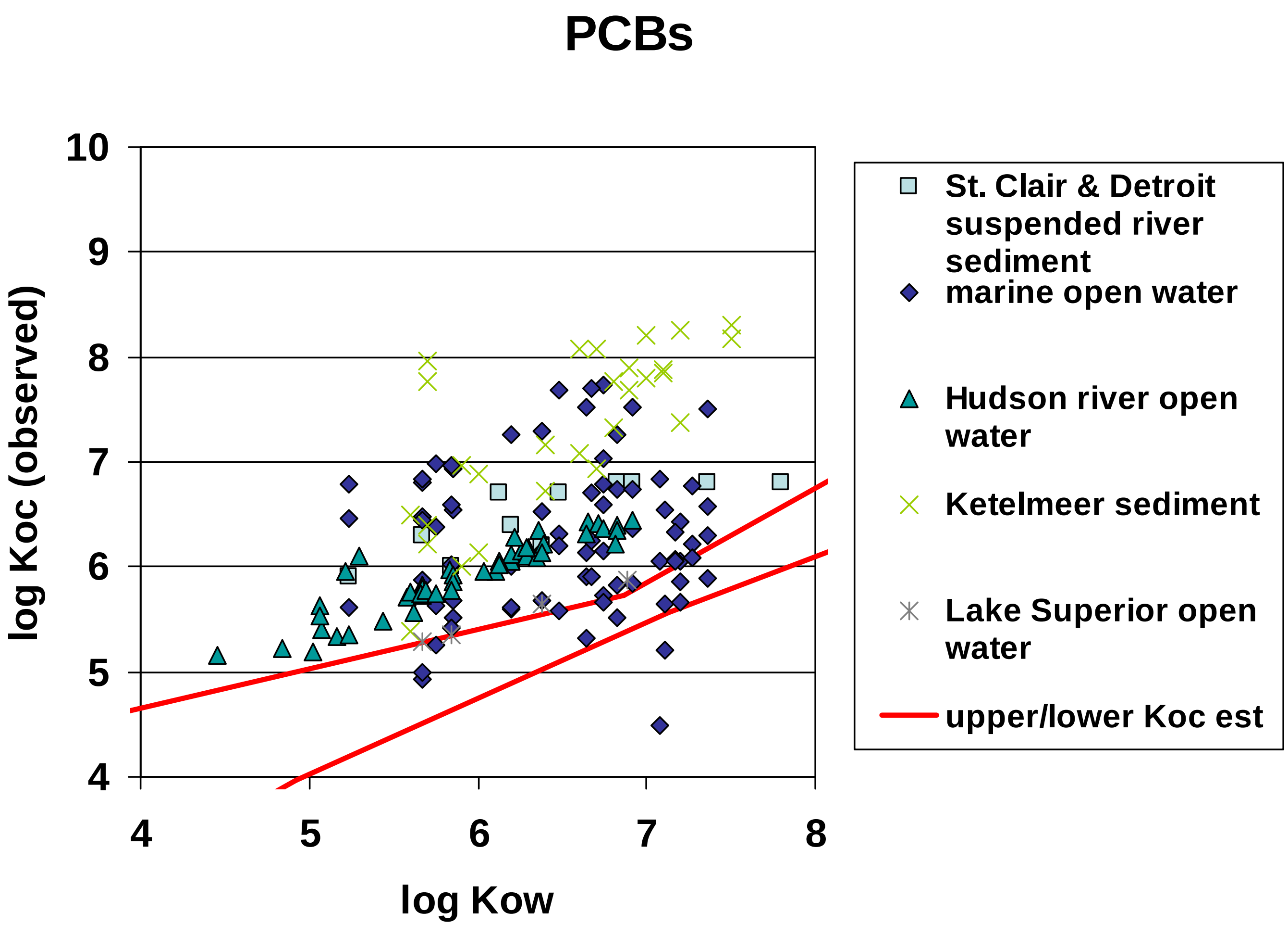
- Sorption competition between different solutes and non-linear sorption isotherms (Pignatello & Xing 1996)
- Multiphasic desorption kinetics (Cornelissen et al. 1997)
- Variable bioto-to-sediment accumulation factors (BSAFs) (Moermond et al. 2005)
- Limited bioremediation potential (Alexander 2000)
- Elevated affinities to solid organic matter (Gustafsson & Gschwend 1998; Bucheli & Gustafsson 2001)

Underestimation of field observed K_{oc}´s based on OMP model



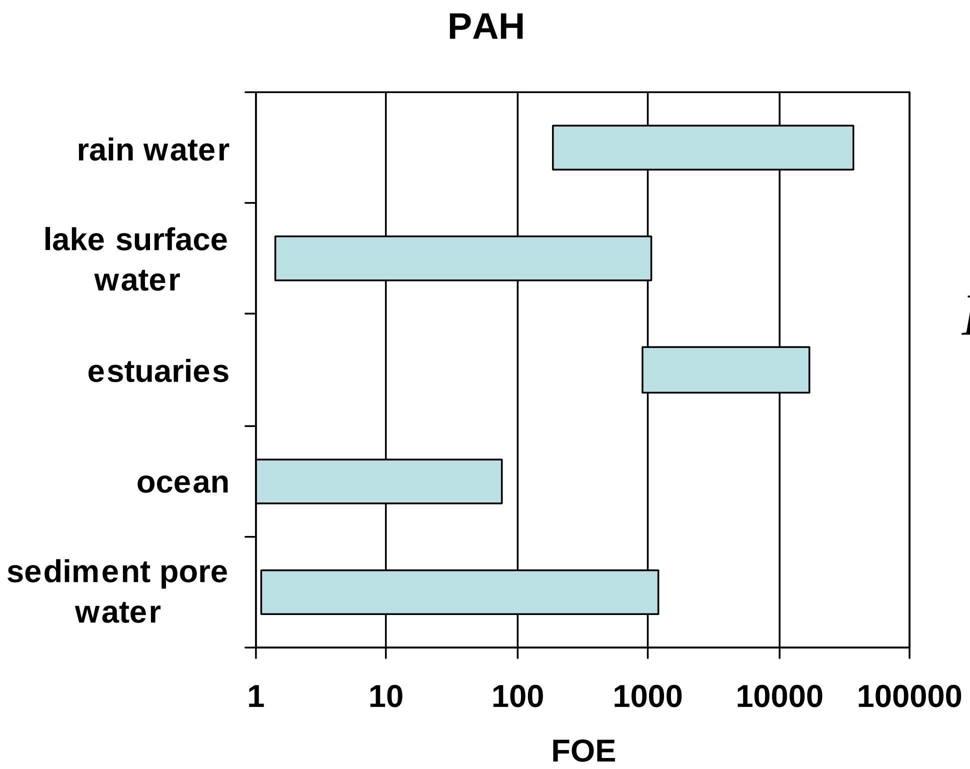
References in Gustafsson & Gschwend 1998

Underestimation of field observed K_{oc}´s based on OMP model



References in Bucheli & Gustafsson 2001

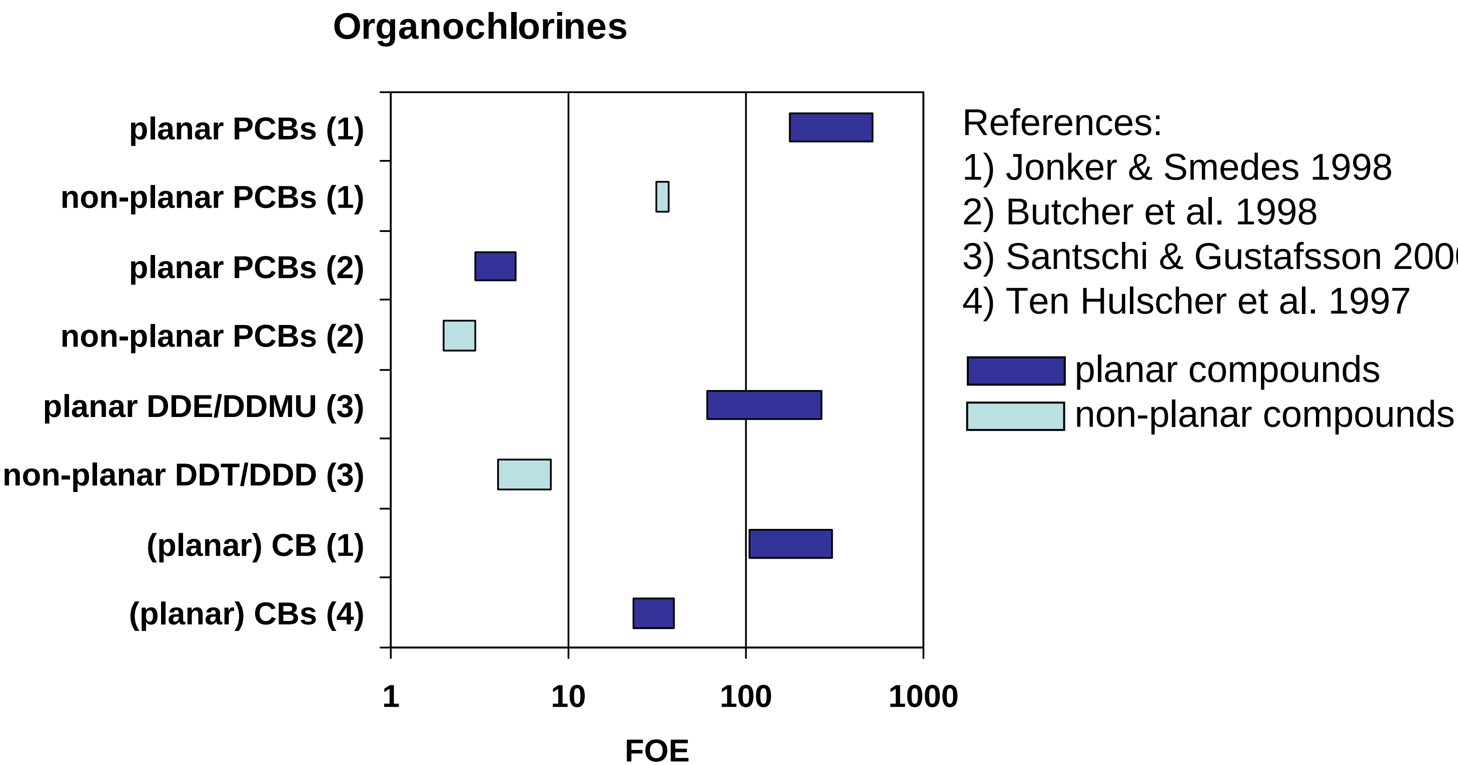
Factors of Overestimated Dissolved Exposures (FOE)



$$FOE = \frac{(c_{water})_{pred}}{(c_{water})_{obs}} = \frac{(K_{oc})_{obs}}{(K_{oc})_{pred}}$$

References in Gustafsson & Gschwend 1998

Factors of overestimated dissolved exposures (FOE)



References:
1) Jonker & Smedes 1998
2) Butcher et al. 1998
3) Santschi & Gustafsson 2000
4) Ten Hulscher et al. 1997

Bucheli & Gustafsson 2001

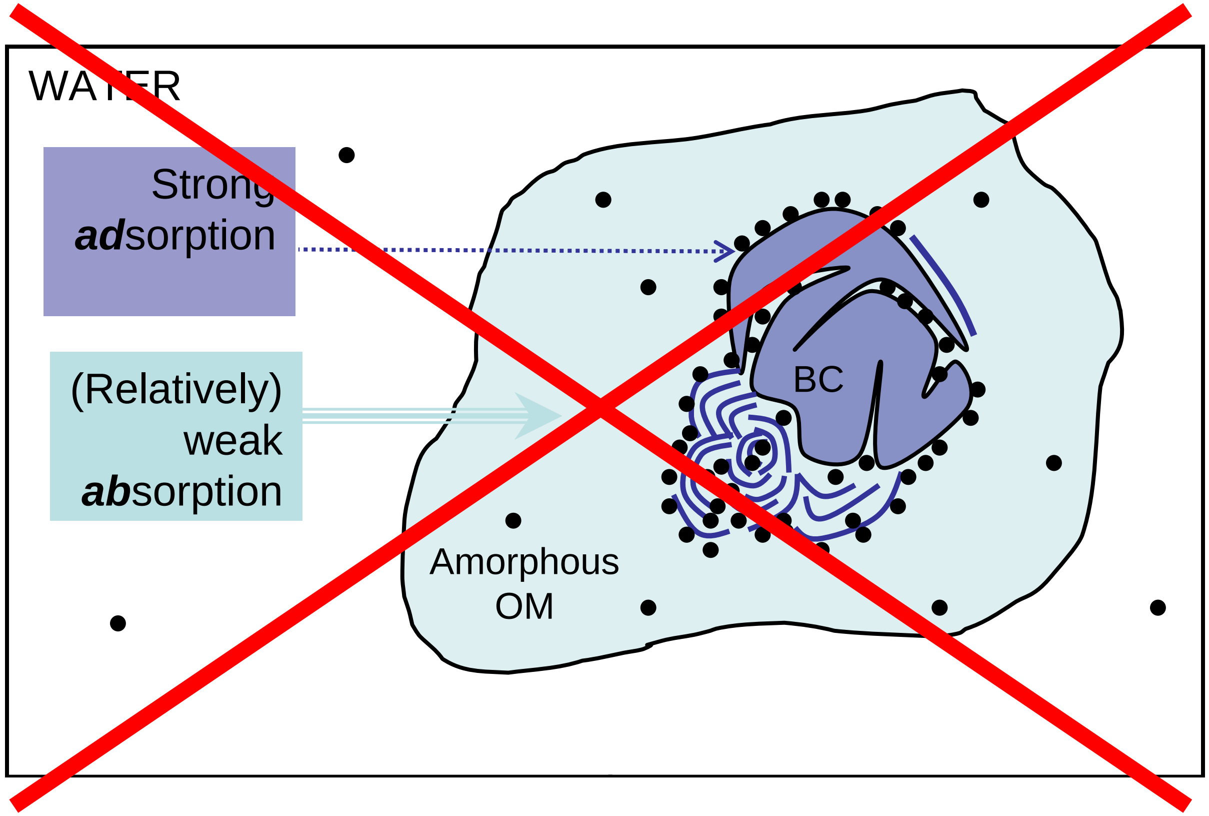
Reasons for divergence of observed K_{oc}´s with OMP model

- Mainly derived from laboratory sorption experiments
- Insufficient equilibration time
- Elevated solute concentrations
- OMP model simply too simple

BC: „the reverse of its dark side“…

Enhanced, BC inclusive, dual mode distribution model

Visualization of the enhanced, BC inclusive, dual mode distribution model



Modified after Cornelissen et al. 2005

Enhanced, BC inclusive, dual mode distribution model

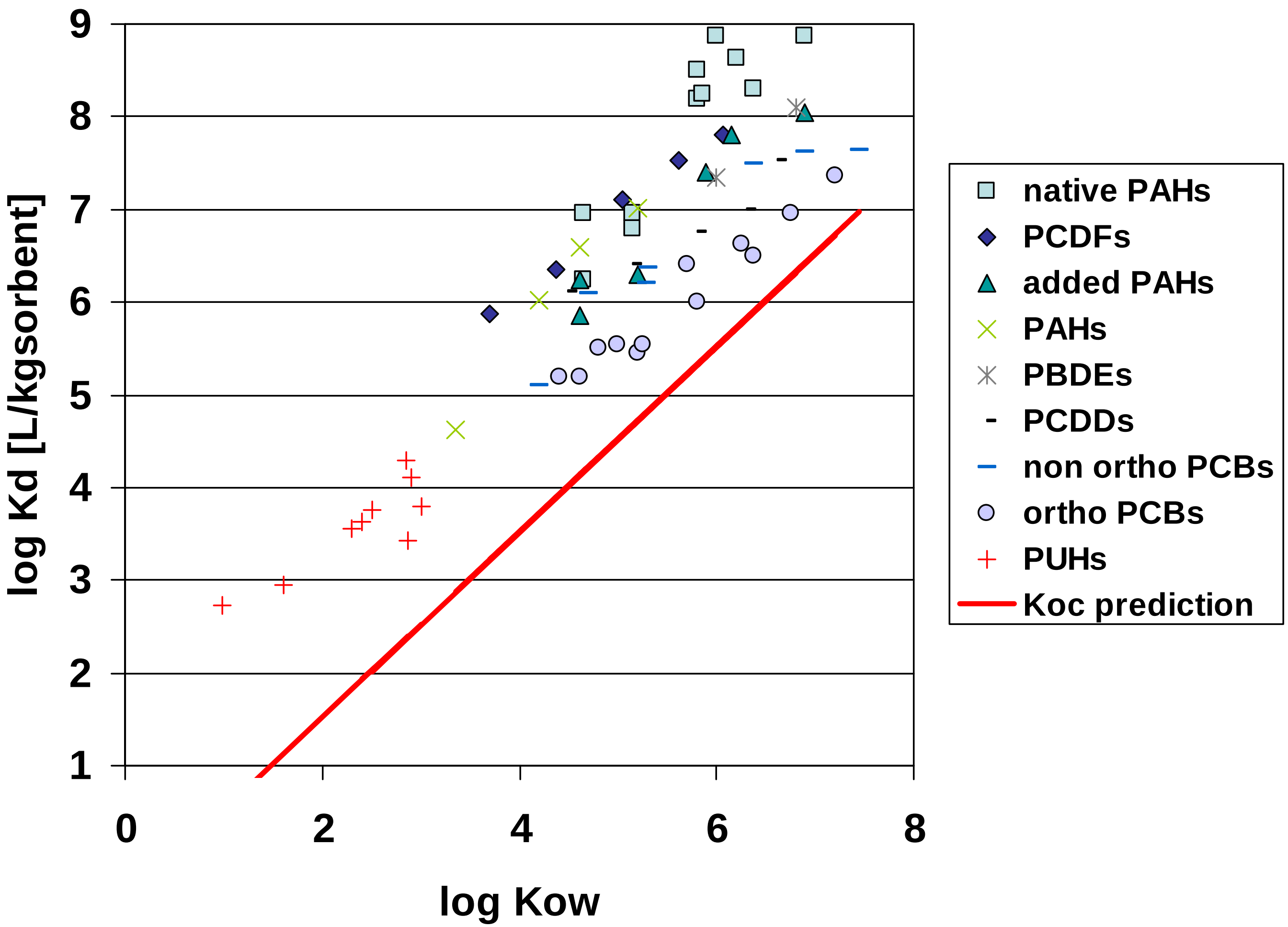
$$K_d = \frac{c_{solid}}{c_{water}} = f_{oc} \cdot K_{oc} + f_{bc} \cdot K_{bc} \cdot c_w^{n-1}$$

- K_d: solid-water partition coefficient [L_{water}/kg_{solid}]
- f_{oc}: fraction of organic carbon [$g_{oc}/g_{total\ solid}$]
- K_{oc}: organic carbon normalized partition coefficient [L_{water}/kg_{oc}]

- f_{bc}: fraction of soot carbon [$g_{soot\ carbon}/g_{total\ solid}$]
- K_{bc}: black carbon normalized distribution coefficient [L_{water}/kg_{sc}]
- n: Freundlich exponent

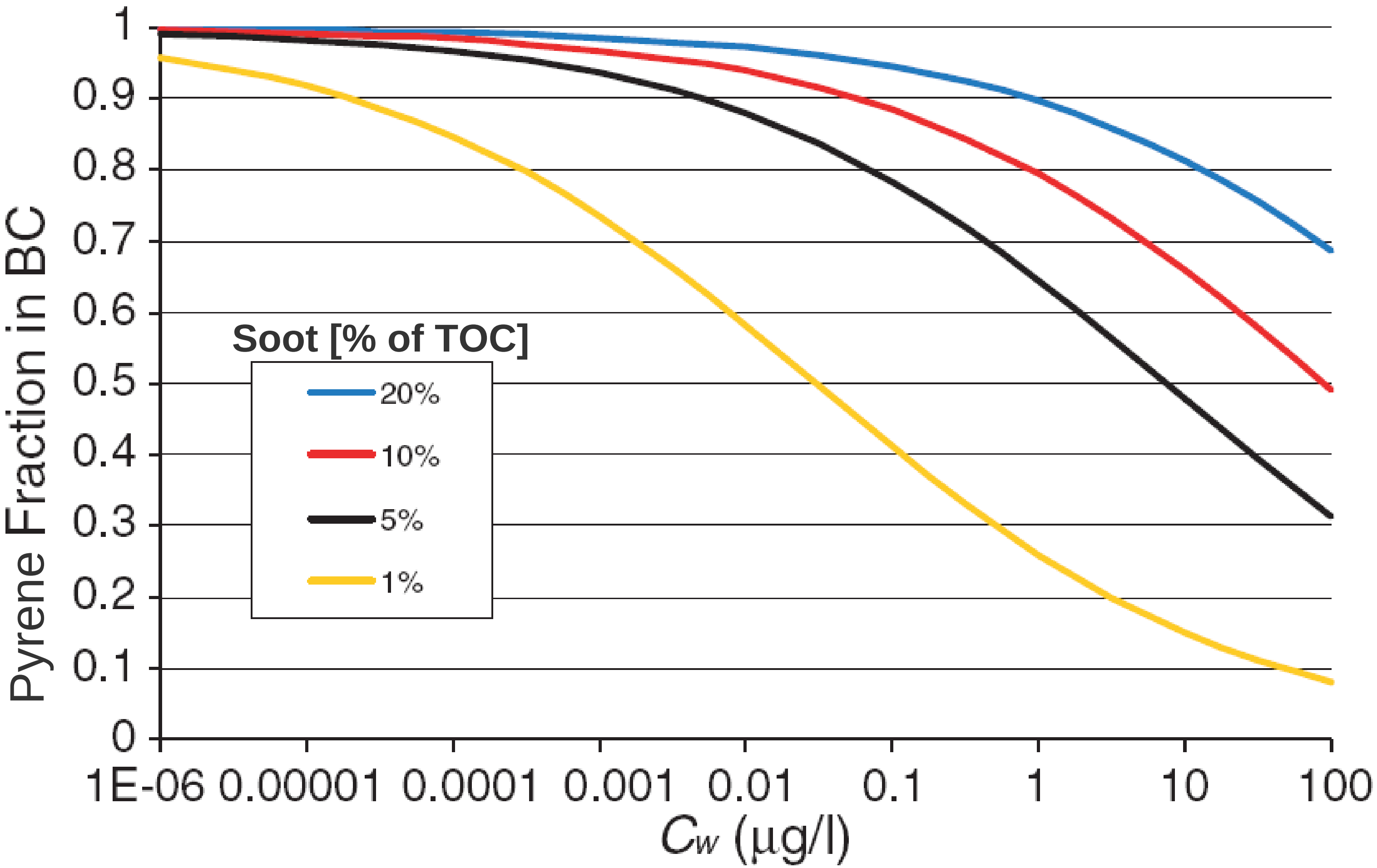
Accardi-Dey & Gschwend 2002

K_{bc} of organic pollutants: BC as a super-sorbent



References in Koelmans et al. 2006 & Sobek et al. 2009

BC determines the distribution of organic pollutants

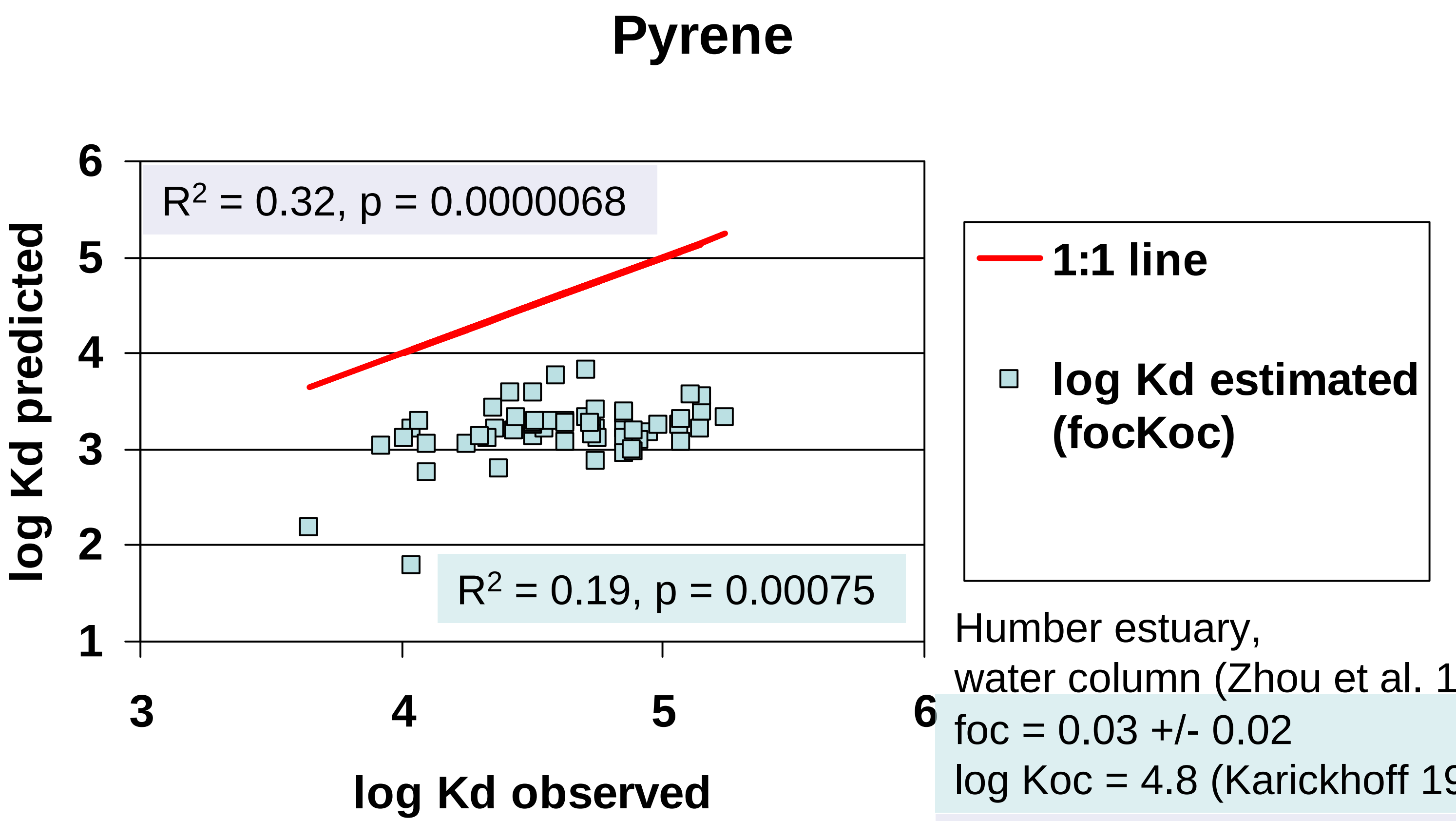


Koelmans et al. 2006

BC: „the reverse of its dark side"…

Consequences for risk assessment

Improved predictability of solid-water distribution coefficient K_d (PAHs)



Humber estuary,
water column (Zhou et al. 1999)

foc = 0.03 +/- 0.02
log Koc = 4.8 (Karickhoff 1981)

fbc = 0.0022 +/- 0.0010
log Kbc = 7.0 (Bucheli & Gustafsson 2000)

Bucheli & Gustafsson 2001

Improved predictability of solid-water distribution coefficient K_d (PCDD/Fs)

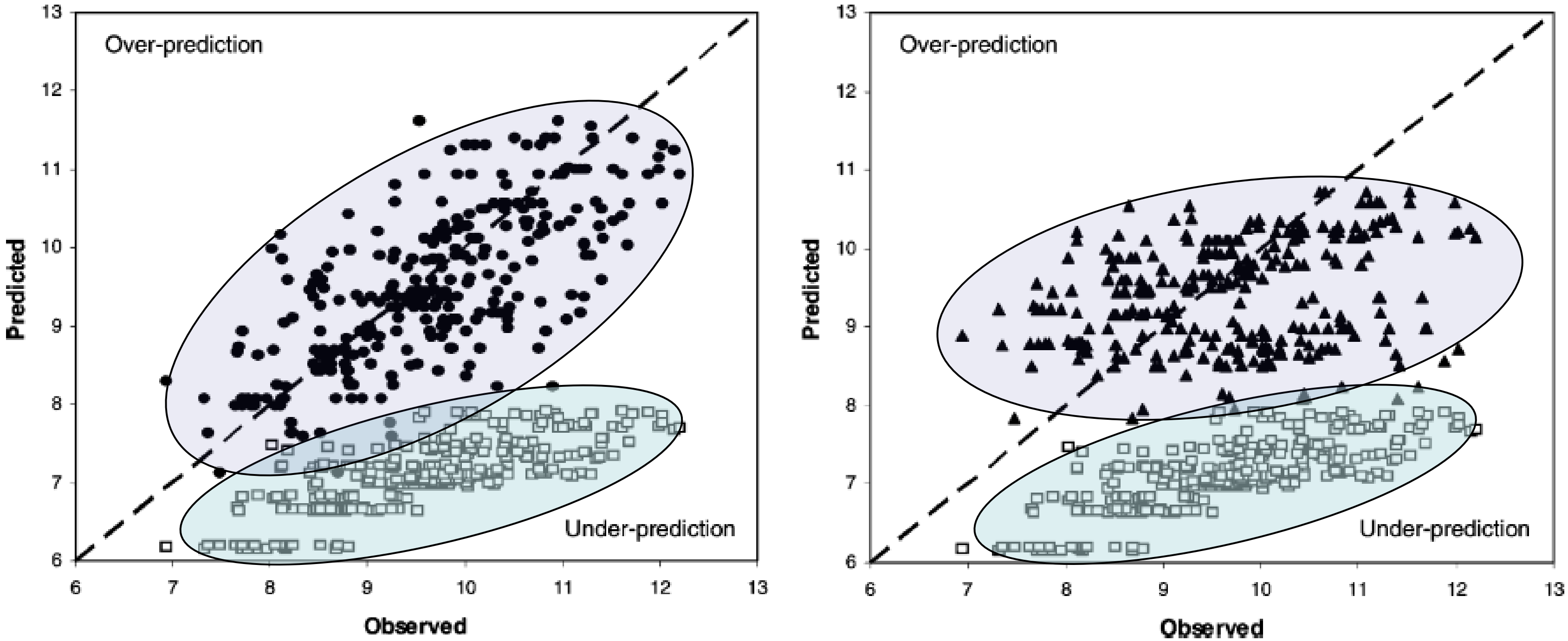
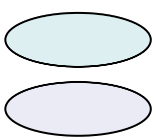


FIGURE 2. Predicted versus observed organic carbon–water partition coefficients (log K_{TOC}, L/kg) for the AOC-only model (open square), AOC + Langmuir sorption isotherm (closed circle) and AOC + Freundlich sorption isotherm (closed triangle) in all boxes with observations for all congeners. Observed data represent discrete samples taken from 1998 to 2000 across the model domain.

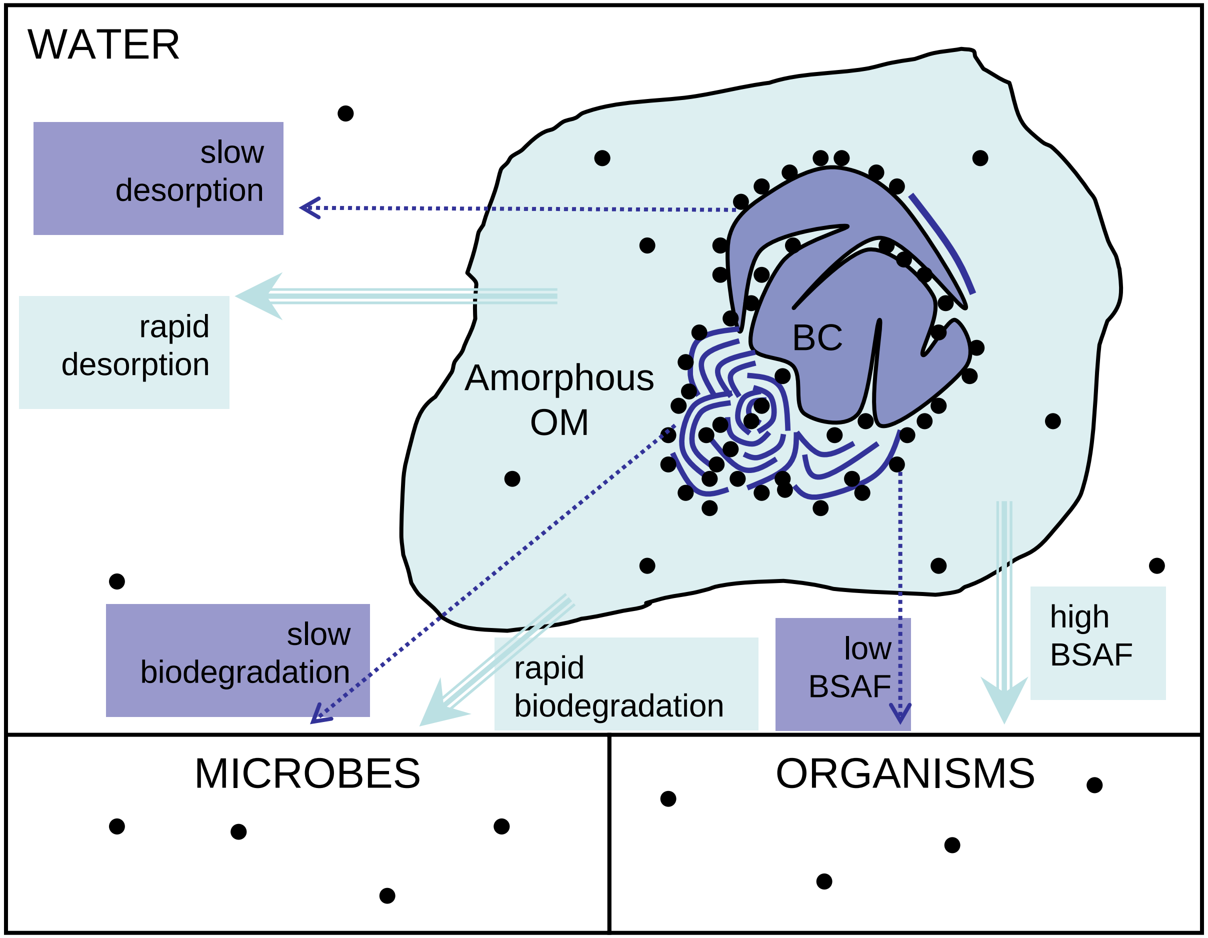


Kd predicted focKoc

Kd predicted focKoc + fbcKbc

Armitage et al. 2008

Enhanced, BC inclusive, dual mode distribution model: kinetic aspects



Modified after Cornelissen et al. 2005

Reduced fast desorbing fractions in the presence of BC

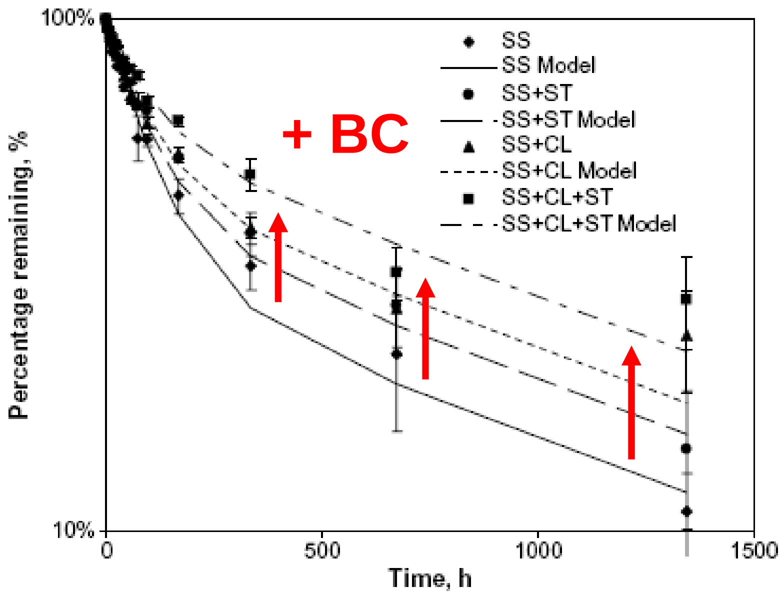


Fig. 1. Biphasic desorption of freshly spiked HCB on four artificial sediments. S_t/S_0: the sediment-bound (non-desorbed) fraction of HCB at time t; Points: experimental data; Line: model fitting to the biphasic desorption kinetics depicted by Eq. (2) with average r^2 of 0.98. SS: standard OECD sediment; SS + CL: standard OECD sediment + 15% montmorillonite clay; SS + ST: standard OECD sediment + 0.5% lamp black soot; SS + CL + ST: standard OECD sediment + 15% montmorillonite clay + 0.5% lamp black soot.

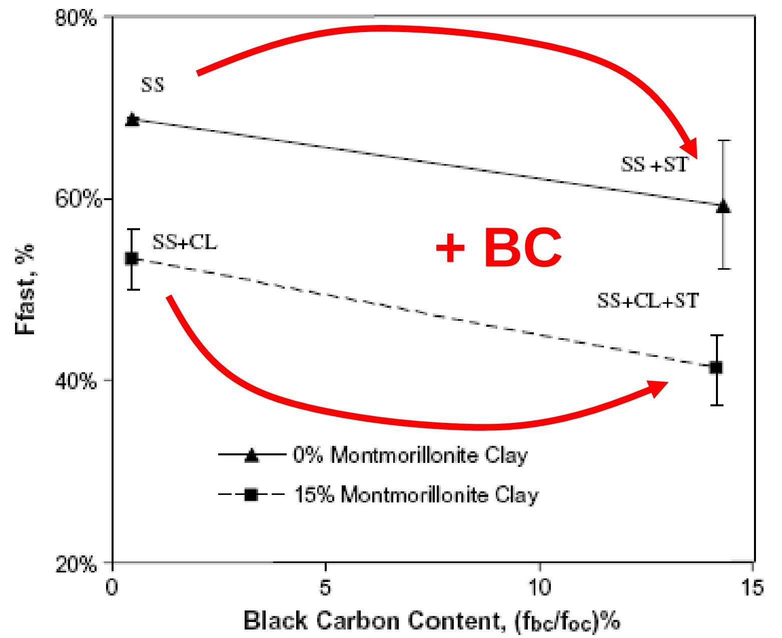
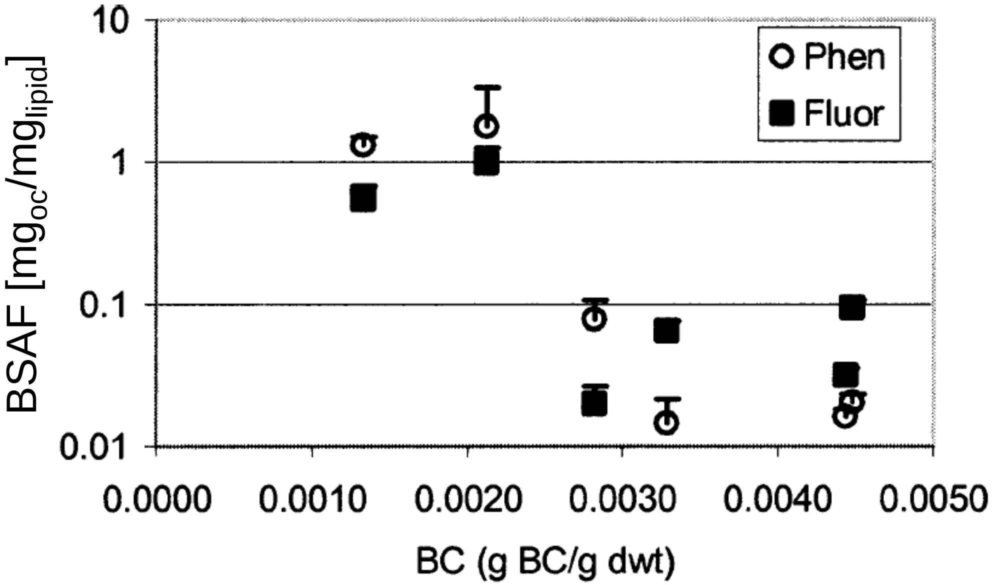


Fig. 2. Effects of black carbon content in sediments on the desorption of sediment-bound HCB. F_{fast}: fast desorbing fraction; SS: standard OECD sediment; SS + CL: standard OECD sediment + 15% montmorillonite clay; SS + ST: standard OECD sediment + 0.5% lamp black soot; SS + CL + ST: standard OECD sediment + 15% montmorillonite clay + 0.5% lamp black soot.

Chai et al. 2007

Black carbon reduces biota to sediment accumulation factors (BSAF)

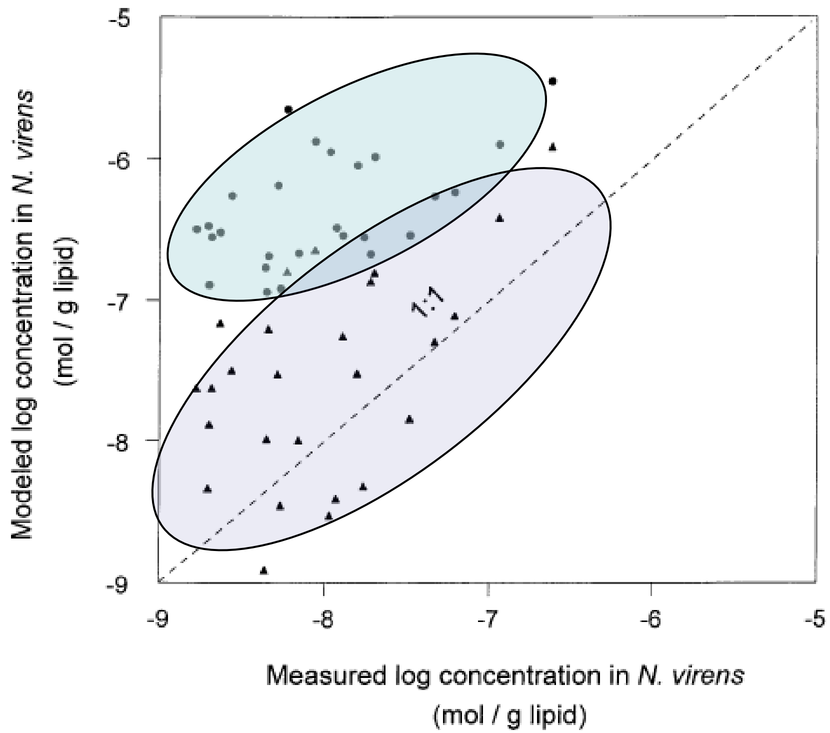
Monoporeia affinis



65 d exposition of *Monoporeia affinis* to sediments from six stations with varying BC content in and around Stockholm

Sundelin et al. 2004

Improved predictability of tissue concentrations (PAHs)



conc predicted focKoc

conc predicted focKoc + fbcKbc

Fig. 2. Comparison of measured *Nereis virens* pyrene and phenanthrene lipid-normalized tissue concentrations ($C_{org,lip}$; mol/g lipid) with tissue concentrations estimated by the bioaccumulation model: $C_{org,lip} = K_{lipid} \cdot C_{diss}$. The freely dissolved pyrene and phenanthrene pore water concentrations (C_{diss}) were estimated via two sediment partitioning models (EqP_{NPOC} and $EqP_{NPOC,BC}$). Nonpyrogenic organic carbon = NPOC; black carbon = BC.

Vinturella et al. 2004

BC: „the reverse of its dark side"…

Application: AC amendment

AC amendment to contaminated sediment (PCBs)

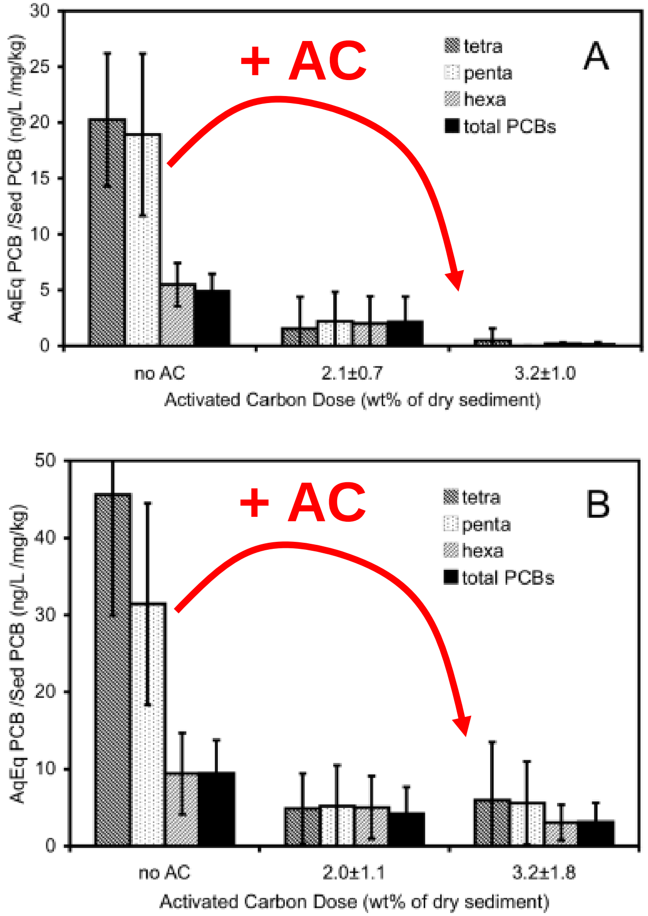


FIGURE 2. AC dose−response relationship for aqueous equilibrium PCB concentrations normalized by sediment concentration: (a) Plot D and (b) Plot F. Each column and error bar represents the mean and one standard deviation ($n = 5$).

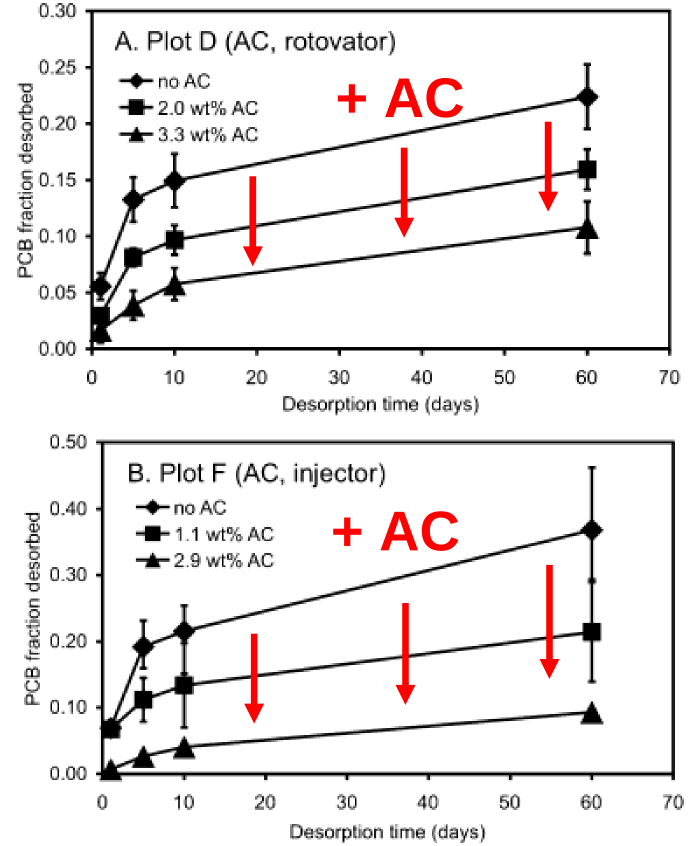


FIGURE 3. PCB desorption for sediment samples collected from two AC-treated plots. The graphs show the fraction of PCBs desorbed for samples with different activated carbon (AC) contents. Each data point represents the mean and one standard deviation ($n = 1-2$, analytical replicates).

Cho et al. 2009

AC amendment to contaminated soil (PAHs)

Table 3

Reduction (in %) of the freely dissolved aqueous concentration in the soil/water suspensions of activated carbon (powdered AC: PAC, granular AC: GAC) amended soils compared to non-amended systems

	Urban soil, PAC	Urban soil, GAC	Creosote soil, PAC	Creosote soil, GAC
FLU	99.8[c]	96.0[c]	20.3	−24.3[a]
PHE	99.7[c]	92.4[c]	15.0	−33.8[a]
ANT	99.7[c]	90.9[c]	35.8[c]	−49.2[a,c]
FLT	99.1[c]	81.9[c]	66.9[c]	−62.8[a,c]
PYR	98.6[c]	79.6[c]	60.5[c]	4.9
BaA	98.4[c]	64.6[c]	70.4[c]	5.3
CHR	98.6[c]	63.9[c]	63.4[c]	3.4
BbF	96.0[c]	38.3	70.2[c]	6.1
BkF	96.1[c]	34.3	70.7[c]	16.1
BaP	93.6[c]	36.4	63.5[c]	−24.7[a]
IND	93.5[c]	17.4	59.3[c]	11.2
BPE	81.3[c]	21.2	66.1[c]	33.4[a,c]
Median	99	64	63	4
IQR[b]	95–99	36–84	53–68	−27–7

+ AC

[a] Negative values indicate an increased concentration in AC amended systems, probably due to soil heterogeneity.
[b] IQR: inter-quartile-range.
[c] Significant reduction compared to non-amended systems.

Brändli et al. 2008

AC amendment: potential limitations and drawbacks

- Ecotoxicity
- Nutrient availability
- Alteration of physical characteristics of soils and sediments (permeability, etc.)
- NOM attenuation may impair effectiveness of AC sorption
- Time to reach equilibrium
- Long-term stability unknown

Conclusions

- BC is ubiquitous in the environment
- BC comes in many forms
- BC is a strong sorbent for organic pollutants
- Solid-water distribution of organic pollutants is dominated by BC
- Desorption and bioavailability of organic pollutants is dominated by BC
- Current risk assessment tools and legislations do not yet account for BC
- Promising application of AC to immobilize pollutants

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  - Swiss National Science Foundation
  - Marie Curie Intra-European Fellowship

Thank you for your attention !!!