Sorption made simple

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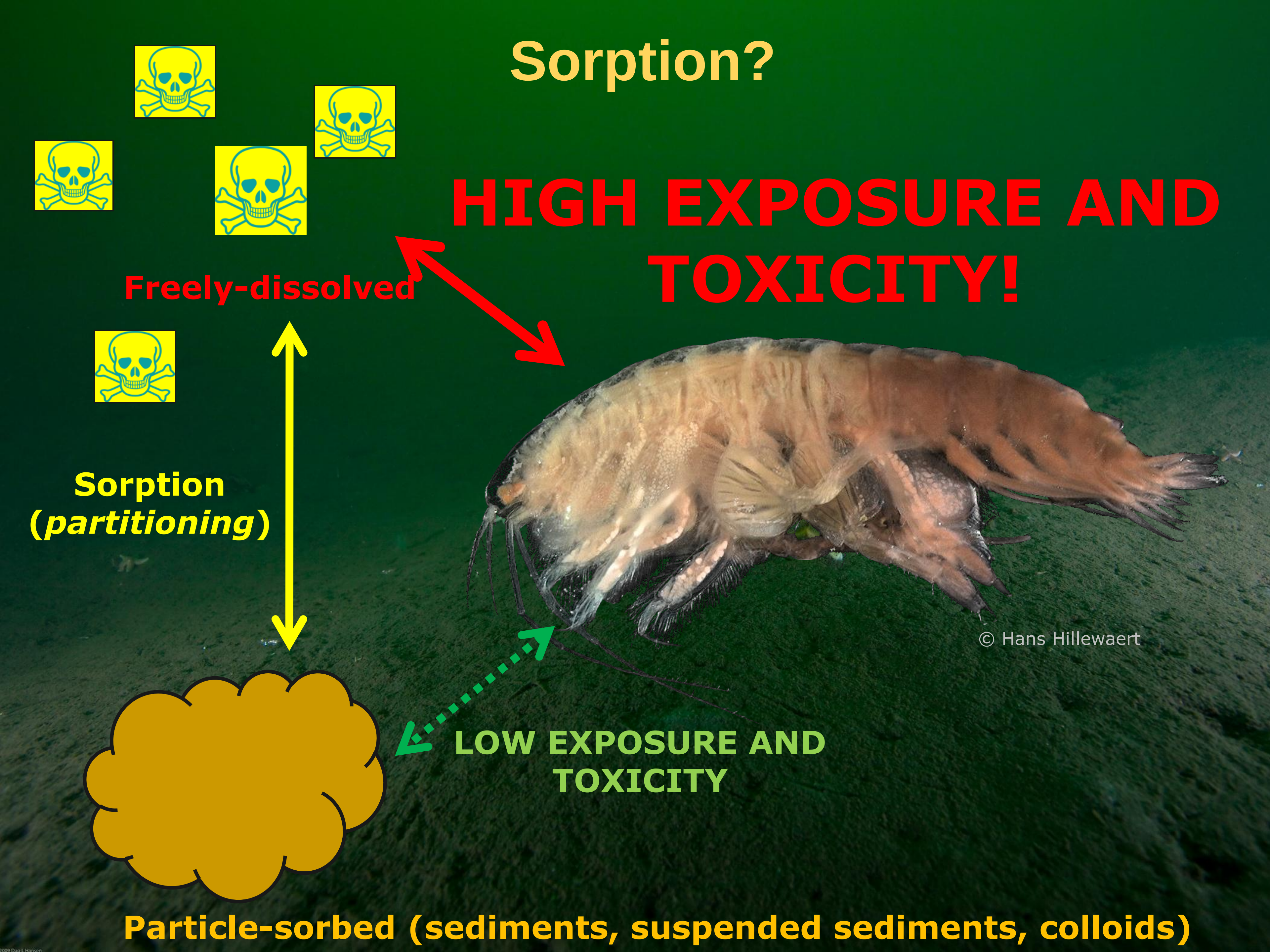
NGI

NORDROCS 2012

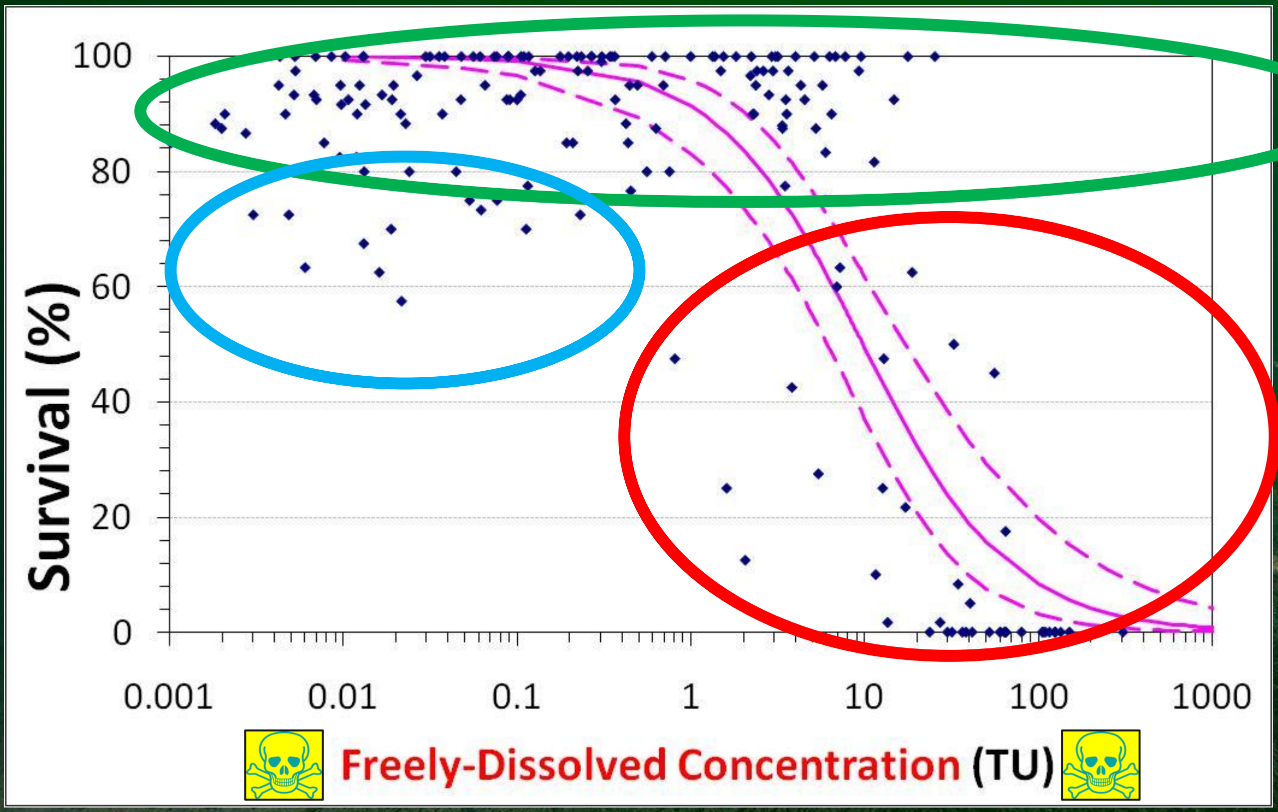
18. September, Oslo Norway

1

Sorption and contamination


Sorption?
HIGH EXPOSURE AND TOXICITY!
Freely-dissolved
Sorption (partitioning)
© Hans Hillewaert
LOW EXPOSURE AND TOXICITY
Particle-sorbed (sediments, suspended sediments, colloids)

Why is sorption important?

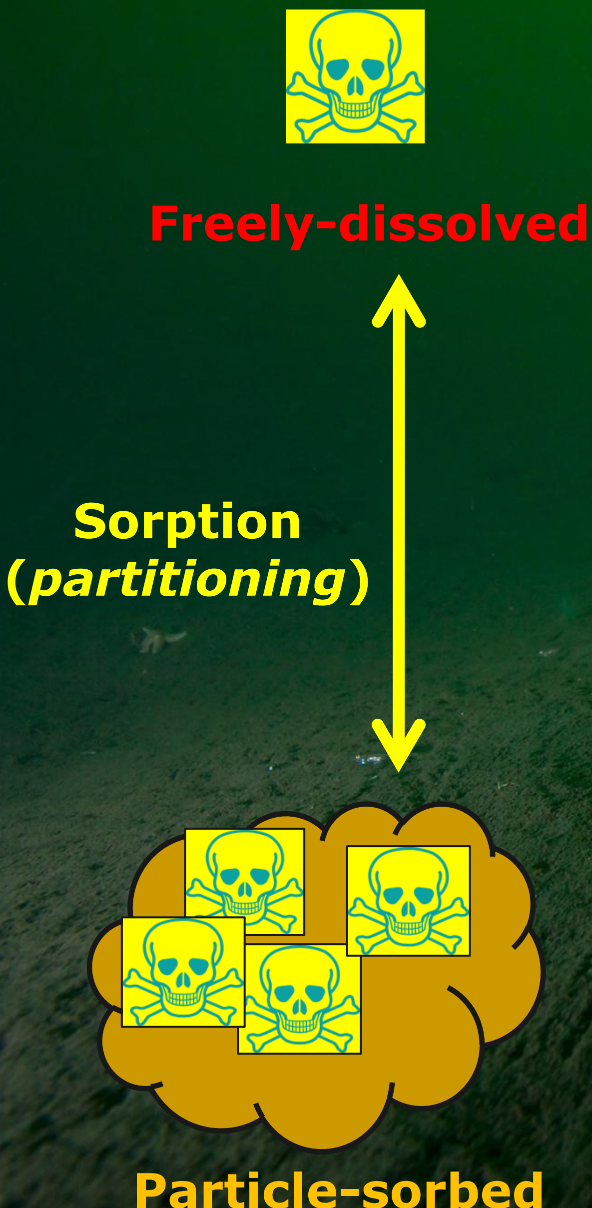


Healthy!

Stress (not due to contamination)

Severe Stress (Contamination)

Sorption?



$$K_D = C_{sed} / C_{water}$$

at equilibrium

2

History of sorption theory

IN THE BEGINNING…

In the 1960s – 1970s, laboratory experiments found sorption of pesticides was

a) related to the total organic carbon (TOC) content of soil

$$K_D = f_{TOC}\, K_{TOC}$$

b) dependant on the chemical.

In 1979:

SORPTION OF HYDROPHOBIC POLLUTANTS ON NATURAL SEDIMENTS

Samuel W. Karickhoff, David S. Brown and Trudy A. Scott
Environmental Research Laboratory, U.S. Environmental Protection Agency, College Station Road, Athens, GA 30605, U.S.A.

(*Received* 4 *September* 1978)

A Physical Concept of Soil-Water Equilibria for Nonionic Organic Compounds

SCIENCE, VOL. 206, 16 NOVEMBER 1979

Cary T. Chiou
Louis J. Peters
Virgil H. Freed

$$\log K_{TOC} = \log K_{OW} - 0.21$$

$$\log K_{oc} = 1.00 \log K_{ow} - 0.21\ (R^2 = 1.00) \qquad (6)$$

$$\log K_{TOC} = 4 - 0.56 \log S_L$$

$$\log G = 4.040\ (\pm 0.038) - 0.557\ (\pm 0.012) \log S \qquad (2)$$

with $r^2 = 0.988$ and $n = 15$ (where G is

TOTAL ORGANIC CARBON (TOC)?

$$K_D = f_{TOC} K_{TOC}$$

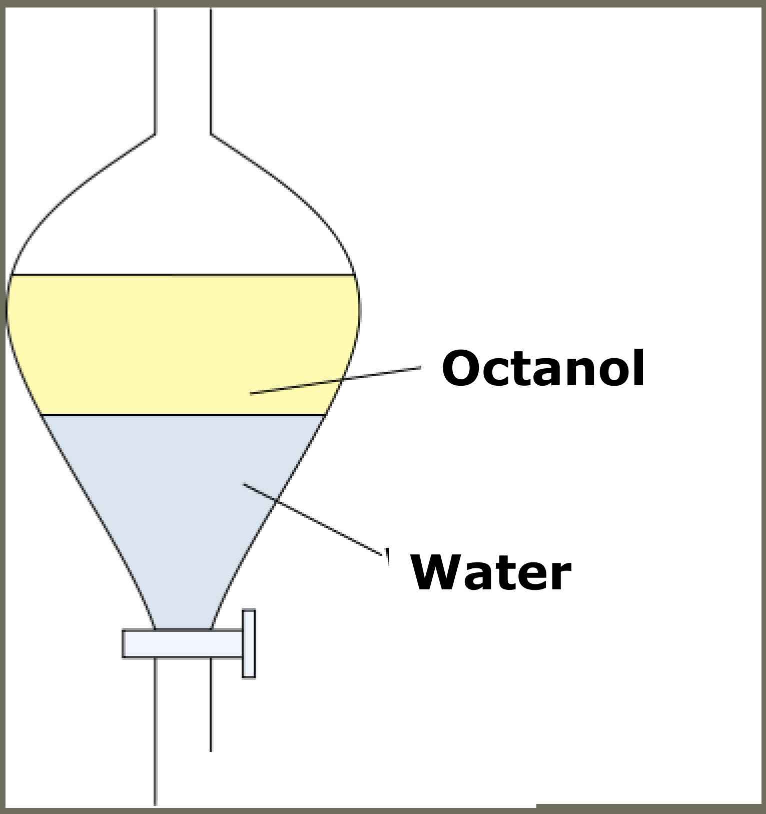
Total Organic Carbon =

Mass Fraction of all carbon in a soil or sediment that is not CO_2 or Carbonate (CO_3^{2-}) - removed in the lab with 1 M HCl

f_{TOC} = mass TOC/ mass sediment

http://www.soil.ncsu.edu/lockers/lindbo/Soil%20Photos/Micromorphology%20slides/Stoops%20Collection/docs/ch6_cmp.html

Octanol-water partitioning (K_{ow})?



$$\log K_{TOC} = \log K_{OW} - 0.21$$

Used in pharmaceutical industry to mimic sorption to fat (lipids).

Used also for low food chain organisms ($K_{lipid} = K_{ow}$)

<u>The hypothesis for soil/sed:</u>

Octanol is a proxy for TOC (as it is for lipids)

Subcooled-liquid solubility (S_L)

$$\log K_{TOC} = 4 - 0.56 \log S_L$$

www.odec.ca

Solubility =
Maximum amount that can be dissolved per volume of water.

Subcooled-liquid =
Solubility of melted solids (at room temperature), to account for the fact in the environment solid crystals of contaminants do not form.

The hypothesis:

TOC partitioning follows Raoult's Law for ideal mixtures

$$K_{TOC} = (MW_{TOC}\ S_L)^{-1}$$

3

The end of simplicity?

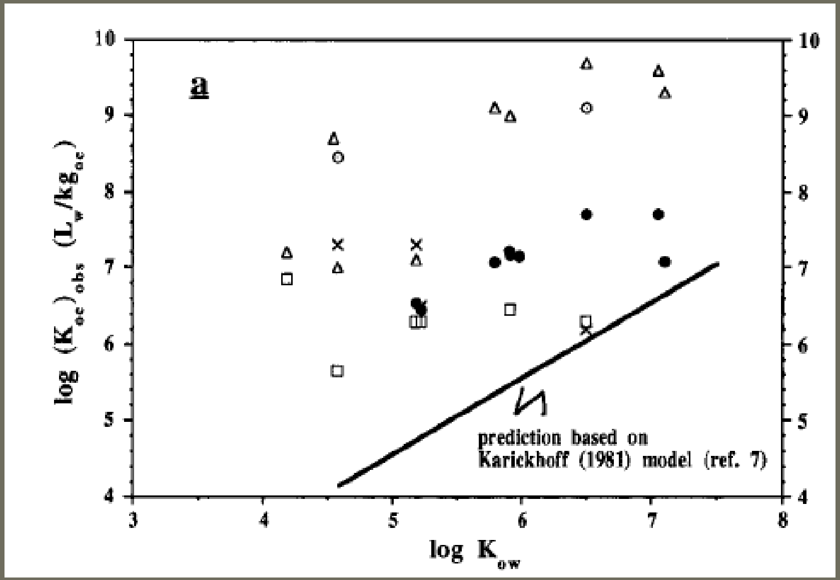
Problems with the simple models # 1.

Sorption from contaminated field sites was much stronger than artificial lab experiments when:

1) No lab spike was used to add the contaminants (i.e. real world contaminanted samples used)

2) Techniques got better for removing *colloids* (very small, suspended particles) and *DOC* (dissolved organic carbon, like humic material, organic molecules and micelles)

3) Pore water detection improved



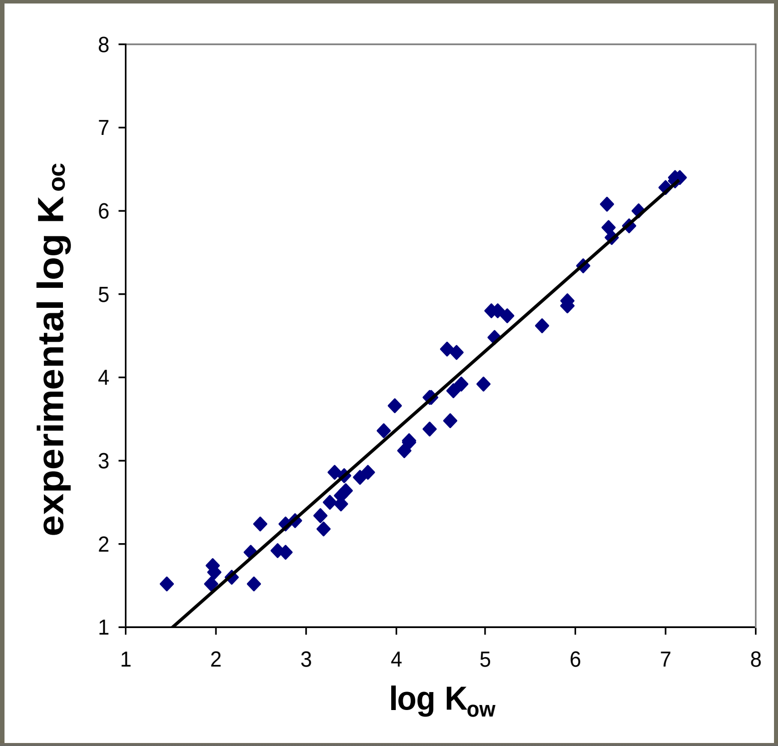
Gustaffson ES&T 2000

Common to find K_{toc} of PAHs, PCBs and dioxins > 10 to 10000 times larger than K_{ow}!!!!

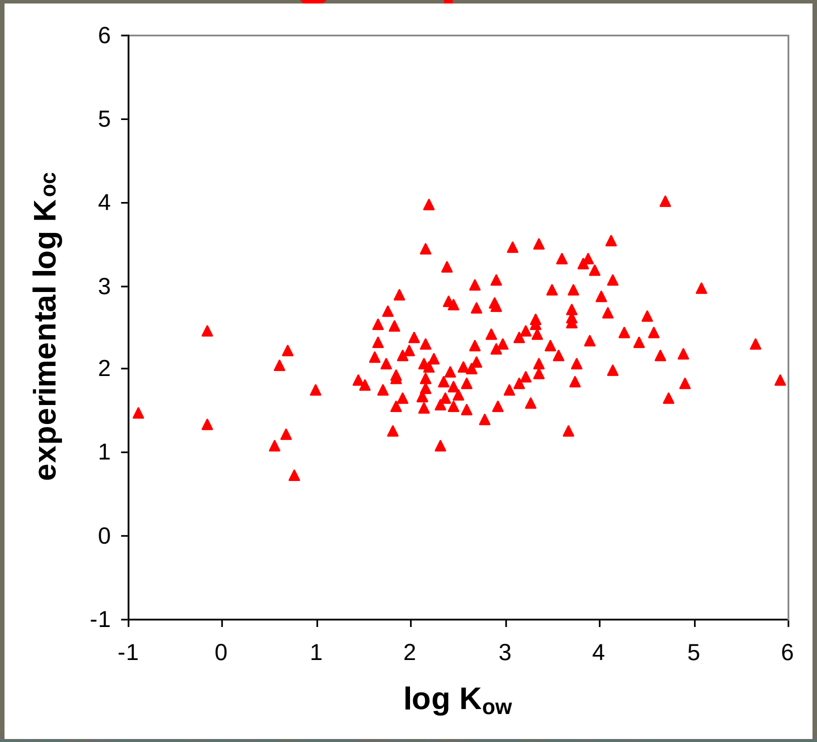
Problems with simple models # 2.

Traditional models ONLY worked with HOCs

hydrophobic organic chemicals



polar chemicals including 50 pesticides



Kai-Uwe Goss, UFZ Leipzig

Research in environmental sorption since 1980

Sorption made...complex!

SORBENT

Is TOC too simple to account for soil and sediment variability?

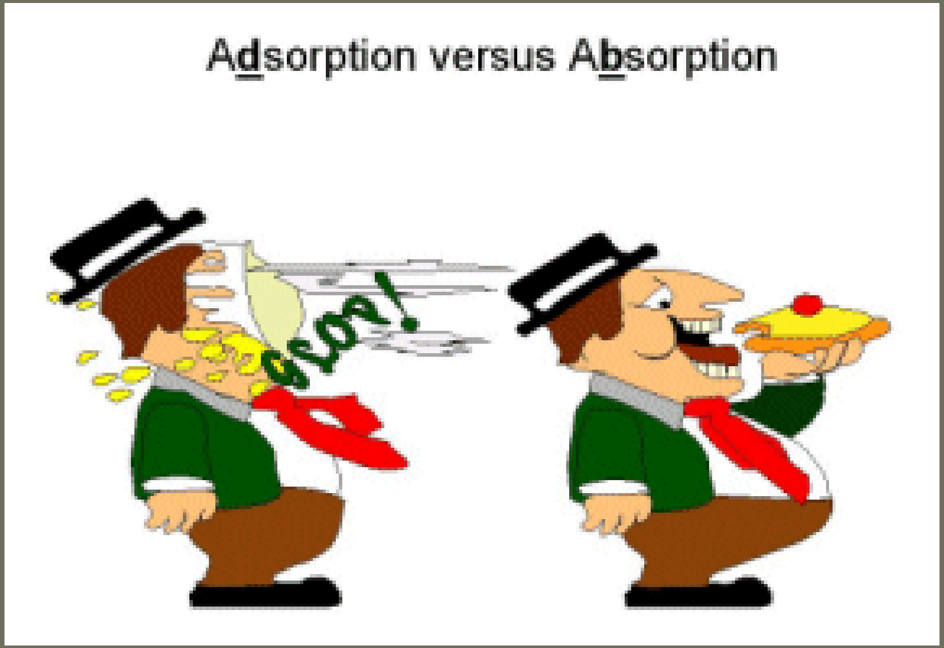
SORBATE

Is K_{OW} and S_L too simple to account for contaminant variability?

4

Sorbent Variability

Sorbent Variability: AD vs AB



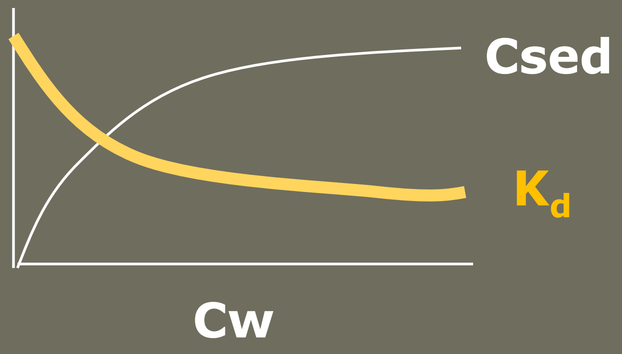
ADSORPTION
On the surface:
Surface area
(Porosity)

ABSORPTION
Inside the material:
Volume
(Crystallinity)

http://mrselliott.wordpress.com/tag/volumetric-analysis/

Sorbent Variability: Concentration Effect

Concentration effect



-Typical effect from factor 2- 10 (soils,sediments) to >100 (activated carbon)

- More commonly attributed to **ADsorption processes** (surface coverage, surface attenuation, pore blockage, etc.) though also for Absorption (e.g. crystallinity)

-Many models (Freundlich, Langmuir, BET…)

Example model (Freundlich):

$$K_D = C_{sed} / (C_w^{n-1})$$

Sorbent Variability: Particle Heterogeneity

Sequestration of Hydrophobic Organic Contaminants by Geosorbents

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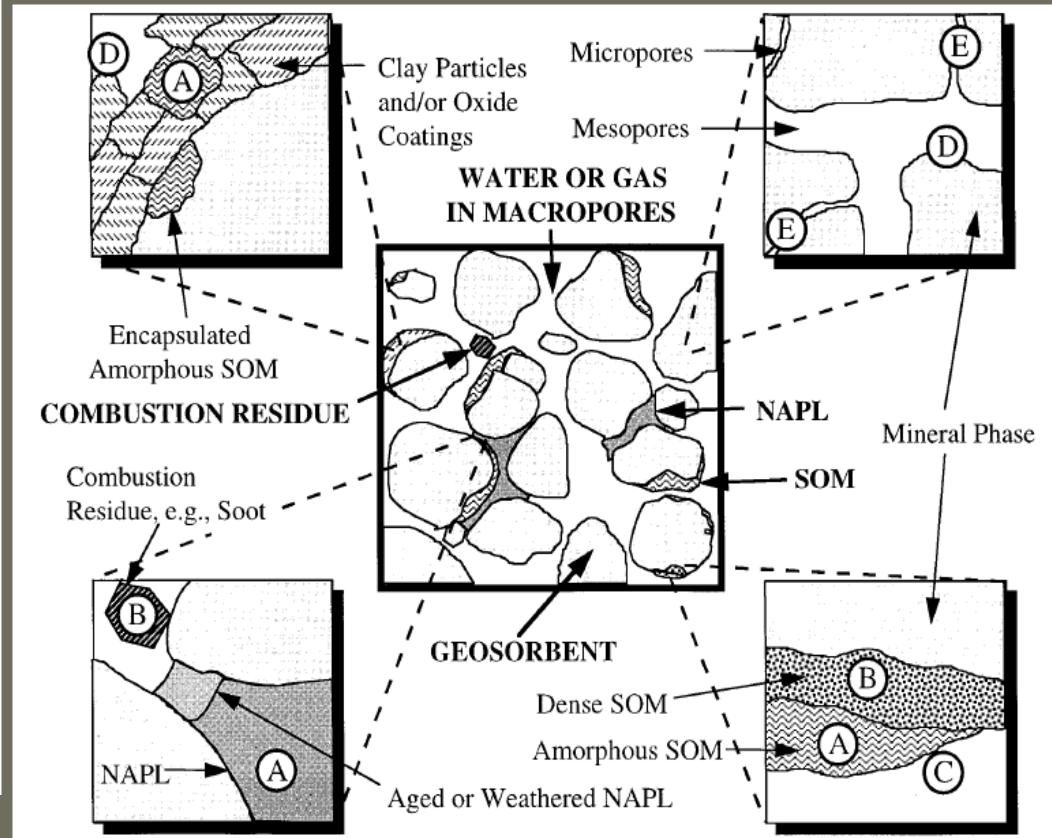
Department of Chemistry, Oregon State University, Corvallis, Oregon 97331



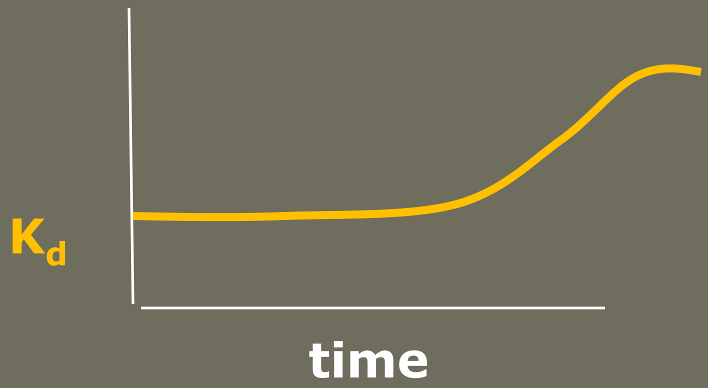
VOL. 31, NO. 12, 1997 / ENVIRONMENTAL SCIENCE & TECHNOLOGY ■ 3341

$$(q_e)_{\text{total SOM}} = (q_e)_{\text{natural SOM linear}} + (q_e)_{\text{natural SOM nonlinear}} + (q_e)_{\text{anthropogenic SOM linear}} + (q_e)_{\text{anthropogenic SOM nonlinear}} \quad (2)$$

$$K_D = f_A K_A + f_B K_B + f_C K_C + f_D K_D + f_E K_E + \ldots$$

Sorbent Variability: Weathering Phenomina

Kinetic / ”Weathering” phenomina



-Increase by a factor 2 to 100

-Observation from old field sites of extremely strong sorption for small contaminants (e.g. benzene)

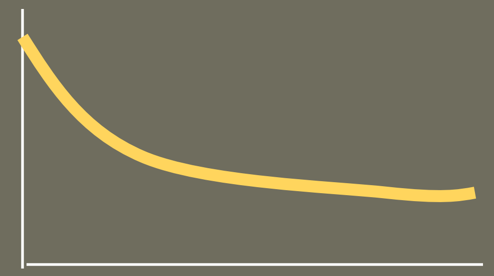
- **Kinetics?** Takes time for contaminants to find strong sorping areas?

- **Weathering?** Caused by changes in the soil/sed with time.

-Likely diverse processes

Sorbent Variability: Temperature Effect

Temperature effect



- Increase temperature, decrease K_d.

- Described by the van't Hoff equation

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H^{\ominus}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right).$$

- Generally minor for water-soil and water-sediment systems.

- Generally major for air-soil, air-sediment systems (also air-water)

Sorption made complex!

Many complex influences on sorption!

How to account for these in the real world?

Example attempt:
The Black Carbon hypothesis.

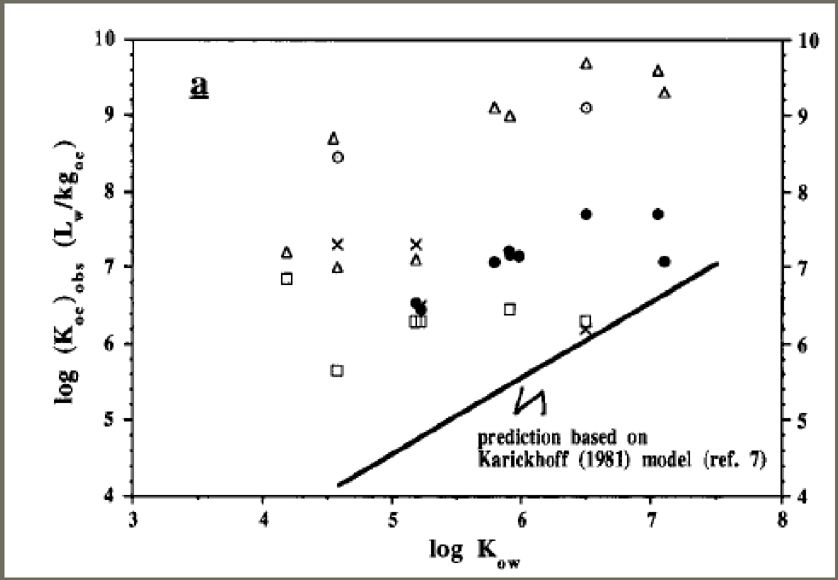
Sorbent Variability: The Black Carbon Hypothesis

Quantification of the Dilute Sedimentary Soot Phase: Implications for PAH Speciation and Bioavailability

ÖRJAN GUSTAFSSON, FARNAZ HAGHSETA, CHARMAINE CHAN, JOHN MACFARLANE, AND PHILIP M. GSCHWEND*

R. M. Parsons Laboratory, MIT 48-415, Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Environ. Sci. Technol. **1997**, *31*, 203–209



Where was the extra sorption coming from?

$$K_d = f_{oc}K_{oc} + f_{sc}K_{sc}$$

Soot – they were after all looking at PAHs

The BC sorption hypothesis is born!

~~$K_D = f_{TOC} K_{TOC}$~~

$$K_D = f_{AOC} K_{AOC} + f_{BC} K_{BC} C_w^{nF-1}$$

Where:

f_{BC} = fraction of BC determined usually by the chemical-thermal oxidation method (375°C) (i.e. CTO-375 BC)

f_{AOC} = fraction of ”amorphous organic carbon”, i.e. TOC – BC

nF = ”Freundlich coefficient” to account for sorption non-linearity (i.e. concentration effect)

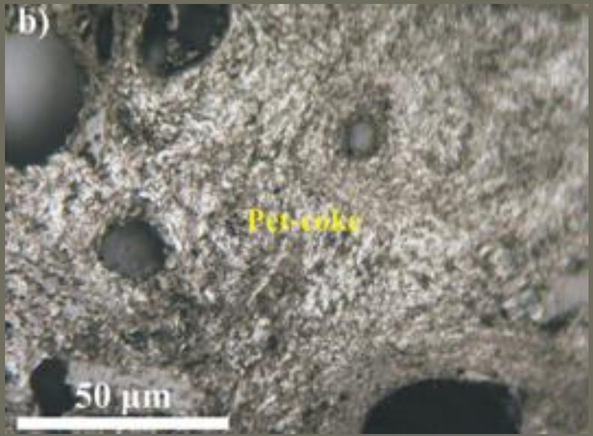
AMORPHOUS ORGANIC CARBON (AOC)?

Amorphous Organic Carbon
= Mass Fraction of all Carbon that is not CO_2, Carbonate (CO_3^{2-}) or <u>Black Carbon</u>

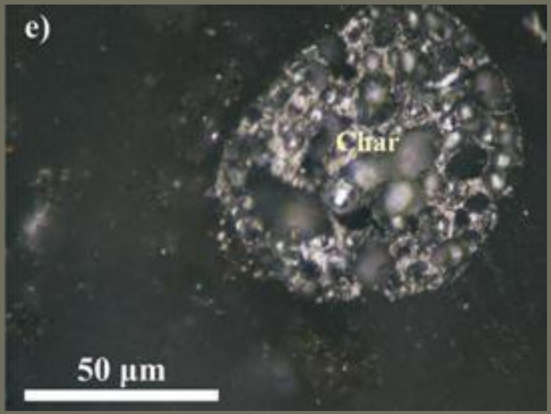
http://www.soil.ncsu.edu/lockers/lindbo/Soil%20Photos/Micromorphology%20slides/Stoops%20Collection/docs/ch6_cmp.html

BLACK CARBON (BC)?

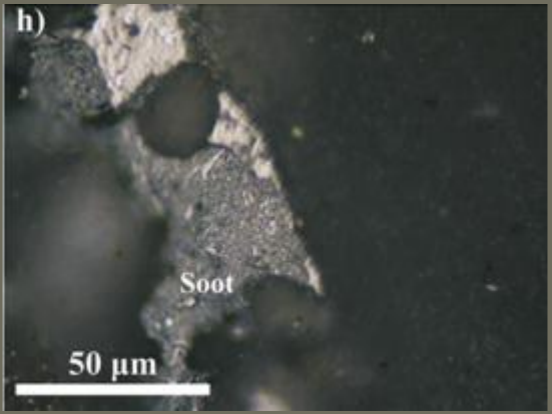
Coal



Coke

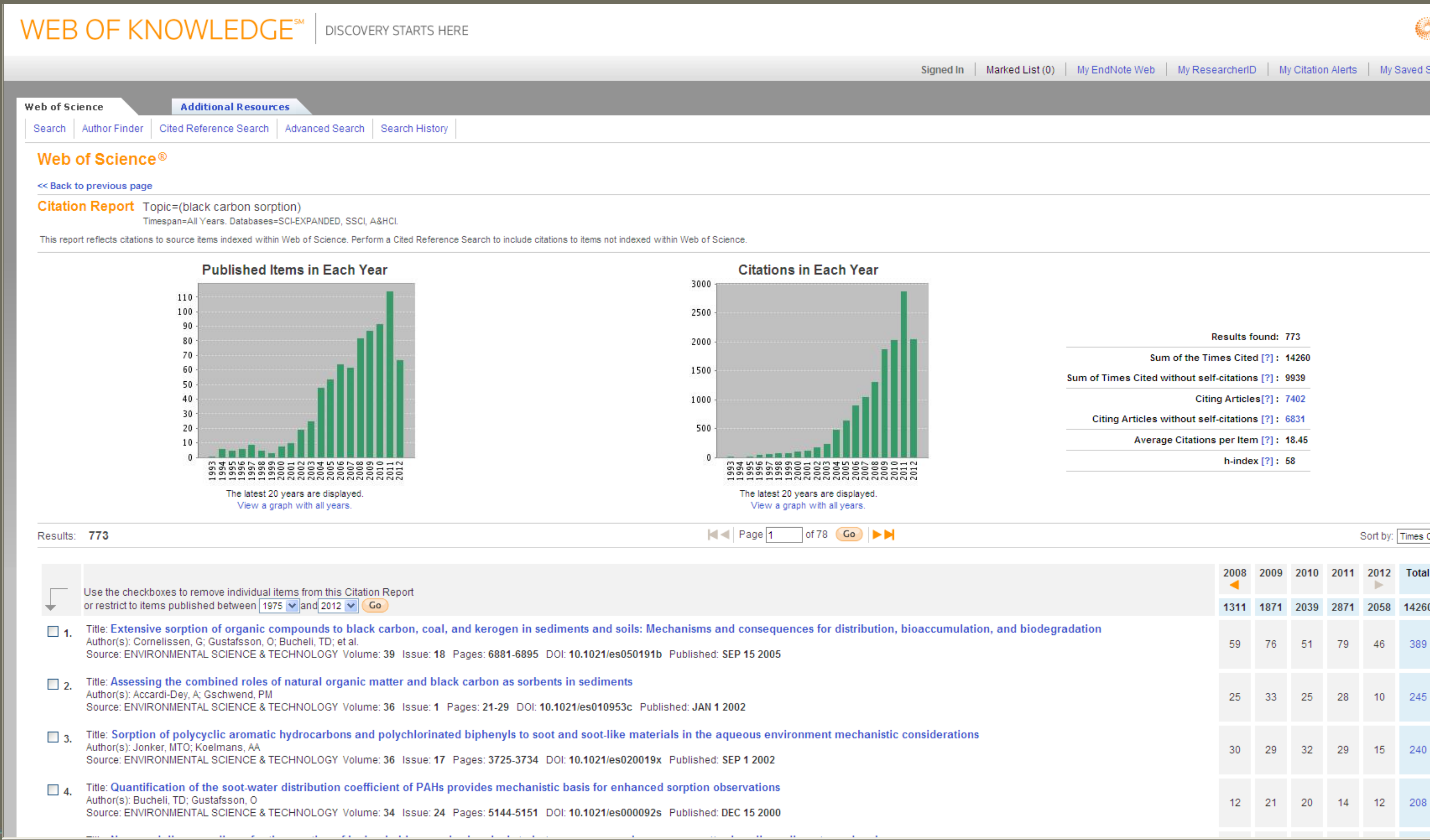


Char



Soot

The BC sorption hyptothesis takes off!



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	2008	2009	2010	2011	2012	Total
	1311	1871	2039	2871	2058	14260
1. Title: Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: Mechanisms and consequences for distribution, bioaccumulation, and biodegradation Author(s): Cornelissen, G; Gustafsson, O; Bucheli, TD; et al. Source: ENVIRONMENTAL SCIENCE & TECHNOLOGY Volume: 39 Issue: 18 Pages: 6881-6895 DOI: 10.1021/es050191b Published: SEP 15 2005	59	76	51	79	46	389
2. Title: Assessing the combined roles of natural organic matter and black carbon as sorbents in sediments Author(s): Accardi-Dey, A; Gschwend, PM Source: ENVIRONMENTAL SCIENCE & TECHNOLOGY Volume: 36 Issue: 1 Pages: 21-29 DOI: 10.1021/es010953c Published: JAN 1 2002	25	33	25	28	10	245
3. Title: Sorption of polycyclic aromatic hydrocarbons and polychlorinated biphenyls to soot and soot-like materials in the aqueous environment mechanistic considerations Author(s): Jonker, MTO; Koelmans, AA Source: ENVIRONMENTAL SCIENCE & TECHNOLOGY Volume: 36 Issue: 17 Pages: 3725-3734 DOI: 10.1021/es020019x Published: SEP 1 2002	30	29	32	29	15	240
4. Title: Quantification of the soot-water distribution coefficient of PAHs provides mechanistic basis for enhanced sorption observations Author(s): Bucheli, TD; Gustafsson, O Source: ENVIRONMENTAL SCIENCE & TECHNOLOGY Volume: 34 Issue: 24 Pages: 5144-5151 DOI: 10.1021/es000092s Published: DEC 15 2000	12	21	20	14	12	208

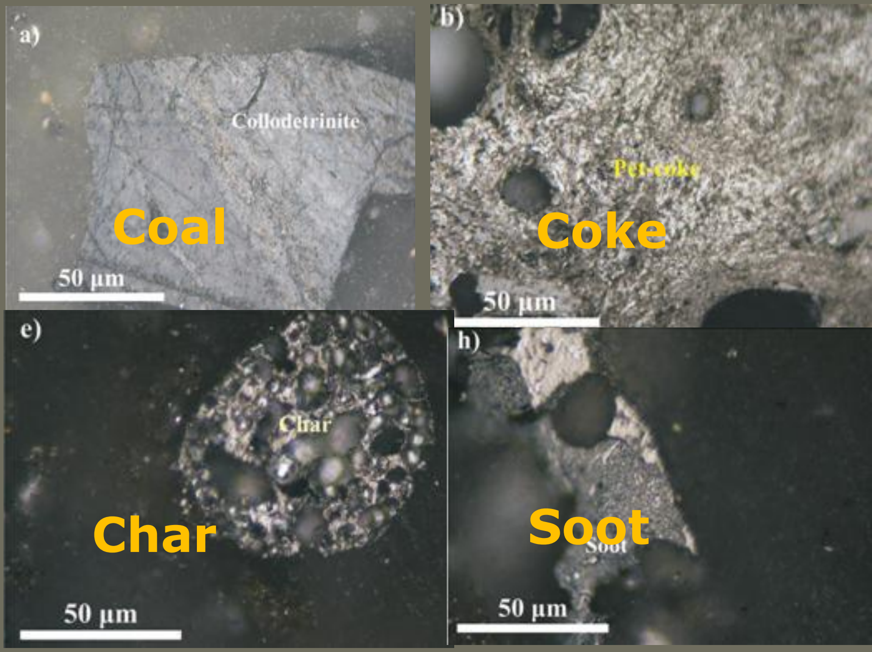
"CRITICISM 1": What is BC?

Critical Review

Extensive Sorption of Organic Compounds to Black Carbon, Coal, and Kerogen in Sediments and Soils: Mechanisms and Consequences for Distribution, Bioaccumulation, and Biodegradation

GERARD CORNELISSEN,[†,‡] ÖRJAN GUSTAFSSON,[*,†]
THOMAS D. BUCHELI,[§] MICHIEL T. O. JONKER,[∥]
ALBERT A. KOELMANS,[⊥] AND
PAUL C. M. VAN NOORT[#]

VOL. 39, NO. 18, 2005 / ENVIRONMENTAL SCIENCE & TECHNOLOGY ■ 6881

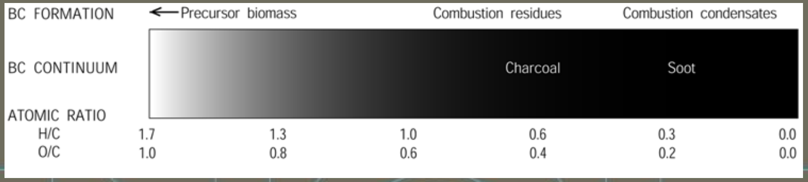


Strong Sorption of Native PAHs to Pyrogenic and Unburned Carbonaceous Geosorbents in Sediments

GERARD CORNELISSEN,[†,*]
GIJS D. BREEDVELD,[†]
STAVROS KALAITZIDIS,[‡]
KIMON CHRISTANIS,[‡]
ANNE KIBSGAARD,[†] AND AMY M. P. OEN[†]

VOL. 40, NO. 4, 2006 / ENVIRONMENTAL SCIENCE & TECHNOLOGY ■ 1197

Chars, coals and coke not stable under CTO-375.

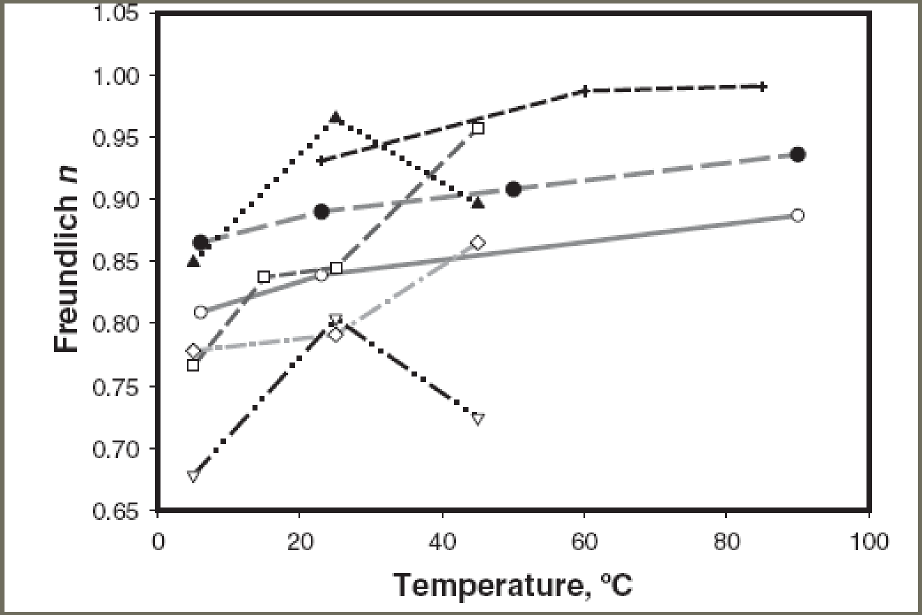


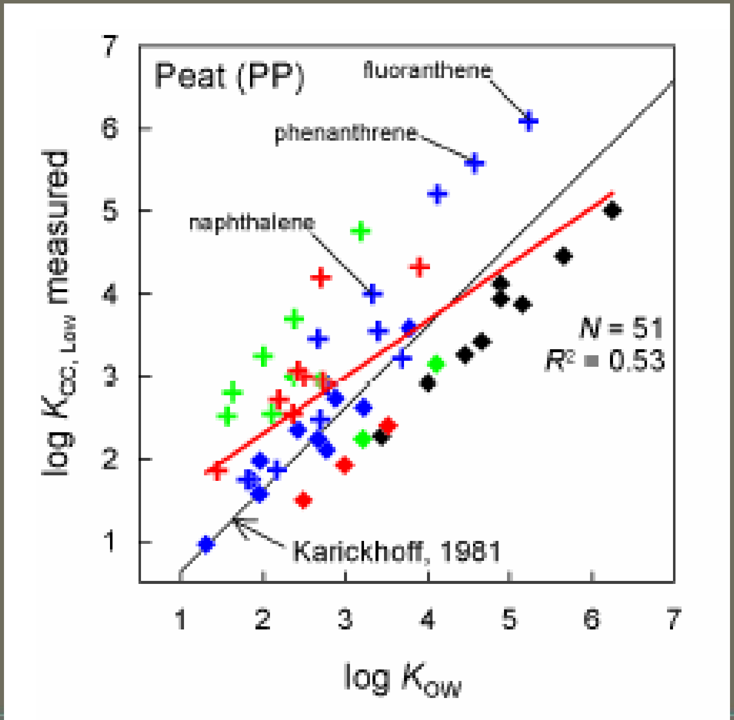
CRITICISM 2: Concentration effect in AOC.

$$K_D = f_{AOC} K_{AOC} C_w^{nF^*-1} + \sout{f_{BC} K_{BC} C_w^{nF-1}}$$

nF values in AOC < 1

at low concentration strong sorption in Pahokee Peat



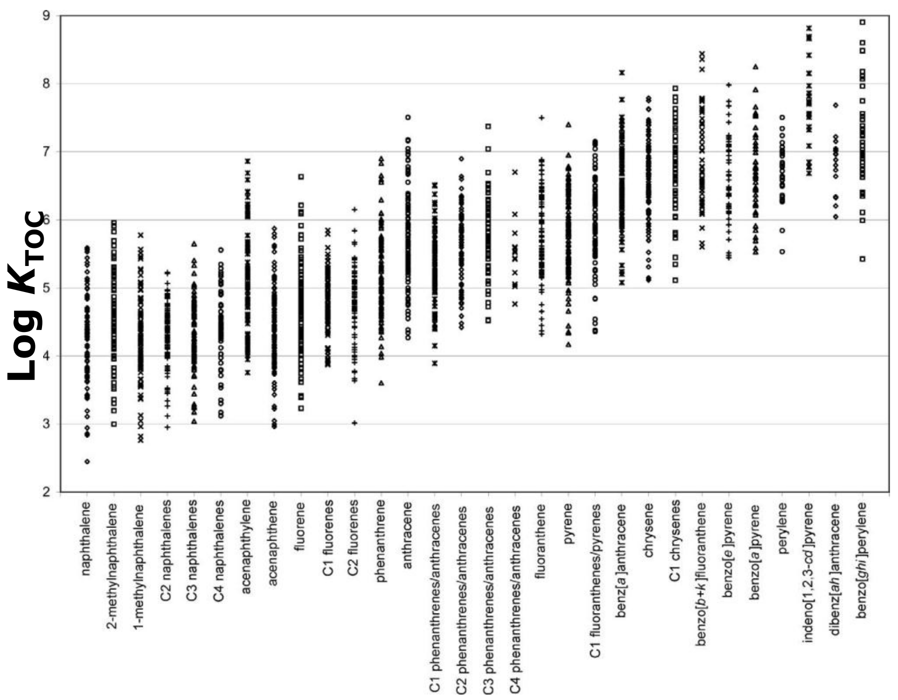


Pignatello et al. J. Environ. Qual. 2006

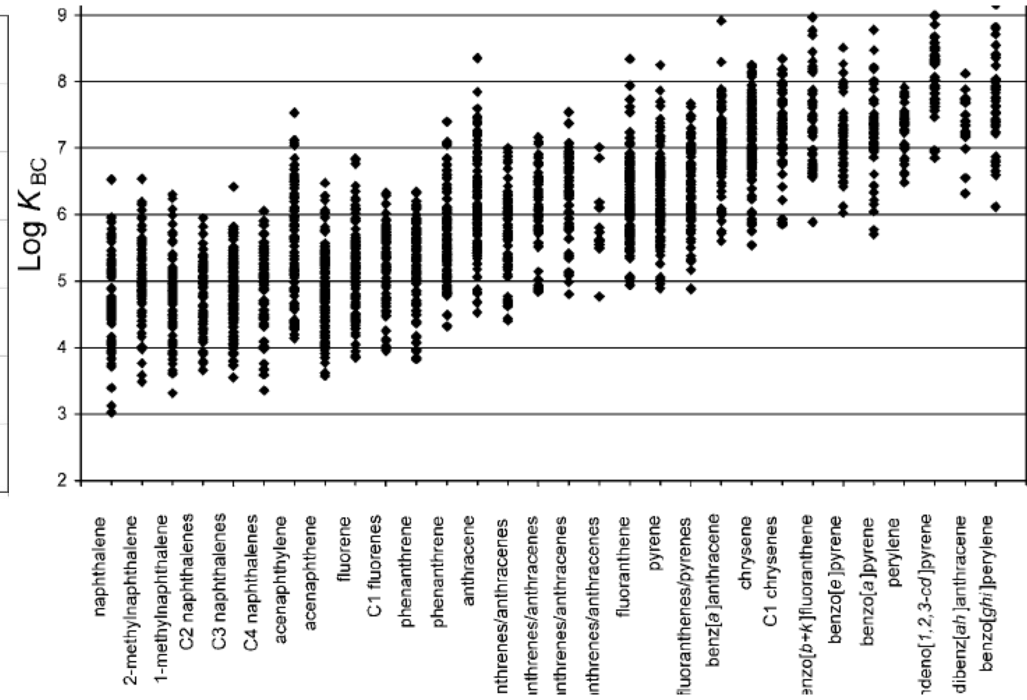
Endo et al. ES&T 2009

CRITICISM 3: No Gain from Extra Parameters

Hawthorne et al. ET&C 2006

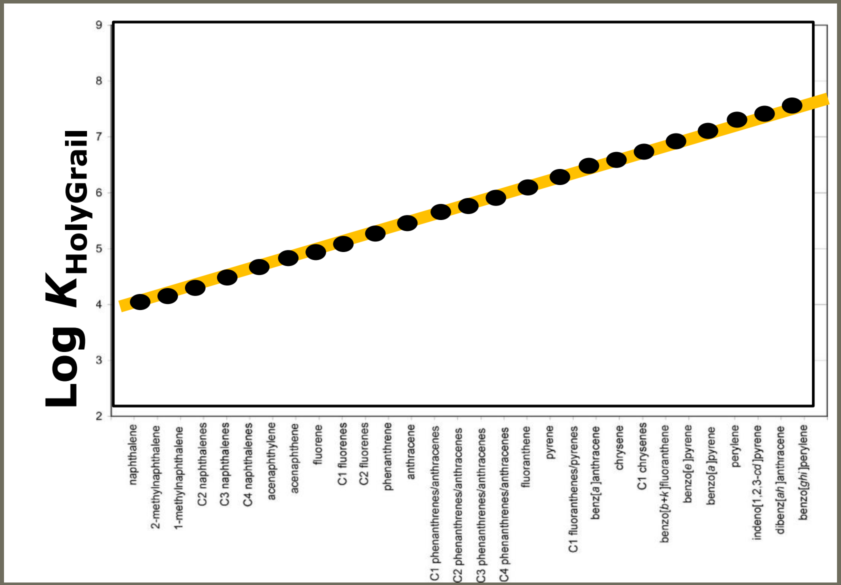


Hawthorne et al. ET&C 2007



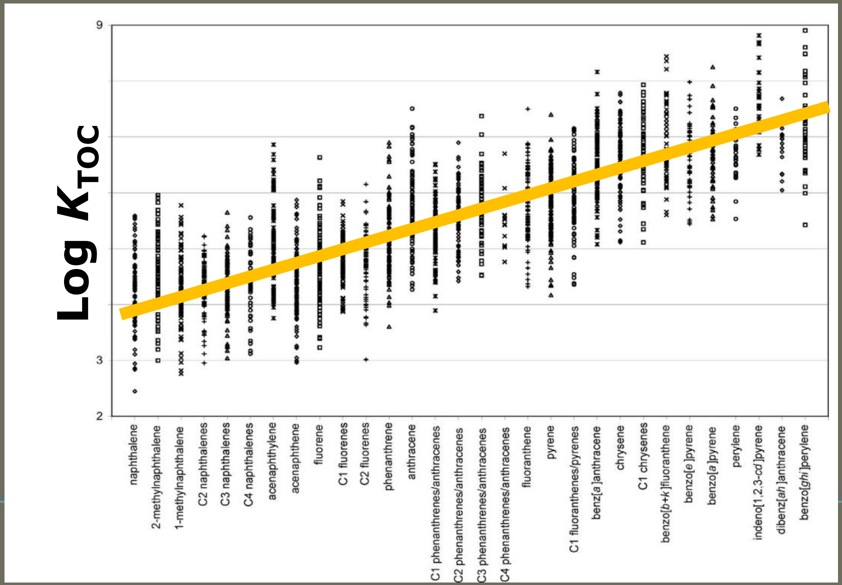
For PAHs, both K_{TOC} and K_{BC} in field sediments scatter by over three orders of magnitude (n = 114)

How to make sorption simple again?



Strategy 1: "The Holy Grail"

- find the critical parameter(s) that condense the data to the uncertainty of particle physics



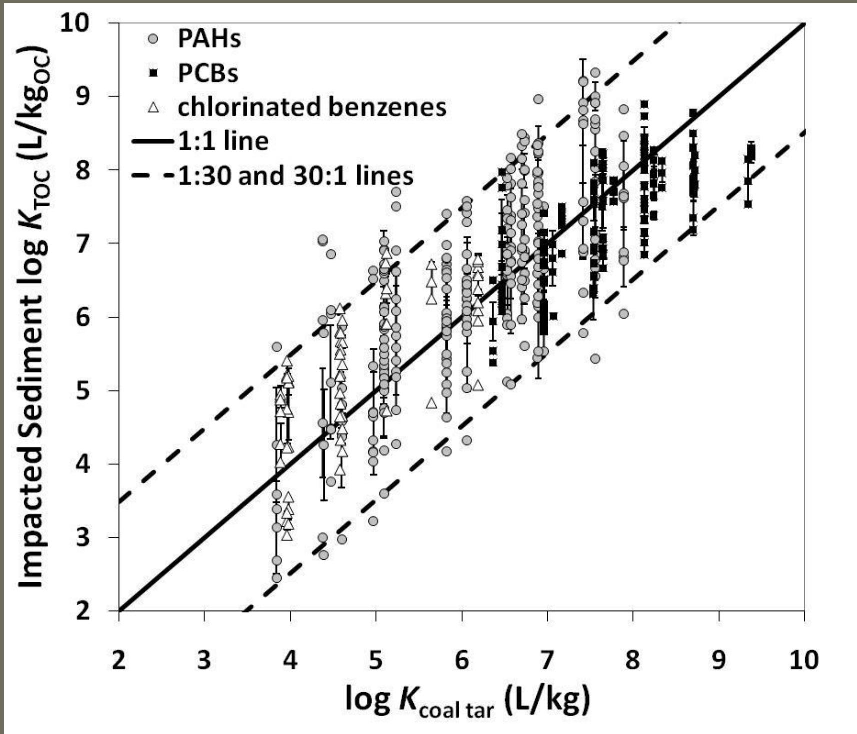
Strategy 2: "Live with it"

Live with the variability of TOC. Find a good proxy, better than K_{ow}, to represent the median of field values.

What makes a good TOC sorption proxy

What proxy gives $K_{TOC\text{-}proxy(lab)} = K_{TOC\text{-}field}$?

Proxy =

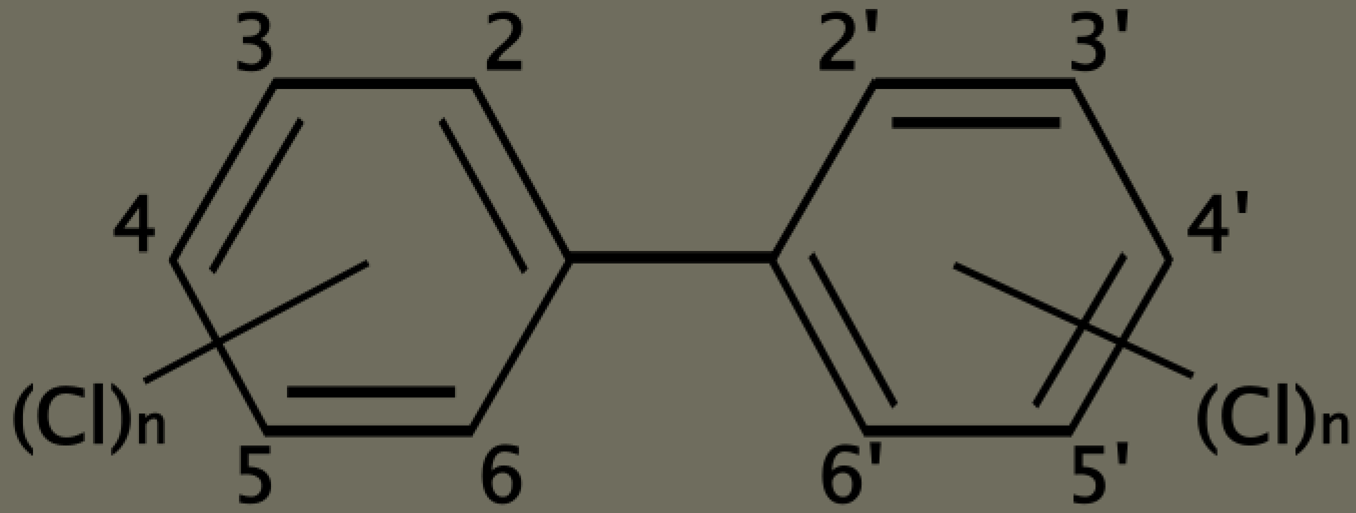


- coal tar
- peat (low concentration)
- peat (high concentration)
- sedimentary NOM
- leonardite humic acid
- hexadecane
- diesel
- n-octanol
- granular activated carbon (low concentration)
- granular activated carbon (high concentration)

Arp et al. *ES&T* 2009

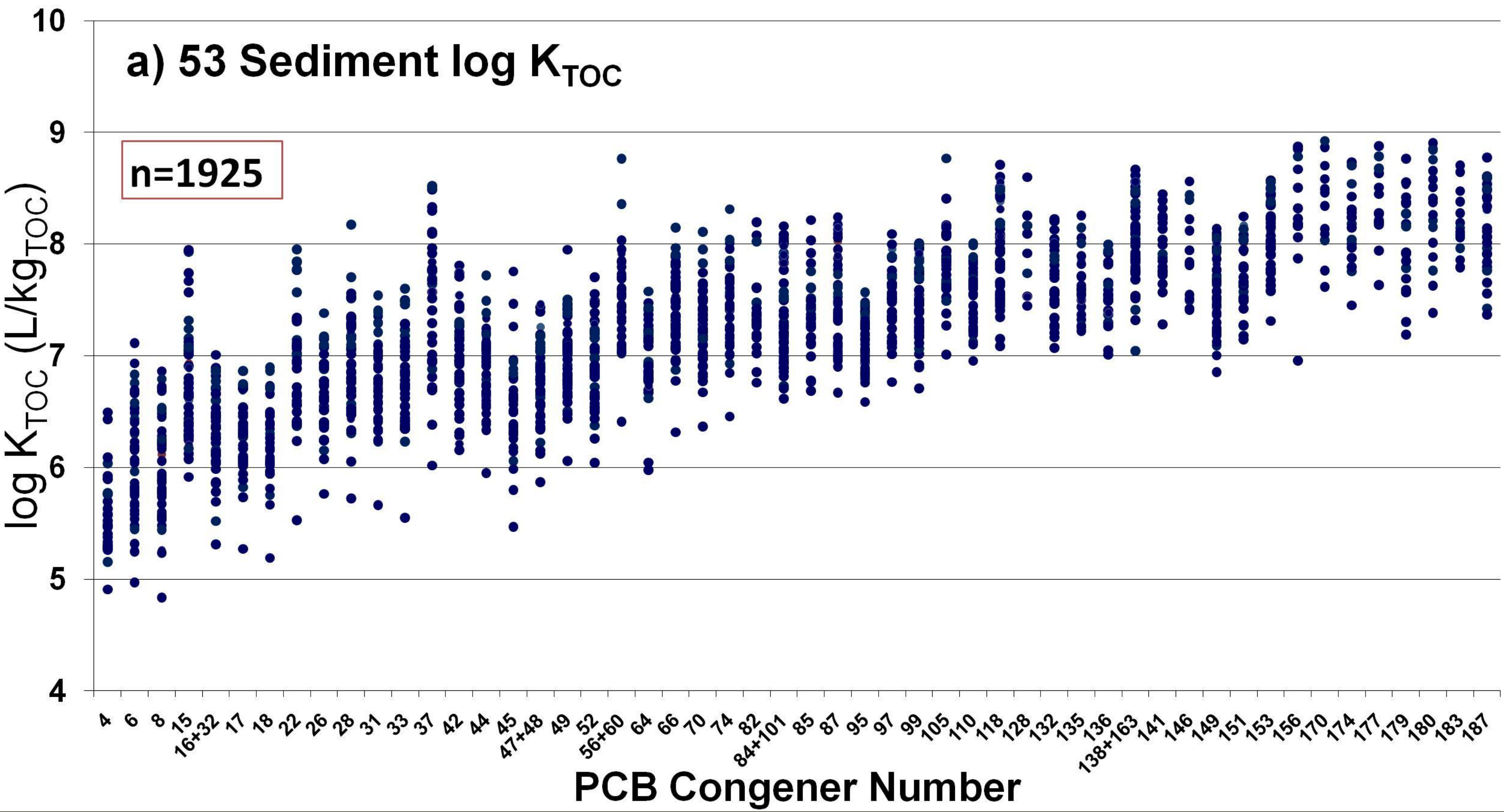
Hypothesis: Coal tar is the new octanol

Test: Real World K_{TOC} data for PCBs

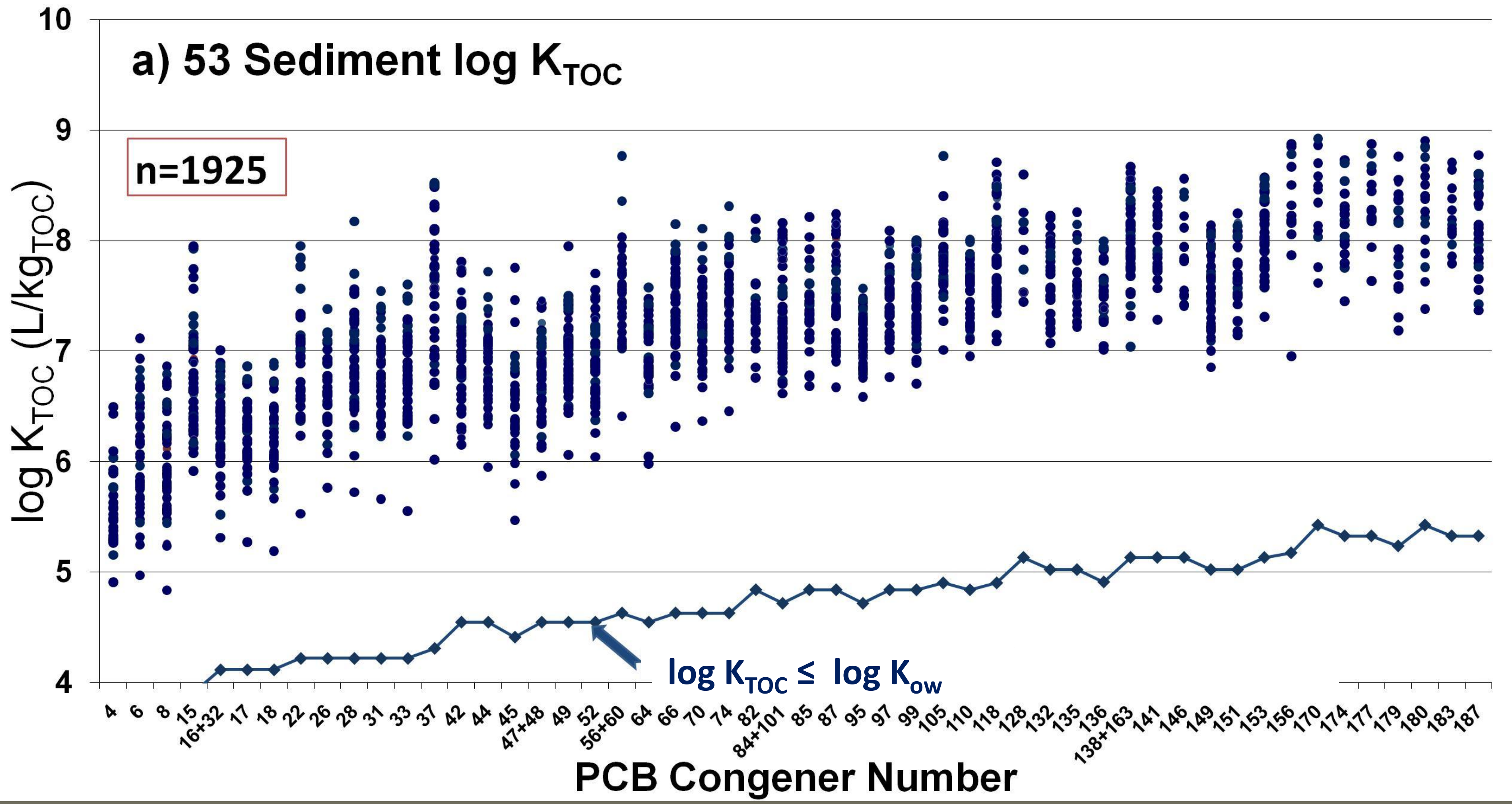


53 contaminanted sediment samples from 10 urban and rural water ways in the United States and Canada

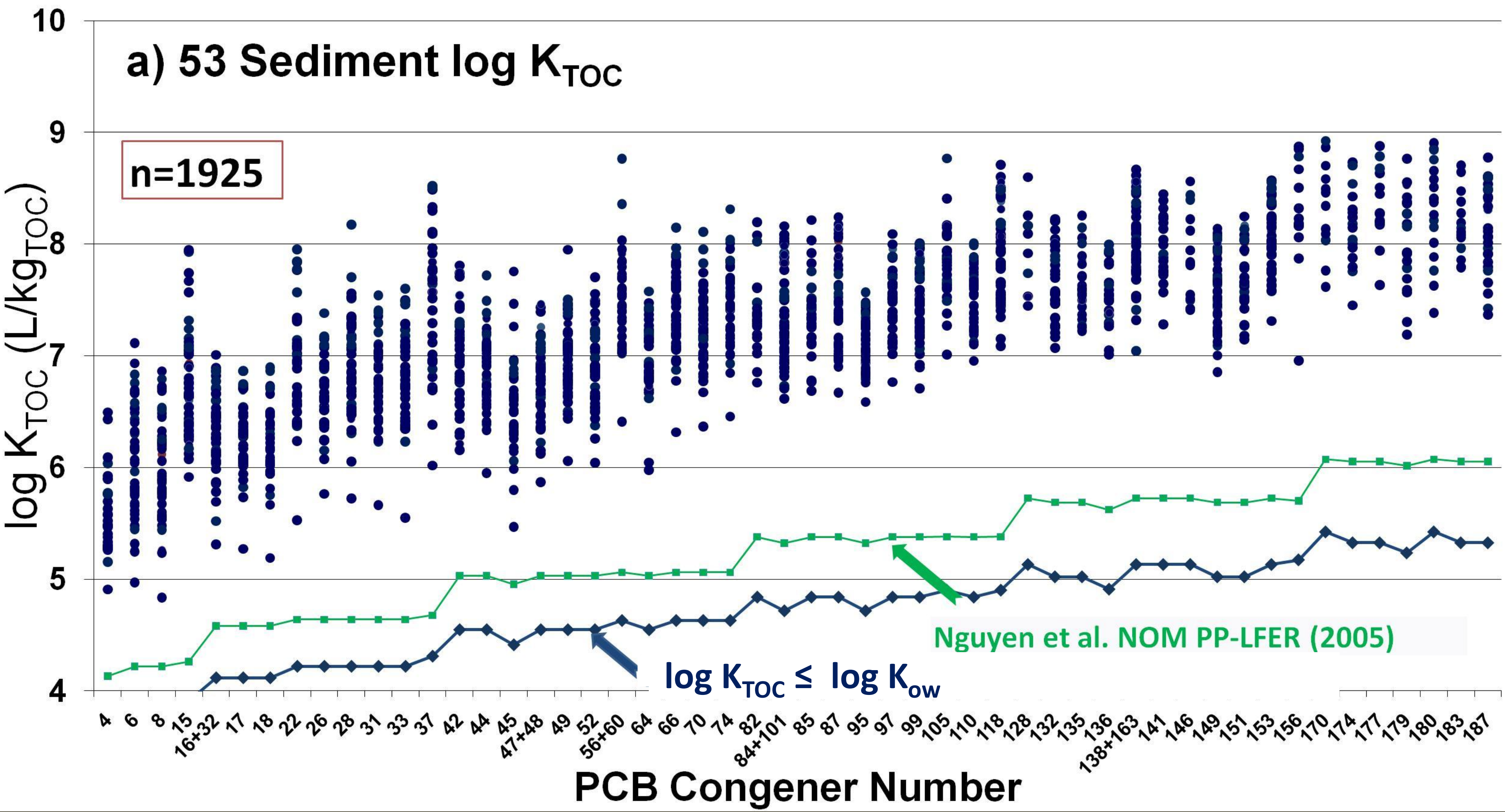
Hawthorne, Arp et al. *ES&T* 2011



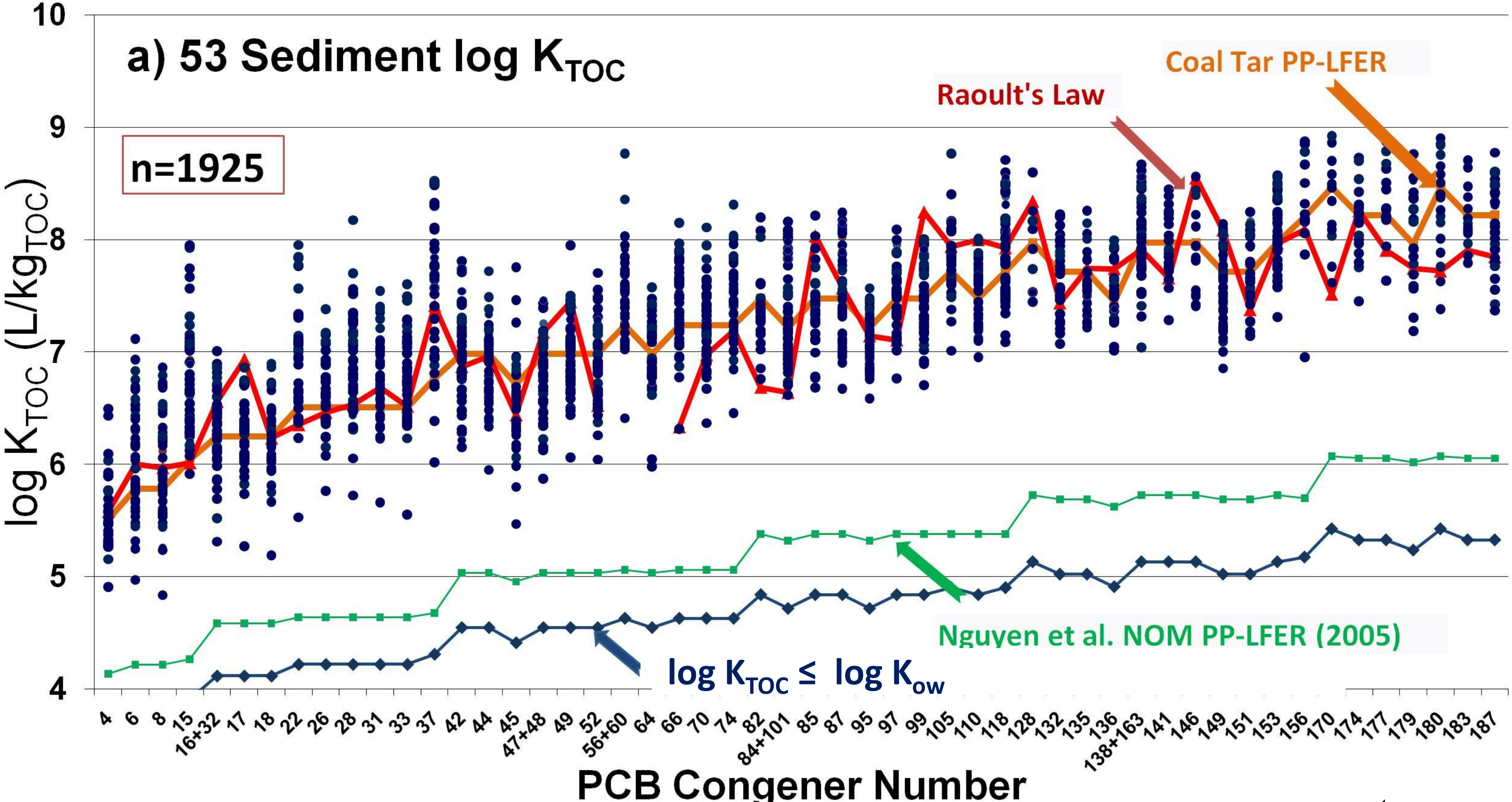
a) 53 Sediment log K_{TOC}
n=1925
log K_{TOC} (L/kg_{TOC})
10
9
8
7
6
5
4
4
6
8
15
16+32
17
18
22
26
28
31
33
37
42
44
45
47+48
49
52
56+60
64
66
70
74
82
84+101
85
87
95
97
99
105
110
118
128
132
135
136
138+163
141
146
149
151
153
156
170
174
177
179
180
183
187
PCB Congener Number



a) 53 Sediment log K_{TOC}
n=1925
log K_{TOC} (L/kg_{TOC})
10
9
8
7
6
5
4
log K_{TOC} ≤ log K_{ow}
4
6
8
15
16+32
17
18
22
26
28
31
33
37
42
44
45
47+48
49
52
56+60
64
66
70
74
82
84+101
85
87
95
97
99
105
110
118
128
132
135
136
138+163
141
146
149
151
153
156
170
174
177
179
180
183
187
PCB Congener Number



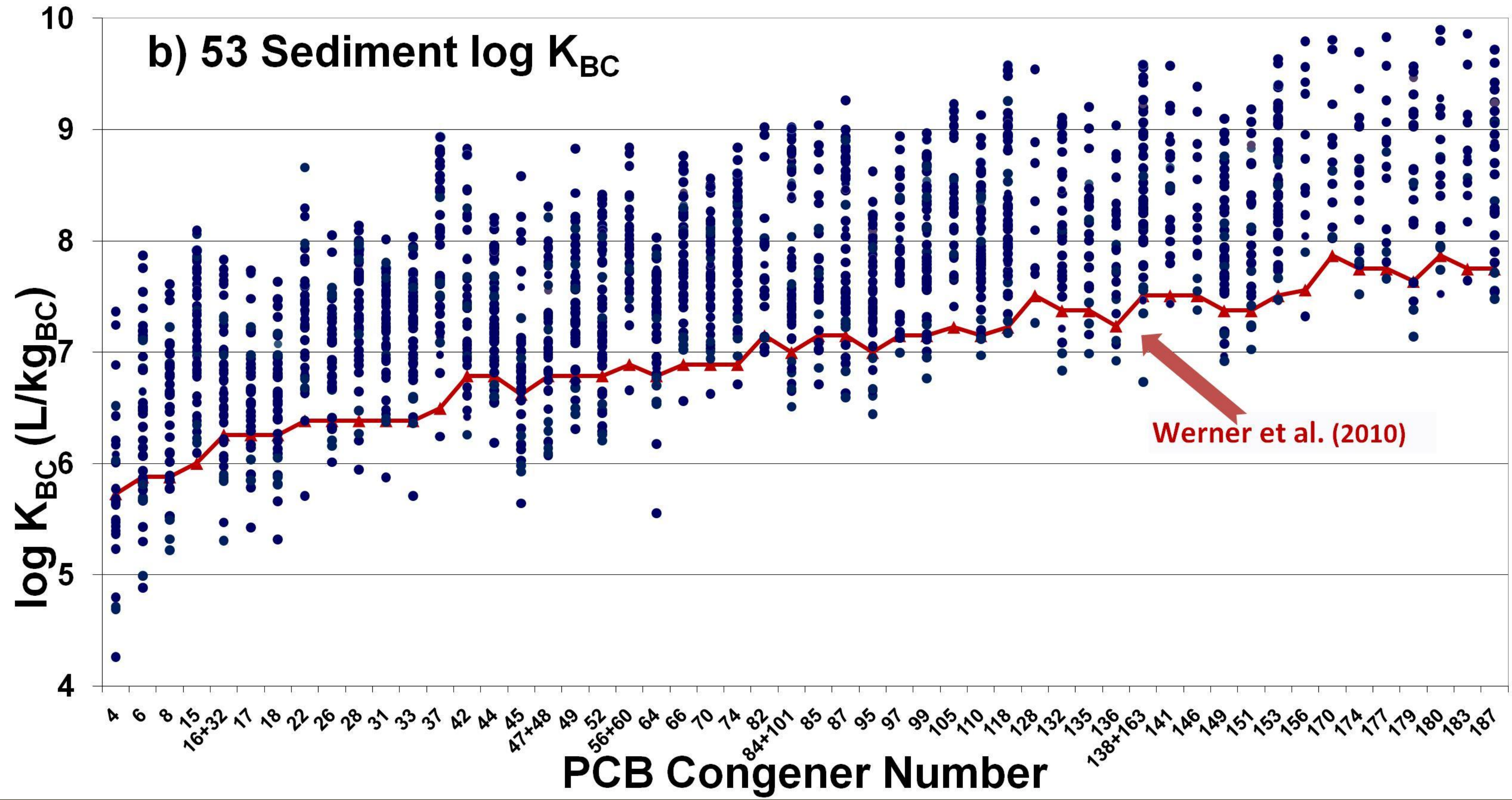
a) 53 Sediment log K_{TOC}
n=1925
log K_{TOC} (L/kg_{TOC})
PCB Congener Number
Nguyen et al. NOM PP-LFER (2005)
log K_{TOC} ≤ log K_{ow}
4 6 8 15 16+32 17 18 22 26 28 31 33 37 42 44 45 47+48 49 52 56+60 64 66 70 74 82 84+101 85 87 95 97 99 105 110 118 128 132 135 136 138+163 141 146 149 151 153 156 170 174 177 179 180 183 187



The Raoult's Law Coal Tar model:

$$\log K_{TOC,\ coal\ tar} = -\log(0.22\ S_L)$$

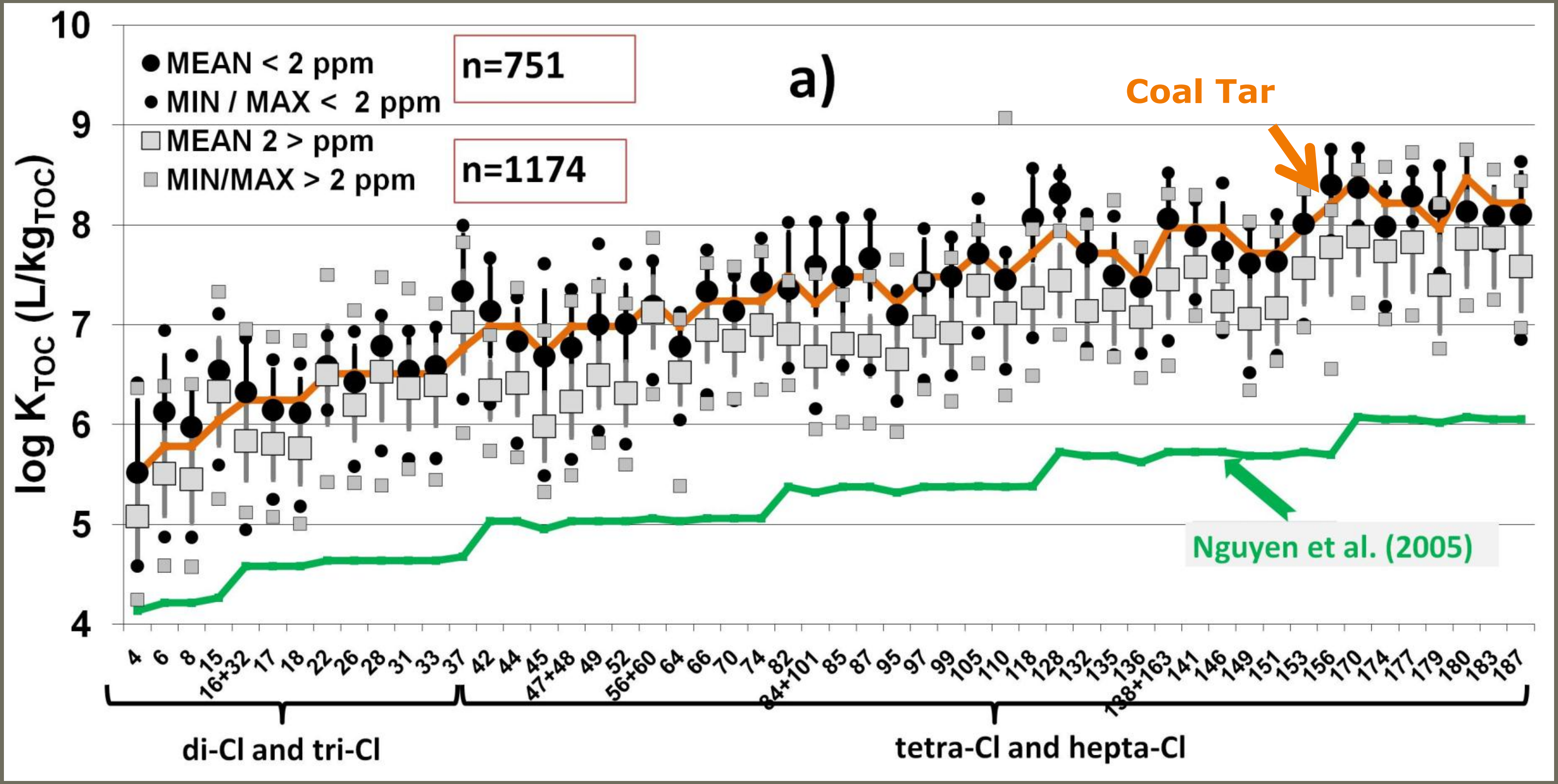
simple



$$K_D = K_{AOC}f_{AOC} + K_{BC}f_{BC}$$

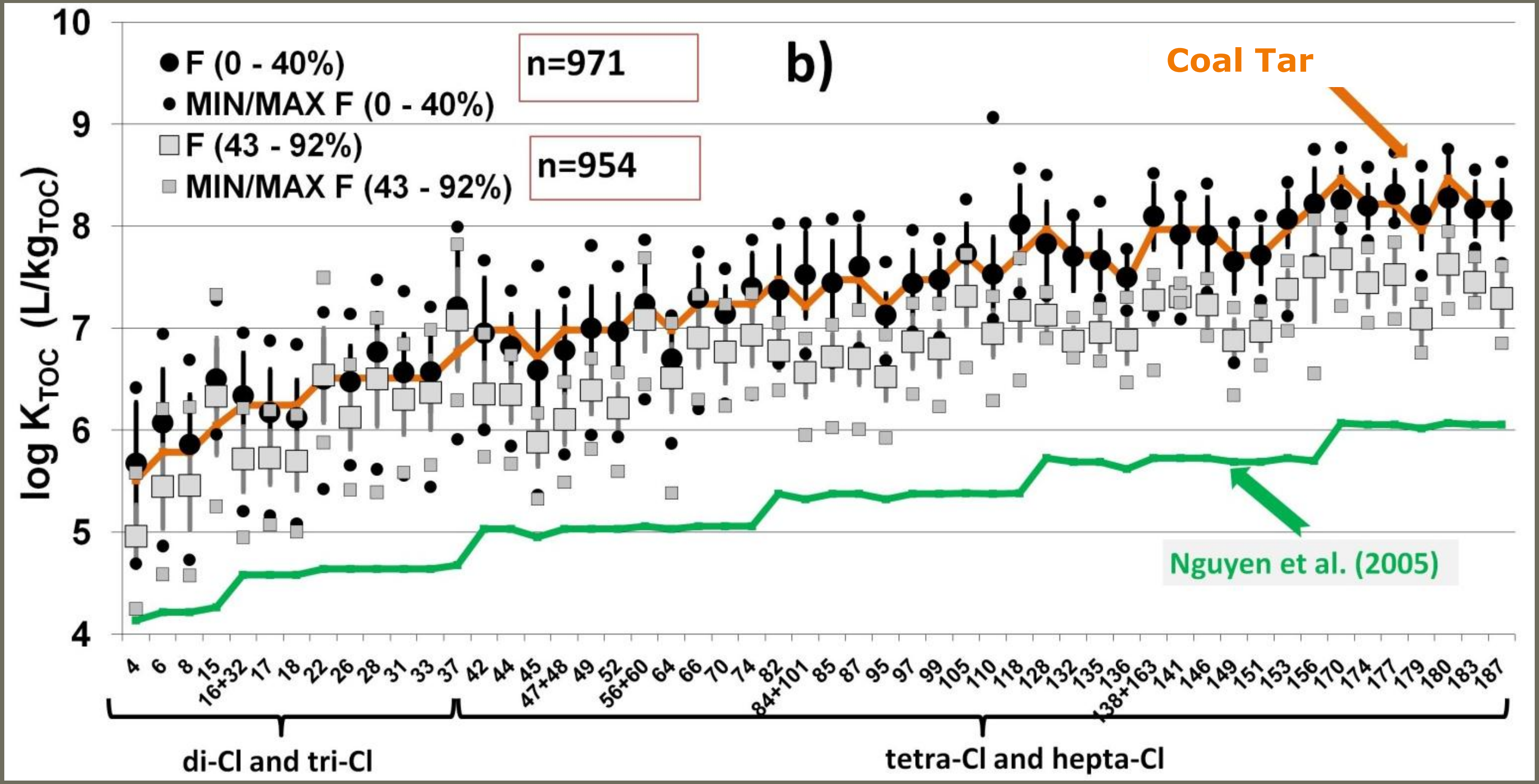
BC as defined by the CTO-375

ROLE OF CONCENTRATION?



-Low concentration follows coal-tar closely
-High concentration samples sorb less, but not significantly

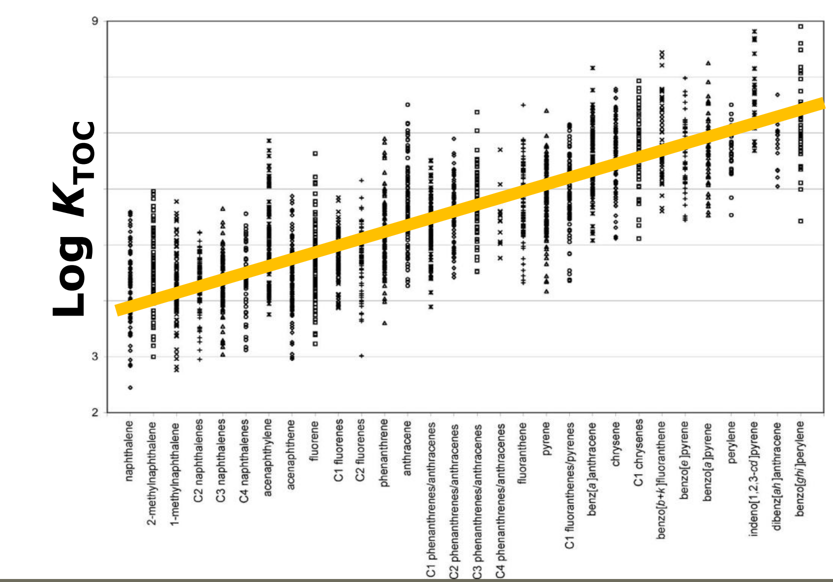
ROLE OF WEATHERING?



NON-CALIBRATED OR FITTED MODEL!
Accuracy factor 3 – 72%, factor 10 - 97%

- **Weathered sediments follow coal-tar sorption closely**

Sorbent Variability - made simple



Strategy 2: "Live with it"

-Estimate the median of field K_{TOC}

-Understand the macro (not micro) trends (e.g. concentration, weathering)

But is live with it strategy good enough to estimate toxicity?

Find out after the break….

5

Is simple good enough regarding toxicity?

Toxicity of PAHs in Pyrogenic Residues

Manufactured Gas Plant

Toxic Sediment Layer

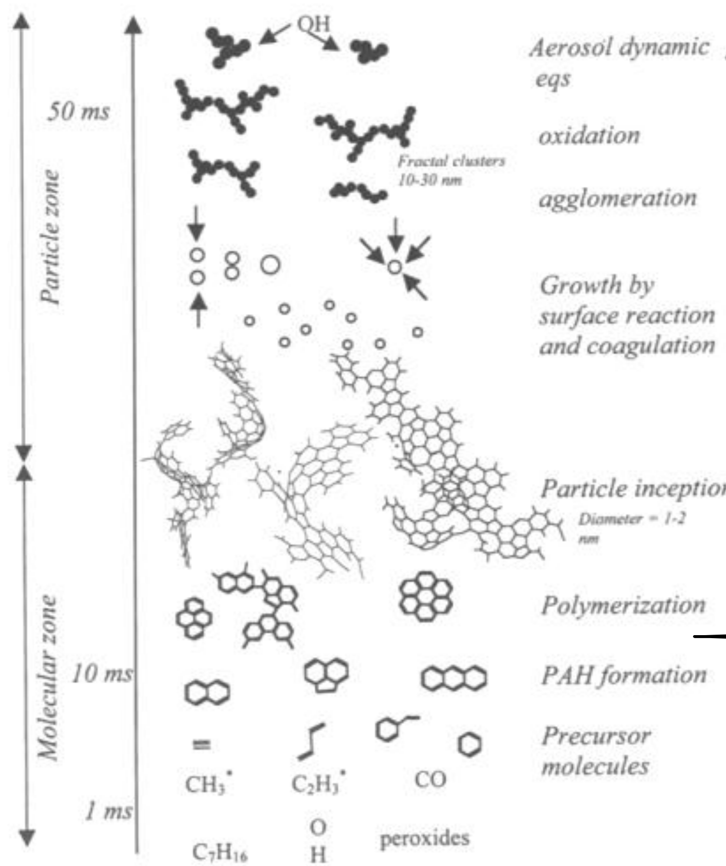
Polycyclic Aromatic Hydrocarbons

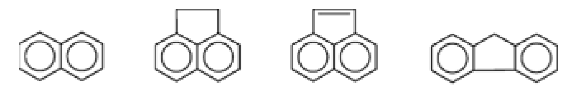
Formed by incomplete combustion processes

Tars

Black Carbon (i.e. soot)

PAH, alkyl-PAH





New list:

EPA – 34

18 parent PAHs
16 clusters of alkyl PAHs

(several hundred compounds)

EPA-16 (parents) subset of > 10,000 parent and alkyl PAHs

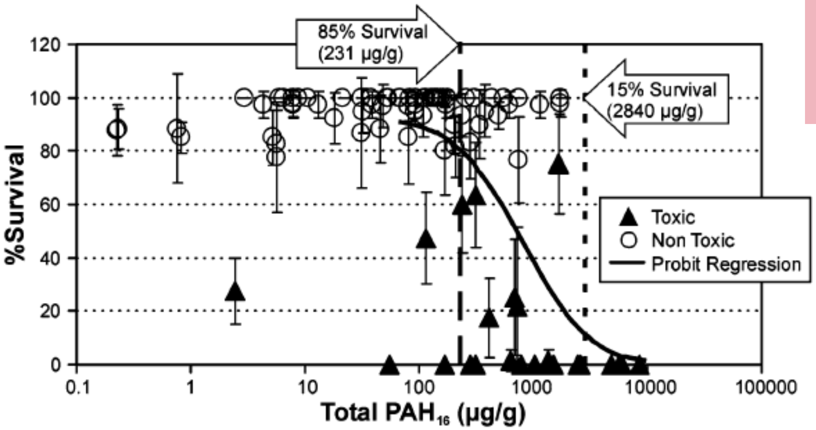
Figure Credit: Pugmire, R. J.et al. (n.d.). *Soot Formation Process*. Department of Chemical & Fuels Engineering, Department of Chemistry, University of Utah. Retrieved from http://www-acerc.byu.edu/News/Conference/2003/Presentations/Pugmire.pdf.

Toxicity: EPA-16 sediments vs EPA-34 porewater

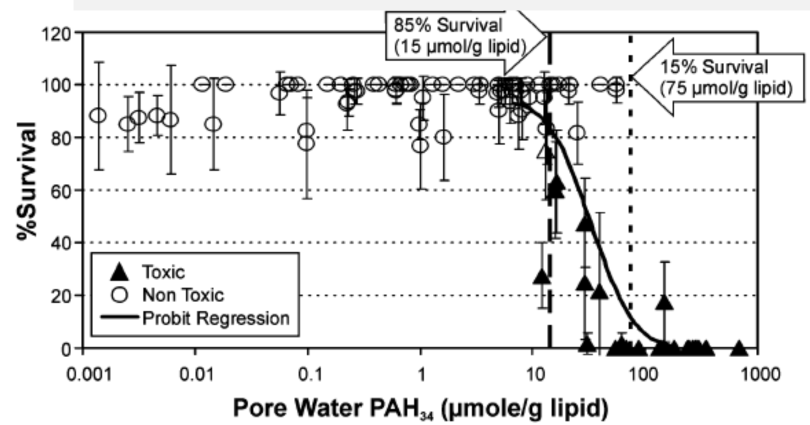
How to get there from here without measuring?

1) Test lab-based K_D models
2) Extrapolate EPA-16 to EPA-34

The "***commonly***" measured **EPA-16** in **sediments**



The "***very rarely***"measured **EPA-34** in **porewater**



Toxicity to Hyalella azteca

Photo credit:
http://en.wikipedia.org/wiki/File:Hyalella_azteca.jpg

Hawthorne et al. *ES&T* 2007

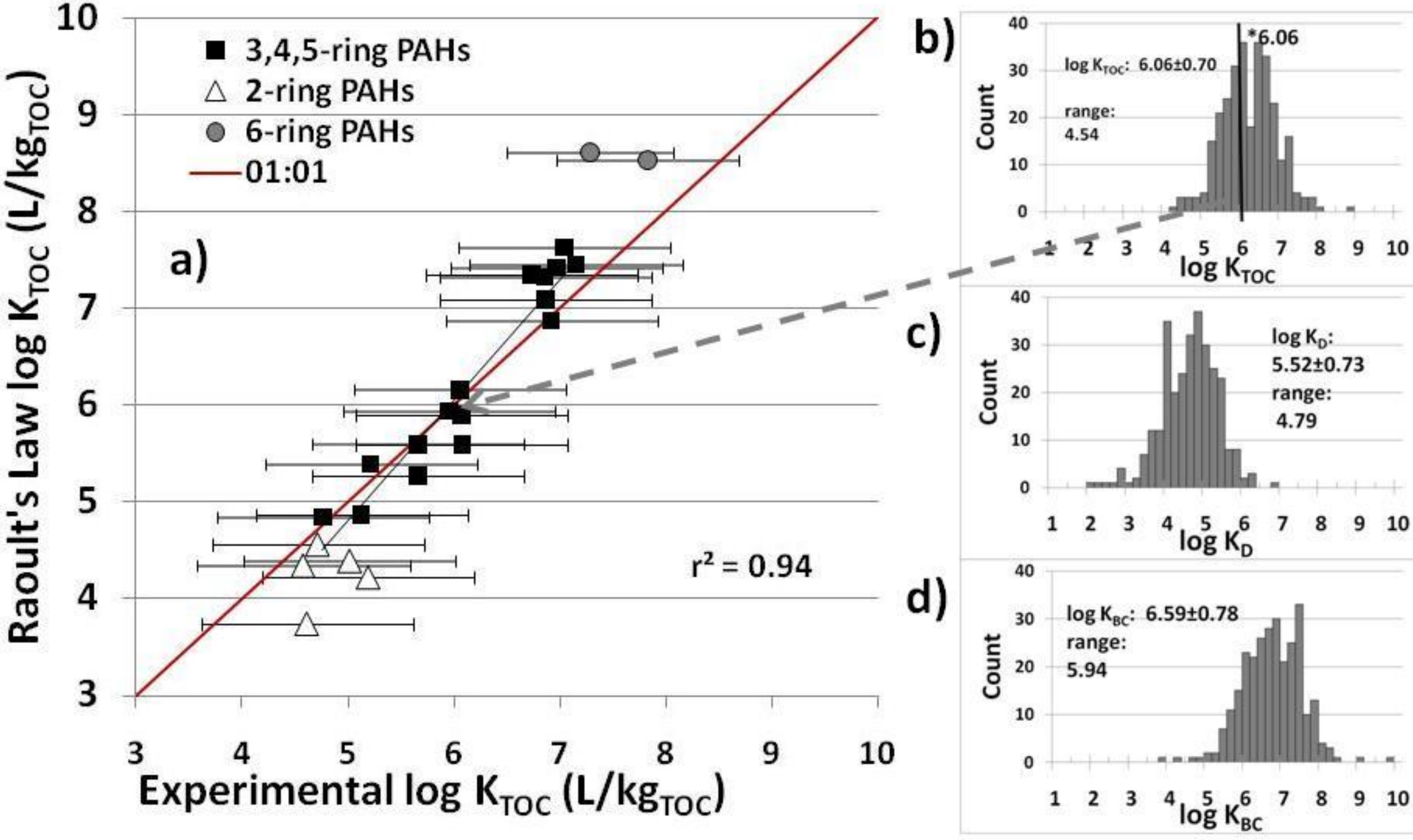
Summary of Sediment Data

Combustion residue source	No. Of Sites	No. of unique location	Conc. Range ΣEPA-34 (mg / kg)
Manufactured Gas Plant	14	256	0.3 – 30,784
Aluminum Smelters	3	59	0.2 – 3,588
Urban Harbour	2	20	39 – 2,000

For all 355 sediments have C_{sed} and C_{pw} fore EPA-34

For 211 sediments have mortality data to *H. azteca*

Arp et al. *ES&T* 2011



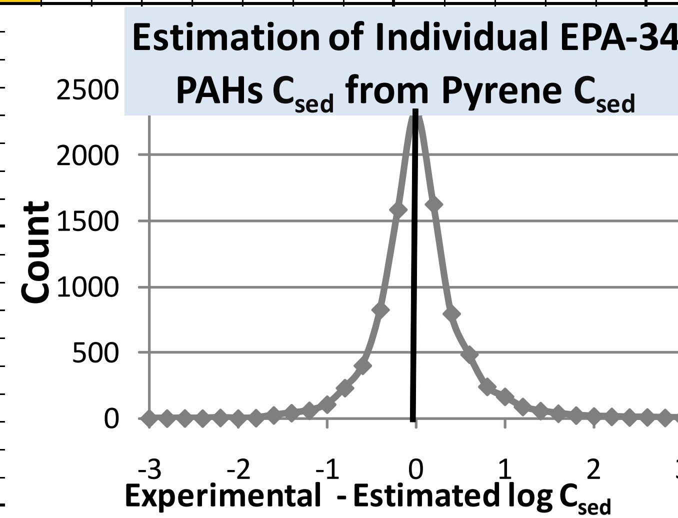
$$\log K_{TOC,\ coal\ tar} = -\log(0.22\ S_L)$$

Extrapolation via Log-Linear Regression

Correlations of all log C_{sed}, log C_{pw} via ***34 x 34 matrix***

e.g. C_{sed}: $\log \mathbf{C_{sed}} (PAH_x) = m \log \mathbf{C_{sed}} (PAH_y) + b$

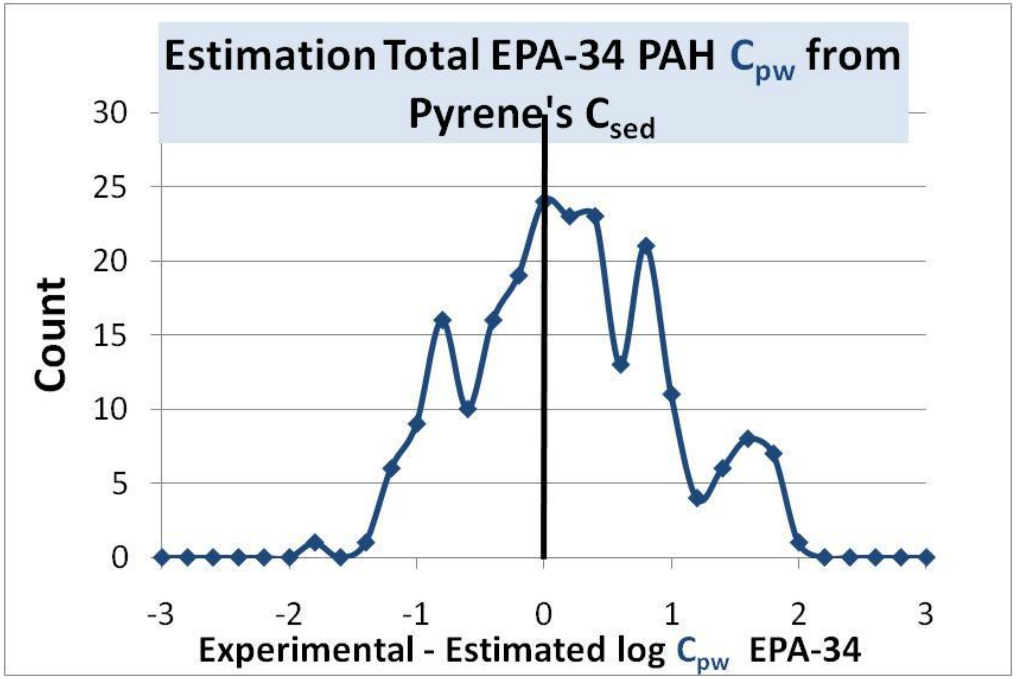
a) C_{sed} r^2		2-ring								3-ring										4-ring									5-ring					6-ring	
		NAP	1MN	2MN	C2N	C3N	C4N	ACE	ACEY	FLU	C1F	C2F	C3F	ANT	PHE	C1P	C2P	C3P	C4P	FLUA	PYR	C1FP	CHR	BAA	C1C	C2C	C3C	C4C	PER	BAP	BBKF	BEP	DAH	IND	BGP
2-ring	NAP	1.00																																	
	1MN	0.87	1.00																																
	2MN	0.96	0.87	1.00																															
	C2N	0.86	0.93	0.88	1.00																														
	C3N	0.81	0.87	0.85	0.96	1.00																													
	C4N	0.34	0.35	0.36	0.43	0.50	1.00																												
	ACE	0.79	0.91	0.80	0.91	0.88	0.37	1.00																											
	ACEY	0.66	0.62	0.67	0.70	0.73	0.37	0.51	1.00																										
3-ring	FLU	0.87	0.89	0.86	0.90	0.87	0.35	0.86	0.66	1.00																									
	C1F	0.80	0.81	0.80	0.91	0.94	0.47	0.80	0.85	0.85	1.00																								
	C2F	0.34	0.37	0.36	0.44	0.50	0.83	0.36	0.45	0.35	0.51	1.00																							
	C3F																																		
	ANT	0.80	0.76	0.80	0.83	0.85	0.43	0.71	0.88	0.87	0.91	0.46		1.00																					
	PHE	0.86	0.83	0.86	0.88	0.87	0.37	0.79	0.76	0.95	0.88	0.38		0.92	1.00																				
	C1P	0.78	0.77	0.80	0.86	0.90	0.46	0.73	0.87	0.84	0.96	0.49		0.95	0.92	1.00																			
	C2P	0.67	0.61	0.69	0.76	0.82	0.43	0.58	0.89	0.67	0.90	0.47		0.88	0.80	0.94	1.00																		
	C3P	0.43	0.40	0.47	0.55	0.61	0.56	0.42	0.58	0.42	0.62	0.65		0.58	0.51	0.64	0.69	1.00																	
	C4P	0.19	0.20	0.22	0.26	0.32	0.64	0.22	0.25	0.18	0.31	0.57		0.27	0.21	0.32	0.34	0.44	1.00																
4-ring	FLUA	0.71	0.64	0.72	0.73	0.77	0.37	0.59	0.87	0.77	0.84	0.41		0.94	0.90	0.92	0.87	0.57	0.25	1.00															
	PYR	0.71	0.64	0.72	0.73	0.78	0.40	0.59	0.90	0.74	0.85	0.43		0.94	0.86	0.94	0.91	0.61	0.30	0.97	1.00														
	C1FP	0.65	0.57	0.67	0.71	0.75	0.41	0.53	0.91	0.66	0.85	0.45		0.89	0.79	0.93	0.95	0.67	0.34	0.92	0.97	1.00													
	CHR	0.63	0.57	0.65	0.67	0.70	0.35	0.50	0.88	0.65	0.78	0.42		0.88	0.81	0.88	0.88	0.61	0.29	0.96	0.97	0.96	1.00												
	BAA	0.62	0.53	0.64	0.66	0.68	0.35	0.49	0.88	0.65	0.78	0.38		0.89	0.80	0.88	0.87	0.59	0.27	0.96	0.97	0.96	0.99	1.00											
	C1C	0.47	0.43	0.51	0.54	0.58	0.44	0.41	0.88	0.49	0.66	0.50		0.72	0.62	0.73	0.75	0.56	0.35	0.76	0.80	0.84	0.83	0.82	1.00										
	C2C	0.20	0.22	0.22	0.26	0.31	0.37	0.22	0.30	0.20	0.32	0.50		0.29	0.22	0.33	0.35	0.45	0.65	0.28	0.33	0.38	0.33	0.31	0.39	1.00									
	C3C	0.19	0.23	0.21	0.26	0.31	0.32	0.24	0.32	0.16	0.34	0.33		0.28	0.18	0.34	0.38	0.32	0.40	0.29	0.36	0.41	0.35	0.33	0.31	0.43	1.00								
	C4C																																		
5-ring	PER	0.52	0.40	0.54	0.55	0.57	0.26	0.37	0.76	0.51	0.64	0.30		0.73	0.69	0.73	0.77	0.55	0.24	0.83	0.82	0.83	0.90	0.88	0.71	0.23	0.32		1.00						
	BAP	0.58	0.48	0.61	0.62	0.65	0.36	0.45	0.87	0.60	0.75	0.38		0.84	0.77	0.85	0.87	0.61	0.30	0.94	0.95	0.95	0.99	0.99	0.84	0.34	0.37		0.90	1.00					
	BBKF	0.56	0.45	0.58	0.59	0.62	0.32	0.42	0.84	0.58	0.71	0.35		0.81	0.76	0.81	0.82	0.57	0.27	0.93	0.93	0.93	0.98	0.97	0.81	0.30	0.34		0.91	0.99	1.00				
	BEP	0.59	0.48	0.60	0.62	0.66	0.33	0.45	0.86	0.60	0.74	0.36		0.82	0.77	0.84	0.86	0.60	0.28	0.93	0.95	0.94	0.98	0.97	0.82	0.32	0.36		0.90	0.99	0.99	1.00			
	DAH	0.50	0.40	0.52	0.46	0.50	0.40	0.37	0.70	0.48	0.55	0.43		0.65	0.59	0.65	0.64	0.44	0.29	0.72	0.73	0.73	0.76	0.75	0.81	0.34	0.28		0.70	0.76	0.76	0.75	1.00		
6-	IND	0.55	0.42	0.56	0.56	0.60	0.30	0.39	0.81	0.54	0.68	0.33		0.77	0.74	0.78	0.81	0.55	0.26	0.90	0.90	0.90	0.96	0.95	0.80	0.31	0.34		0.91	0.97	0.97	0.97	0.78	1.00	
	BGP	0.56	0.44	0.58	0.58	0.62	0.33	0.41	0.82	0.56	0.69	0.35		0.78	0.74	0.80	0.83	0.58	0.28	0.92	0.92	0.91	0.97	0.96	0.81	0.33	0.37		0.91	0.98	0.98	0.98	0.77	0.99	1.00



n=8115

Predicting C_{pw} EPA-34 from C_{sed} Pyrene

$$\log C_{pw}\ (\text{EPA-34}) = m\,(\log C_{sed} / \log K_{TOC}\ (\text{Pyrene})) + b$$



$$+\ n \times \frac{C_{sed}\ (4+5+6\ \text{ring})}{C_{sed}\ (2+3\ \text{ring}}$$

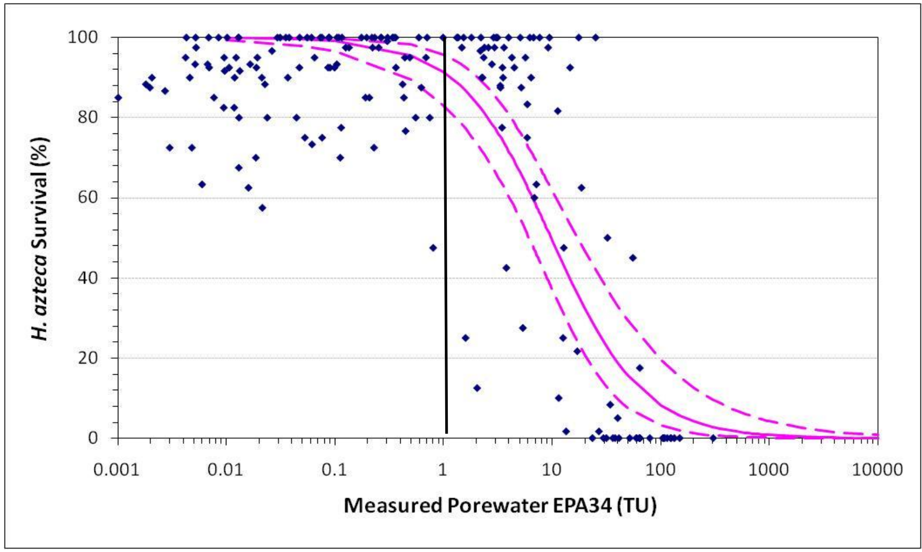
Weathering Factor

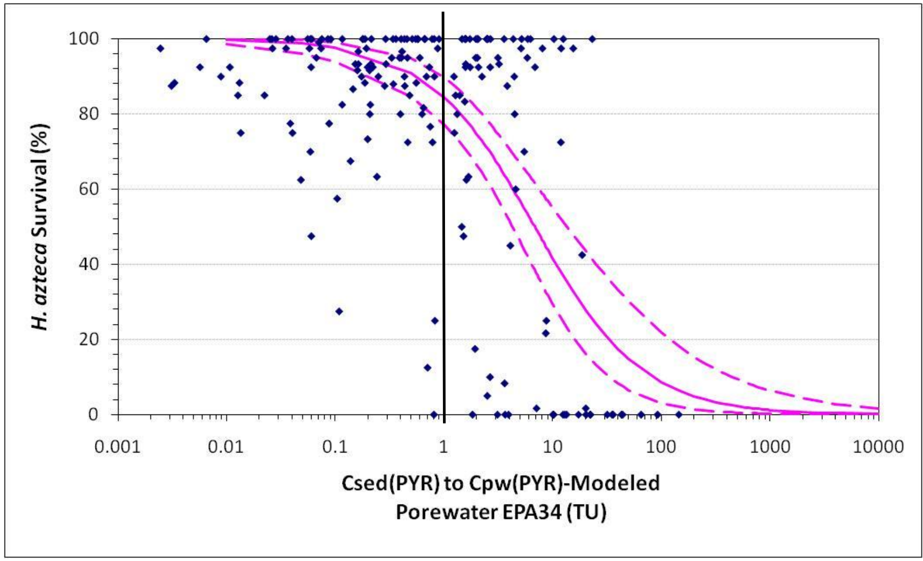
Total Data Points	219
Deviation factor 30	89%
Deviation factor 100	100%

Total Data Points	219
Deviation factor 30	95%
Deviation factor 100	100%

%Survival vs EPA-34 PW

EPA-34 PAHs	**Sensitivity** number of < 80% survival predicted as toxic	**Overall Efficiency** (correctly predicted toxic and non-toxic)	n
Measured **C_{sed}** 1TU = 22.8 mg/kg	94%	41%	211
Measured **C_{pw}** of 1 TU	91%	76%	209
Estimation 1 TU from **C_{pw}** pyrene	94%	77%	184
Estimation 1 TU from C_{sed} pyrene	**89%**	**78%**	**210**





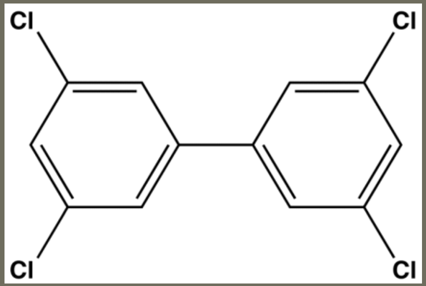
C_{sed} pyrene as good as C_{pw} of all 34 PAHs

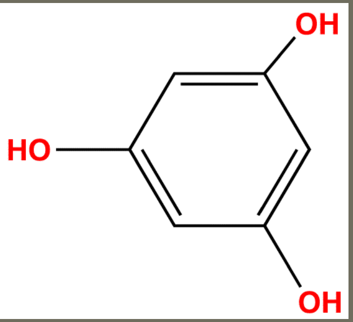
5

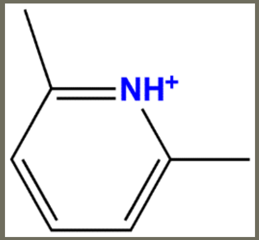
Sorbate Variability

Sorbate Variability

Non-specific (non-polar) interactions	+ specific (polar) interactions	+ pH dependant ionic interactions	+ Complex chemistry dependant on salts and O2







Apolar	Polar	Ionizable	Ionizable and Oxidizable

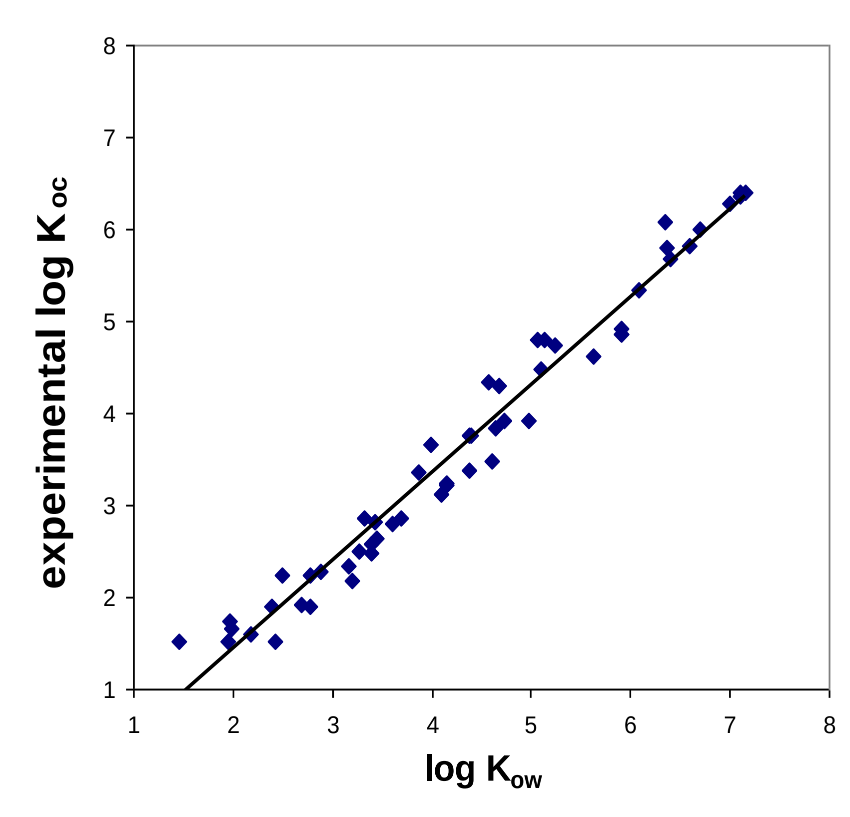
→

Simple → **Complicated**

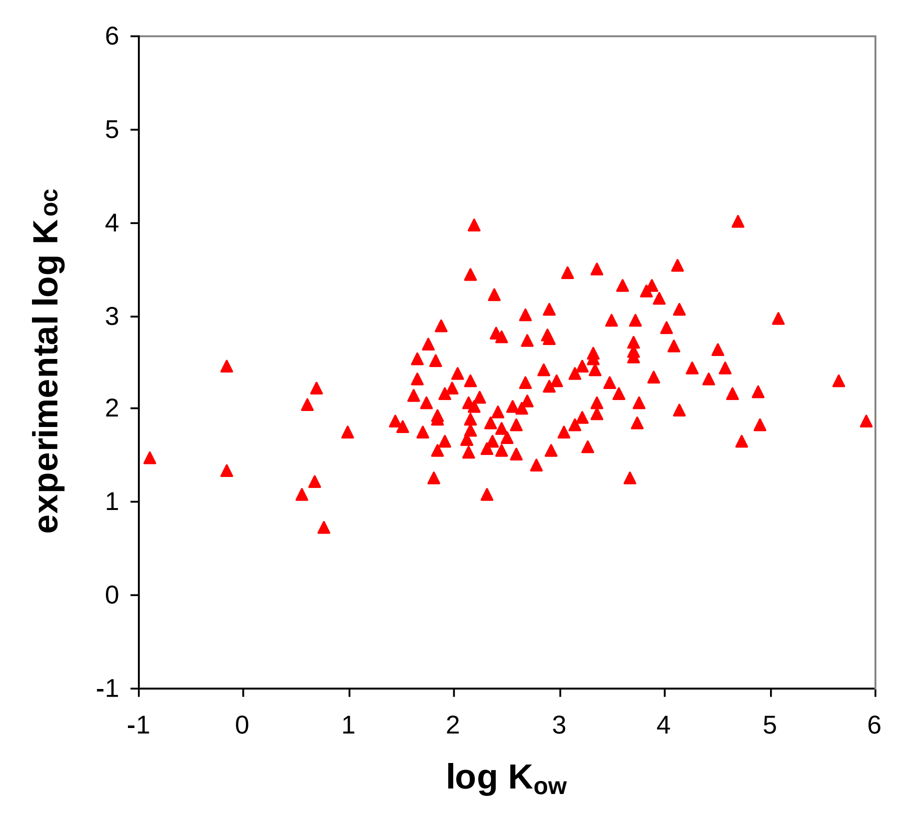
Problems with simple models # 2.

Traditional models ONLY worked with HOCs

hydrophobic organic chemicals



polar chemicals including 50 pesticides



Kai-Uwe Goss, UFZ Leipzig

Approach 1 – QSAR (EPIwin)

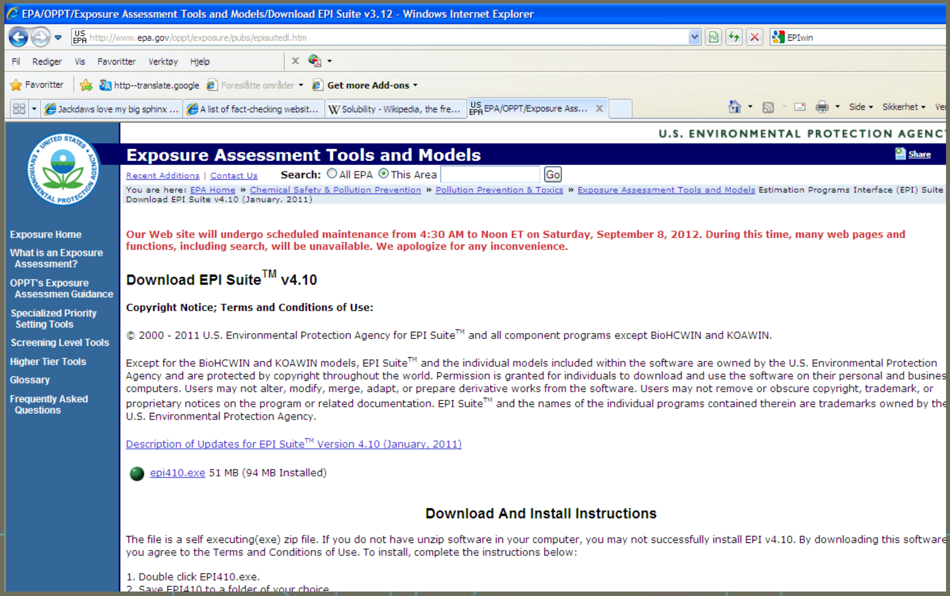
- QSAR = Qualtitative structure activity relationship (e.g. EPIsuite™)

$$K_D = a_c\, nC + a_H\, nH + a_O nO + a_{OH} nOH_C + \ldots$$

http://www.epa.gov/oppt/exposure/pubs/episuitedl.htm

Advantages
-Free
-simple to use
-designed specifically for environmental applications
-also has QSAR for toxicity.

Disadvantages
-No ions
-Varying accuracy (only as good as the data its calibrated with).



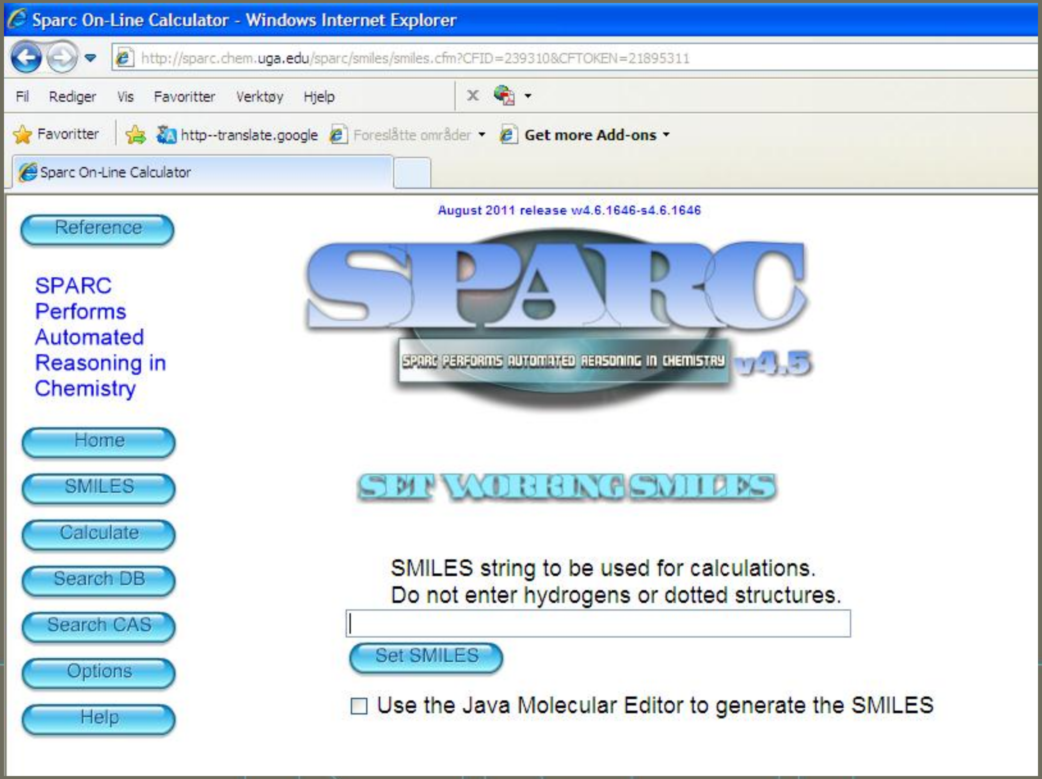
Approach 2 – Expanded QSAR (SPARC Online calculator)

Expanded QSAR – expanded QSAR that accounts for many phase changes (e.g. melting and boiling) and sorption simultaneously. Advantage - Larger calibration data set, more robust.

*www.ibmlc2.chem.uga.edu/**sparc**/*

Advantages
-Free
-Can select any sorbing phase of sorbing phase and contaminant by molecular structure
-ions (pKa)
- generally more accurate than EPIwin

Disadvantages
-harder to use,
-accuracy changes with version.



Approach 3 – PP-LFER

PP-LFER– polyparameter linear free energy relationships.

$$\log K_{TOC} = aA + bB + sS + lL + vV + c$$

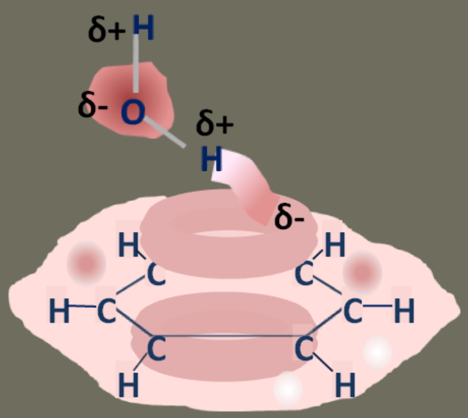
Free energy of polar interactions

Free energy of non-polar interactions

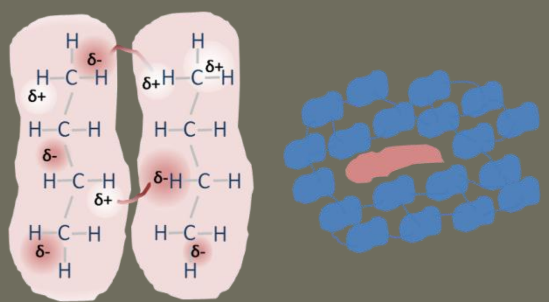
Advantages
-the most accurate
-easily done with excel.

Disadvantages
-compound parameters Needed (A, B, S, L, V)

-sorbent (soil, sed) parameters (a, b, s, l, v, c) needed – but are available!



H-bonding

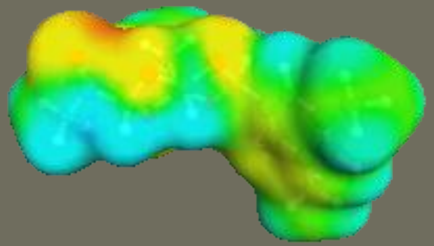


Van der Waals, cavity formation

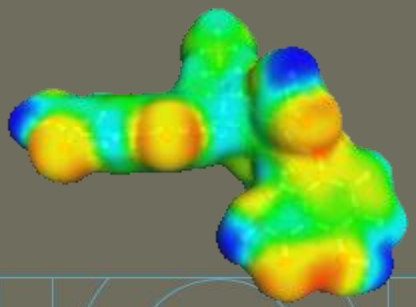
Approach 4 – Quantum Chemistry / Solvation Thermodynamics

COSMOtherm – 1) Use Quantum Chemical calcuations to find optimum structure of contaminant and soil; 2) Use solvation thermodynamics to find the log K.

http://www.cosmologic.de/index.php



Advantages
Very accurate, needs no calibration. Ions OK
Easily done with excel.

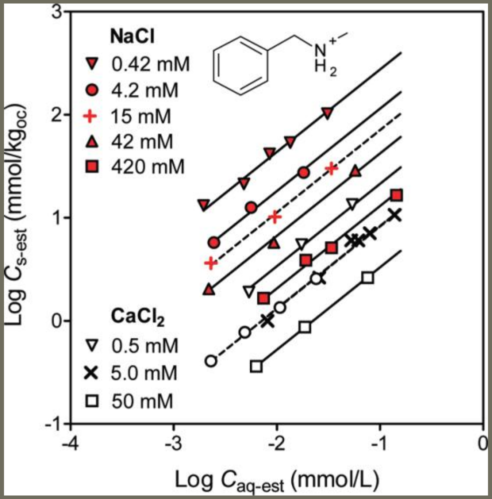


Disadvantages
Extremely complex,
Requires licenses and linux server access.

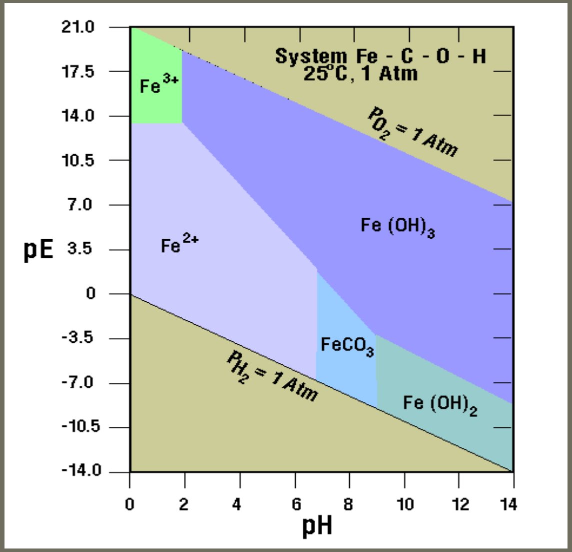
K_D ionic organic compounds and metals

Organic Ions

Droge et al. ES&T 2012



Metals



http://jan.ucc.nau.edu/~doetqp-p/courses/env440/env440_2/lectures/lec14/lec14.html

K_D depends on:

- pH
- concentration effect
- Dissolved salts
- DOM / micelle concentration

K_D depends on:

- Same as organic ions
- pE (Ev) i.e. redox

Not simple

Note for ionic compounds! K_D vs D

K –contaminant has same molecular structure in both phases

$$K_D = \frac{C_{sed}(\text{neutral})}{C_{water}(\text{neutral})}$$

$$K_D = \frac{C_{sed}(\text{PFOS})}{C_{water}(\text{PFOS})}$$

D – contaminant has multiple molecular structures in one or both phases

$$D = \frac{C_{sed}(\text{neutral + ionic})}{C_{water}(\text{neutral + ionic})}$$

$$D = \frac{C_{TOC}(\text{PFOS + PFOS}^-)}{C_{water}(\text{PFOS + PFOS}^-)}$$

$$D = \frac{C_{TOC}(Pb(OH)_2)}{C_{water}(Pb^{2+} + Pb(OH)^-)}$$

Linking sorbent and sorbate variability

Impacted sediments, non-polar compounds

- PP-LFER for coal tar

  ($\log K_{TOC} = -1.2A - 4.5B - 0.35S + 0.5E + 3.9V + 0.16$)

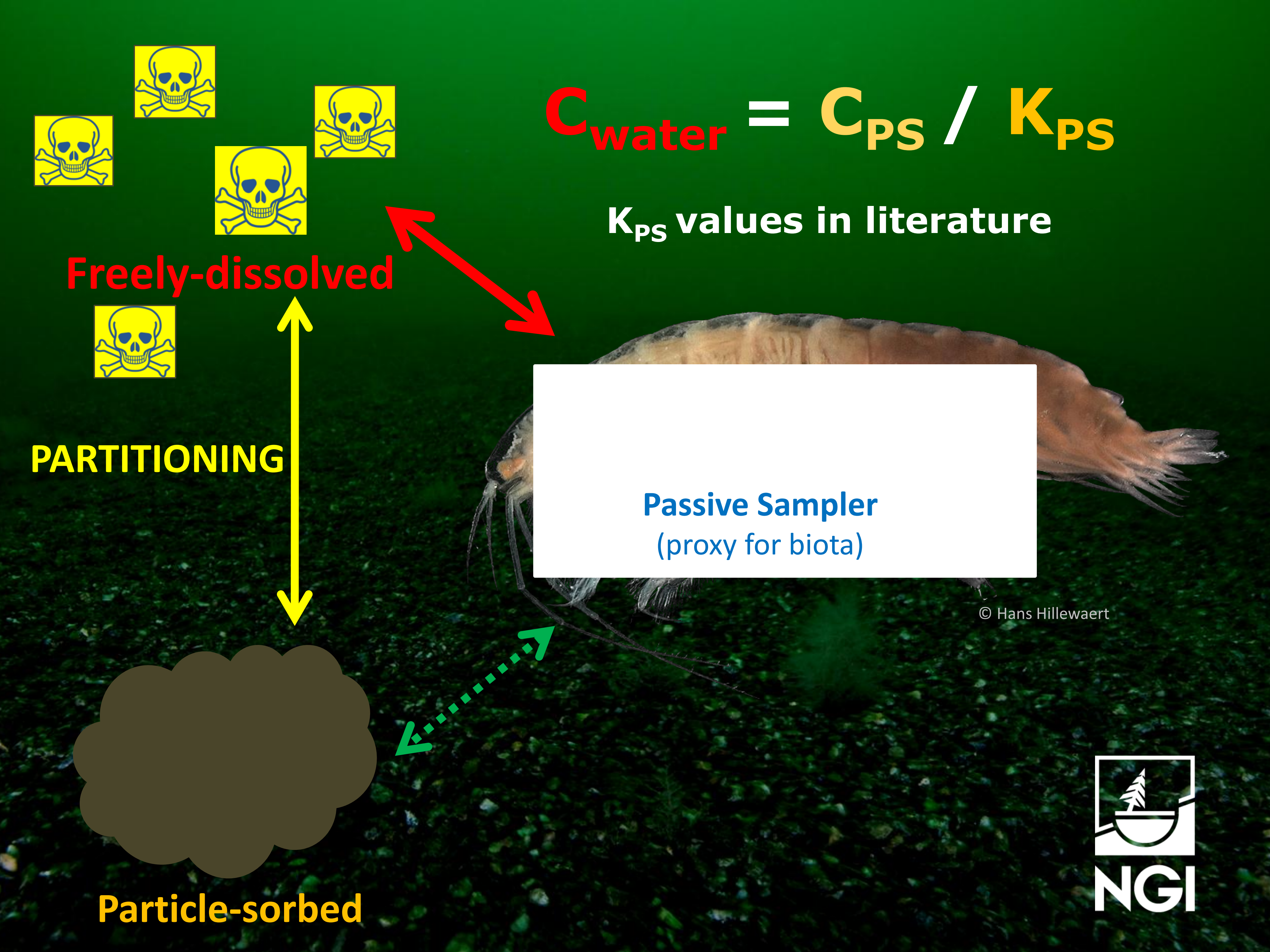
- SPARC / COSMOtherm– find S_L ($\log K_{TOC} = -\log(0.22 S_L)$)

Other sites, polar, ionic and metal compounds

- Site specific K_D value
- Average K_D from similar sites / literature (e.g. Sauve ES&T 2000 for metals)
- If none of the above, try combination of EPIwin, SPARC, PP-LFER for coal tar, soils, etc.

6

Equilibrium Passive Sampling


$C_{water} = C_{PS} / K_{PS}$
K_{PS} values in literature
Freely-dissolved
PARTITIONING
Passive Sampler
(proxy for biota)
© Hans Hillewaert
Particle-sorbed
NGI

Simple Extraction with POM passive sampler for PAH and PCB

Measuring Picogram per Liter Concentrations of Freely Dissolved Parent and Alkyl PAHs (PAH-34), Using Passive Sampling with Polyoxymethylene

Steven B. Hawthorne,[*,†] Michiel T. O. Jonker,[‡] Stephan A. van der Heijden,[‡] Carol B. Grabanski,[†] Nicholas A. Azzolina,[§] and David J. Miller[†]

Anal. Chem. 2011;83(17):6754-61

Simple method!

2 g soil + 0.2 g POM
+ 20 ml $H_2$0

shake for 1 month, extract POM
Cpw = Kpom * Cpom

$$C_{water} = C_{PS} / K_{PS}$$

K_{PS} values in literature

Passive Samplers for polar compounds

Environmental Science & Technology

ARTICLE

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Equilibrium Partition Coefficients of Diverse Polar and Nonpolar Organic Compounds to Polyoxymethylene (POM) Passive Sampling Devices

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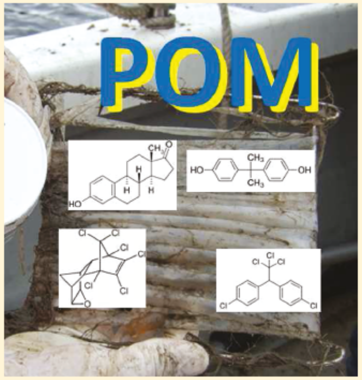
Supporting Information

ABSTRACT: Equilibrium passive samplers (EPS) based on polyoxymethylene (POM) are increasingly used for determining freely dissolved water and pore water concentrations of hydrophobic organic compounds in the environment. Unlike other polymeric materials commonly used as EPS, namely poly(dimethylsiloxane) (PDMS) and low-density polyethylene (PE), POM is a polar polymer, containing repeating H-bond accepting ether units. Thus, POM is expected to be a more sensitive EPS than PDMS and PE for polar, H-bond donating compounds, such as many hormones, pharmaceuticals, and biocides. To better characterize the sorption capacity of POM for diverse polar and apolar compounds, equilibrium POM—water partition coefficients, $K_{POM/w}$, were measured for 56 compounds, including several classes of polar compounds and organochlorine pesticides. Using this data set and literature data, various POM-partitioning models were calibrated and validated for their ability to predict $K_{POM/w}$. The best performing models tested were an Abraham descriptor based polyparameter linear free energy relationship (PP-LFER) (SD = 0.24 log units) and COSMO*thermX* (SD = 0.37 log units). The performance of SPARC (SD = 0.61 log units) and log—log correlations with K_{ow} (SD = 0.49 log units) were lower. A comparison with PDMS and PE confirmed expectations that POM exhibits a higher sensitivity for H-bond donating polar compounds than PDMS and PE do for these compounds. These findings expand the domain of chemicals for which POM can be used as an EPS sampler, and demonstrate that POM is as suitable a passive sampler for many polar organic compounds as it is for hydrophobic organic compounds.



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Conclusions

Sorption made simple

- **Option 1** – for HOCs and sediment, use the coal tar estimation method (or cite specific values)
- **Option 2** – Other contaminants or cites, use cite specific K_D values. Measure them with passive samplers!
- **Option 3** –Use average of literature values, but favour field measurements over lab measurements.
- **Option 4** – Best available model (SPARC, PP-LFER, etc.)

To end on a simple note:

Thank You!

Appendix

More information on equations presented

Single-Parameter Linear Free Energy Relationship (SP-LFER) with K_{ow}

Schwarzenbach et al. Environmental Organic Chemistry 2'nd ed. (2003)

$$\log K_{TOC} = 0.73 \log K_{ow} + 0.15$$

- K_{ow} = octanol-water partitioning coefficient
- K_{TOC} measured by spike tests (32 data for diverse PCBs from the literature)
- always predicts sorption to TOC is < sorption to octanol

Poly-Parameter Linear Free Energy Relationship (PP-LFER) for Natural Organic Matter

Nguyen et al. ES&T 2005

$$\log K_{TOC} = 0.15\,A - 1.98\,B - 0.72\,S + 1.10\,E + 2.28\,V + 0.14$$

- calibrated with 75 apolar and polar compounds from many literature sources
- K_{TOC} measured mostly by spike tests
- A, B, S refer to polar (specific) interaction properties of the molecule
- E,V refer to apolar (non specific) interaction properties of the molecule

Two Carbon Model

Werner et al. ES&T 2010

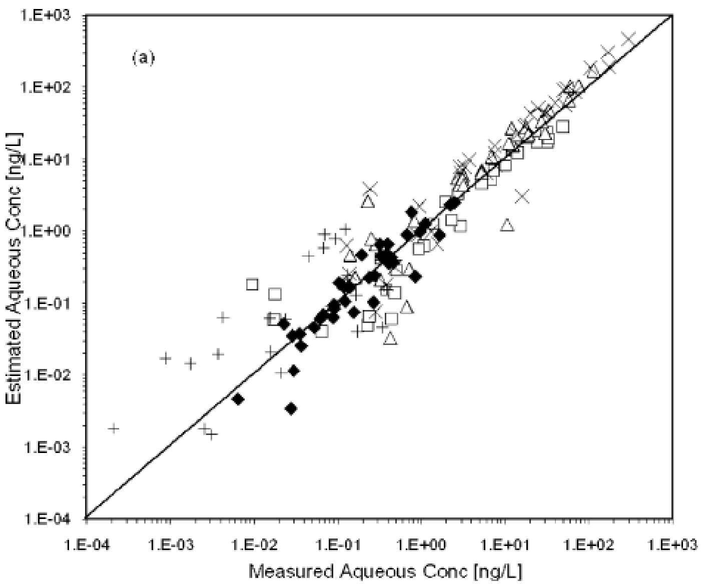
$$K_D = f_{AOC} K_{AOC} + f_{BC} K_{BC} C_{pw}^{nF-1}$$

f_{BC} = fraction of thermoresistent ”black carbon” (at 375 C)
K_{BC} = Freundlich partition coefficient to BC
nF = Freundlich parameter (= 1)
f_{AOC} = ”amorphous” organic carbon (TOC – BC)
K_{AOC} = Koc from the Schwarzenbach 2003 PP-LFER

- Calibrated with 7 historically contaminated

To get:

$$\text{Log } K_{BC} = 0.74 \log K_{ow} + 0.15$$



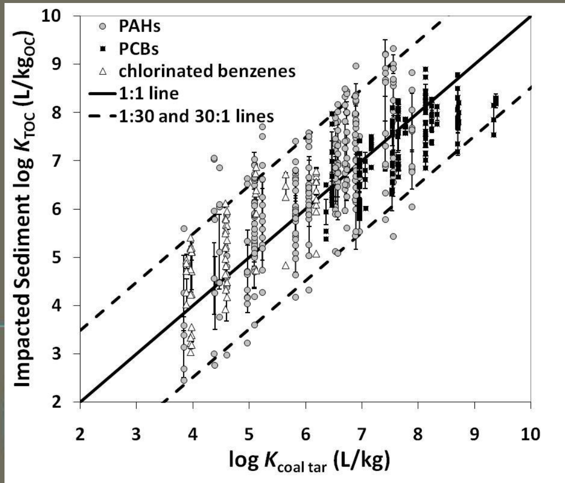
PP-LFER - Coal Tar as TOC Proxy

Arp et al. ES&T 2009

$$\log K_{TOC} = -1.2A - 4.5B - 0.35S + 0.50E + 3.9V + 0.16$$

-Validated (not calibrated!) with historically contaminated sediments for 19 references covering PAHs, PCBs, chlorinated benzenes, dioxins

- Best performing model (accuracy within factor 30)



Raoult’s Law type model

Arp et al. ES&T 2009

$$K_{TOC} = (C_L^{sat} MW_{coaltar})^{-1}$$

- C_L^{sat} = subcooled solubility
- $MW_{coaltar}$ = 0.223 kg/mol
- -**Validated** (not calibrated!) with historically contaminated sediments for 19 references covering PAHs, PCBs, chlorinated benzenes, dioxins
- Second best performing model (accuracy within factor 30)