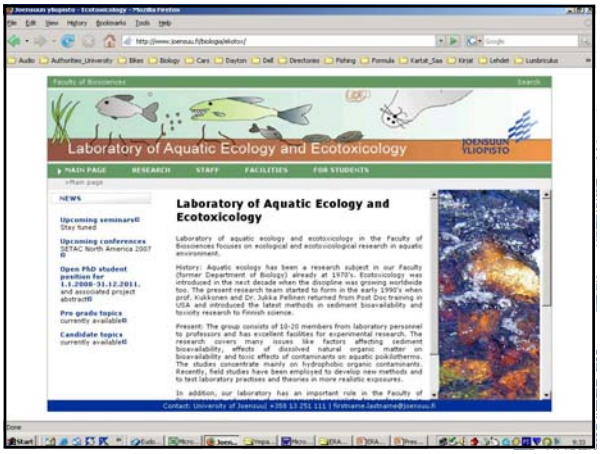
Sedimentit ja vierasaineiden kohtalo: varasto vai uhka eliöstölle?

Matti Leppänen
Joensuun yliopisto
Biotieteiden tdk



Wikipedia:

Sediment *is any particulate matter that can be transported by fluid flow and which eventually is deposited as a layer of solid particles on the bed or bottom of a body of water or other liquid.*

Freshwater sediments in Finland (GTK)

- *In large lakes 30-40% of bottom area*
- *Sediment depth ≈0 - ≥10 m*
- *Mean depth/area*
  - *> 100 km²* *0,82 m*
  - *< 0,1 km²* *1,1 m*
- *Volume*
  - *> 100 km²* *12 000 x 10^6 m^3*
  - *< 0,1 km²* *1800 x 10^6 m^3*
  - *Total* *39 000 x 10^6 m^3*

Properties of sediment

- *Particle size distribution*
  - *surface area*
- *Inorganic matter quality*
  - *clay*
- *Organic matter quality*
  - *organic carbon*
    - *soft - amorphous – rubbery, young*
    - *hard - condensed – glassy, old*
      - *soot, black carbon*

Xenobiotic persistence in sediments

Sediment:

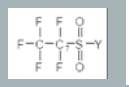
- *Lack of light (no photodegredation)*
- *Low temperature*
- *Only surface oxygenated*
- *Sorption sites (OM)*

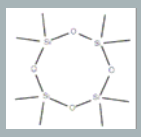
Chemicals:

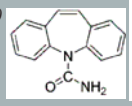
- *Hydrophobic*
- *Resistent to degredation*
- *Sorption to particles*

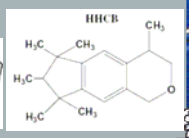
Xenobiotics –
Environmental contaminants

- *Traditional*
  - *DDT/DDE, HCB*
  - *PCBs, Dioxins*
  - *PAHs*
- *New*
  - *PBDEs*
  - *PFCAs, PFSAs*
  - *Fragrances (Musks)*
  - *Siloxanes*
  - *Pharmaceuticals ?*
  - *TBT*









Sediment contamination

- *Defalco 1967: The estuary – Septic tank of megalopolis*
- *Concern of dredging disposal in USA*
  - *management at 1970s*
- *London convention for Ocean disposal*
- *General programs for sediment contamination at 1980s*

Sediment quality assessment (1)
USEPA

- *Reference area comparisons*
- *Equilibrium partitioning*
  - *Sediment concentration that relates $C_{porewater}$ to WQC*
- *Tissue residues*
  - *Sediment concentration that results acceptable tissue concentration*

Sediment quality assessment (2)
USEPA

- *Pore water toxicity*
  - *pore water exposure toxicity quantified*
  - *chemicals responsible for tox identified*
- *Benthic community structure*
  - *alterations in community structure*
- *Whole sediment toxicity and sediment spiking*
  - *whole-sed exposures to measure toxicity*
  - *dose-response relationships when spiked used*

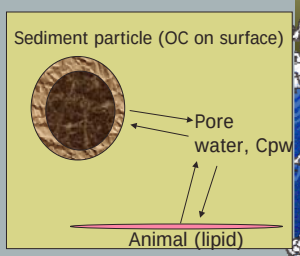
Sediment quality assessment (3)
USEPA

- *Sediment quality triad*
  - *chemical concentrations*
  - *toxicity tests*
  - *benthic community structure*

  ⇒ *search of conc. and effects relationships*

Equilibrium partitioning
EqP

- *Organic chemicals in steady state between OC and Cpw*
- *Pore water conc. dictates toxicity/ bioavailability*



(Shea 1988, Di Toro et al. 1991)

Equilibrium partitioning
EqP

- *Sediment quality criteria = C_{pw} x K_{oc}*
  - *K_{oc} = K_{ow} or K_{oc} = 0.989 x K_{ow}-0.346*
- *Sediment quality criteria = $C_{effect\text{-}conc}$ x K_{oc}*
- *Tissue concentration (lipid) = $C_{pore\ water}$ x BCF*
- *Mixtures; additivity for narcotics*

Equilibrium partitioning
Bioavailability

- *Equal activity between animal lipids and sediment OC at steady state*
- *Biota Sediment Accumulation Factor:*

$$BSAF = (C_a / f_l) / (C_s / f_{OC})$$

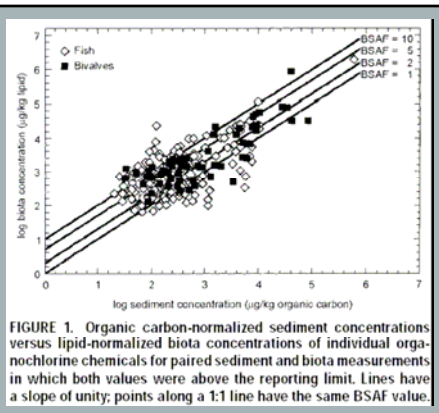


FIGURE 1. Organic carbon-normalized sediment concentrations versus lipid-normalized biota concentrations of individual organochlorine chemicals for paired sediment and biota measurements in which both values were above the reporting limit. Lines have a slope of unity; points along a 1:1 line have the same BSAF value.

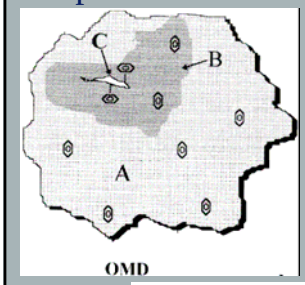
Wong et al. 2001: ES&T 35:1709

Sorption and fate of xenobiotics

- *Sorption will determine available fraction*
- *Bi- (tri) phasic (de)sorption*
- *Unexplained phenomenon:*
  - *slow sorption and concentration dependence*
  - *kinetic hysteresis*

Pignatello & Xing 1996: ES&T 30:1

Sorption and fate of xenobiotics



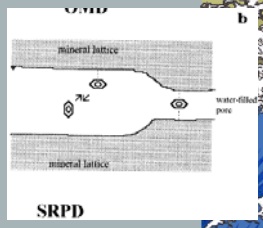
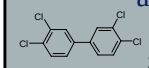
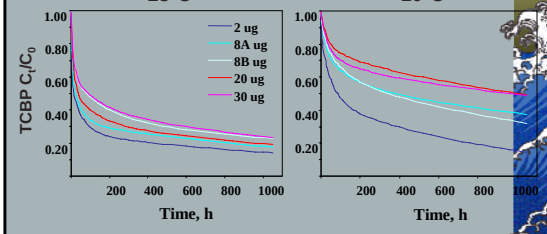


FIGURE 2. Schematic of two models for slow sorption. (a) Organic matter diffusion (OMD), illustrating diffusion through a rubbery phase A, diffusion through a more condensed glassy phase B, and adsorption in a "Langmuir site" C (see text). (b) Sorption-retarded pore diffusion (SRPD). Retardation by rapid-reversible sorption to pore walls, and "enhanced adsorption" in pores of very small diameter due to interaction with more than one surface.

Desorption curves and applied model (PCB-77)

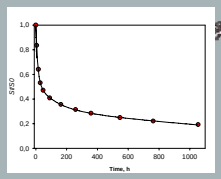




$$C_t / C_0 = F_{fast}(e^{-k_{fast}*t}) + F_{slow}(e^{-k_{slow}*t}) + F_{veryslow}(e^{-k_{veryslow}*t})$$

Desorption and bioavailability

- *Equilibrium partitioning theory revised:*
  - *equal activity between animal lipids and sediment OC at steady state*
  - *not all of the sediment-associated chemical is available*
  - *uptake is kinetically limited due to desorption*



$$BSAF = (C_a / f_l) / ((C_s / f_{OC}) \times F_{rapid})$$

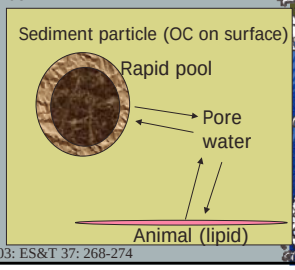
EqP Revised: Kraaij et al. 2003: ES&T 37: 268-274

Pore water and bioavailability

- *Equilibrium partitioning theory revised:*
  - Steady state body burden is a result of bioconcentration:

$$C_b = BCF \bullet C_p$$

$$BSAF_{Porewater} = \frac{BCF \bullet (C_{S,OC} / K_{OC})}{C_{S,OC}}$$



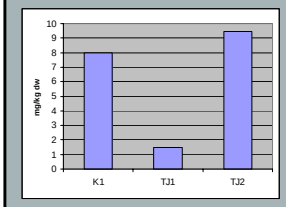
EqP Revised: Kraaij et al. 2003: ES&T 37: 268-274

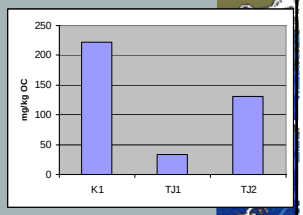
A case study

PCBs in Kernaalanjärvi sediments

- *Tervajoki Oy Papermill (Janakkala)*
  - *PCB oils (Clophen, Aroclor…) 1956- 1984*
- *Study*
  - *PCB (29 congeners) concentrations; 3 sites*
  - *Lab exposed oligochaetes & field collected Chironomidae*
  - *Trad. BSAFs vs. desorption corr. BSAFs*

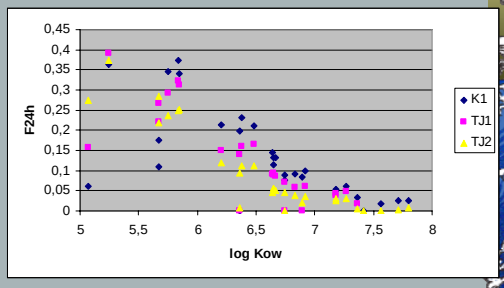
PCB concentrations



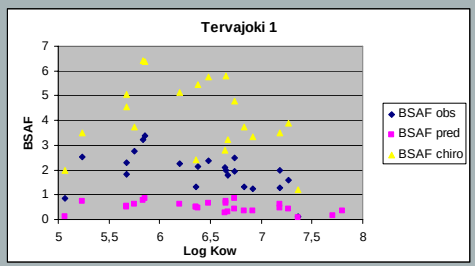


K1 = Kernaalanjärvi
TJ1 = Tervajoki 1
TJ2 = Tervajoki 2

Desorption, fast fraction



Bioavailability
BSAFs



Conclusions
Chemist's view

- *Environmental fate (incl. bioavailbility) of organic xenobiotics is based on partitioning phenomenon determined by sorbent and sorbete properties*

Conclusions
Biologist's view

- *Environmental fate (incl. bioavailbility) of organic xenobiotics is modified with biological processes*
  - *feeding behavior & digestive fluids*
  - *life habit*
  - *life cycle*

Good science

- *Input from chemistry:*
  - *Sorption/desorption major factors affecting bioaccumulation and accessible fraction*
  - *Pore water concentration is a good parameter for estimating bioconcentration/bioaccumulation*
- *Input from biology:*
  - *Bioavailable (accessible) fraction varies from case to case*
  - *Is needed for estimating variance and determining safety factors in risk assessment*

POPs & sediment

- *Sediments are a storage but also a source for biota*
- *Risk assessment/management*
  - *Fast desorbing fraction is a key*
  - *Remediation*
    - *capping vs. dredging*