Desorption of contaminants during resuspension

An important process but hard to model

a short (over)view by Dick Bakker

Climate change and sediments

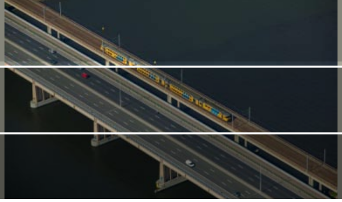
- Climate change (probably) leads to more frequent extremely high river discharges in winters;

- With extremely high river discharges large amounts of (historically) contaminated sediments can be remobilized and deposited downstream, in groyne fields, floodplains or other flooded areas.
  - During transport peak contaminant concentrations can be well above LC50 values for aquatic species;
  - Downstream deposited sediment can affect ecology, cattle, humans;

- Report European Environment Agency ‘Mapping the impacts of natural hazards and technological accidents in Europe ‘:
  - 1998-2009: 213 floods, causing 1126 fatalities and € 52 billion economic losses (of which Elbe basin (2002) € 20 billion);
  - No mention of ‘chemical danger’ due to contaminated sediments;

- (General?) trend: Water quantity (safety) seems more important than water (and sediment) quality.

Statement 1



- River basin management should take into account that extreme river discharges and flooding may present not only physical but also ‘chemical danger’, resulting from the remobilization of historically contaminated sediments.

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Desorption during resuspension

- Several experimental studies have shown that resuspension of contaminated sediment results in:
  - not only high total contaminant concentrations in water;
  - but also high dissolved contaminant concentrations.

- (Initial) dissolved contaminant concentrations are sometimes much higher than predicted by equilibrium partitioning theory;

- Both heavy metals and organic pollutants can show this behaviour, but not always;

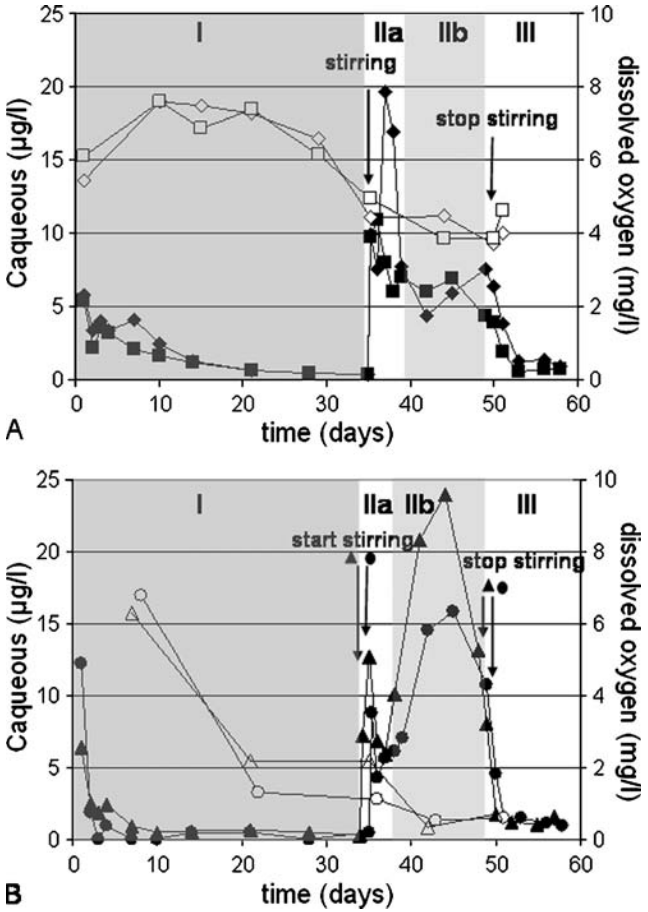
- It is hard to predict (model) the desorption of contaminants during resuspension.

Examples organic pollutants (1)

- De Weert *et al.* (2010)[1]:
  - Dissolved mass transfer of (field-aged) nonyl-phenol from sediment (0,3 µg d^{-1}) increased 100-fold (27-29 µg d^{-1}) in first 8 hours after resuspension;
  - Produced explanation:
    - > Nonyl-phenol from pore water of sediment;
    - > Increase of exchange area (195x for 70 µm and 680x for 20 µm particles);
  - Under resumed settling conditions the dissolved NP concentrations decreased again and were slightly higher than prior to resuspension.

[1] De Weert, J., M. Streminska, A. Langenhoff, H, Rijnaarts, 2010. Nonylphenol mass transfer from field-aged sediments and subsequent biodegradation in reactors mimicking different river conditions. Journal of Soils and Sediments, vol. 10, pp. 77-88.

From De Weert *et al.* (2010)



<u>Upper graph A: sterile conditions</u>
Aqueous nonylphenol concentrations (left Y axis, *filled symbols*) and dissolved oxygen concentrations (right Y axis, *open symbols*). Reactors 1 and 2.

<u>Lower graph B: non sterile conditions</u>
Aqueous nonylphenol concentrations (left Y axis, *filled symbols*) and dissolved oxygen concentrations (right Y axis, *open symbols*). Reactors 3 and 4. Stirring in reactor 4 started 1 day before reactor 3

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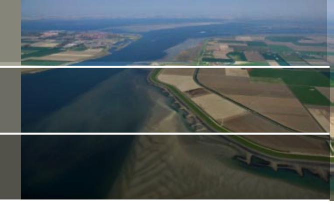
Statement 2

- Resuspension of contaminated sediment can lead to much higher initial dissolved contaminant concentrations than predicted by equilibrium partitioning theory.

Examples organic pollutants (2)

- <u>Feng *et al. (2007)* [2]*:*</u>
  - • 16 PAHs concentration in resuspended particles decreased 4-fold (from 6000 µg kg^{-1} to 1600 µg kg^{-1}) with increasing shear stress applied. Individual PAHs showed similar trend;
  - Produced explanation:
    - > Entrainment of larger size, less contaminated, particles;
    - > Redistribution (desorption) to water phase;
  - Dissolved PAH concentrations showed significant differences depending on molecular weight and applied shear stress:
    - > Naphtalene conc. increased 2-fold
    - > Acenaphtene and Fluorene conc. remained equal;
    - > Phenantrene, Anthracene, Fluoranthene and Pyrene conc. decreased by 30%

[2] Feng, J, Z. Yang, J. Niu and Z. Shen, 2007. Remobilization of polycyclic aromatic hydrocarbons during the resuspension of Yangtze River sediments using a particle entrainment simulator. Environmental Pollution, vol. 149, pp. 193-200.

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Examples organic pollutants (3)

- Birdwell *et al. (2007)* [3]:
  - One of the most used empirical models to obtain release rates is the Two-compartment First-Order Rate Constant (TFRC) model. This model contains a k_{fast} and a k_{slow} to describe desorption;
  - In a large dataset (11 studies, 34 sediments), the authors tried to find relations between k_{fast} and k_{slow} and:
    - > aqueous solubility, $\log K_{oc}$, aqueous diffusivity and f_{oc};
    - > data subsets based on chemical type, geosorbent, field/lab contamination and lab technique (Tenax vs. XAD);
  - Despite wide range of properties, k_{fast} centers on mean value of 5 d^{-1} (1.7-7.2 d^{-1}) and k_{slow} on mean of 0.03 d^{-1} (0.02-0.05 d^{-1})

[3] Birdwell, J., R.L. Cook and L.J. Thibodeaux, 2007. Desorption kinetics of hydrophobic organic chemicals from sediment to water: A review of data and models. Environmental Toxicology and Chemistry, vol. 26, no.3, pp. 424-434.

From Birdwell *et al.* (2007)

J. Birdwell et al.

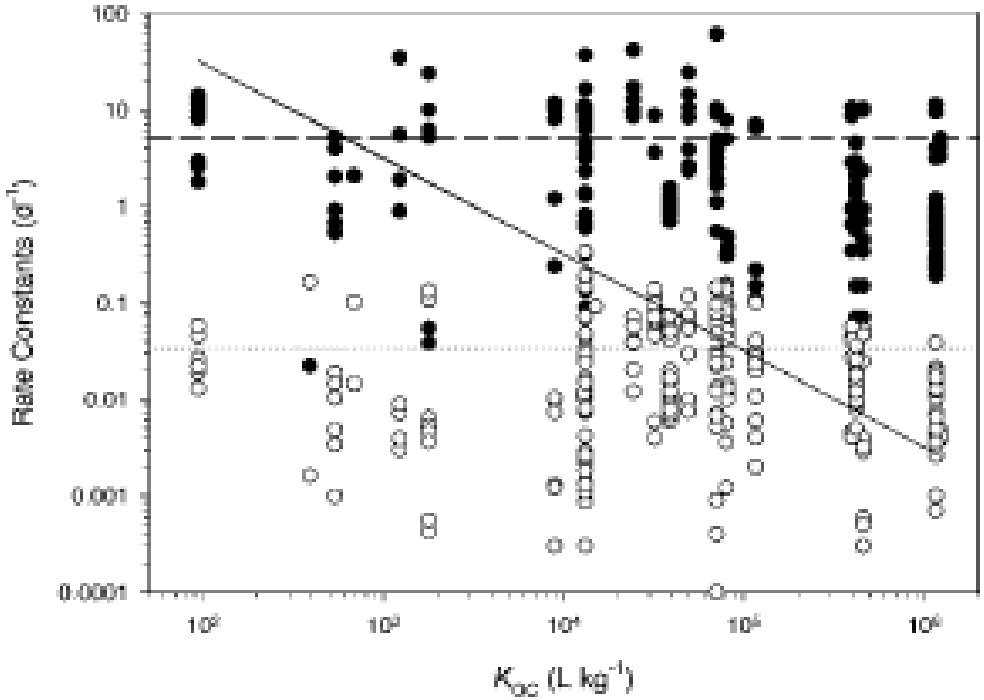

Fig. 2. Correlation plot of fast (●) and slow (○) desorption rate constants with contaminant organic carbon-water partition coefficients. Solid line represents the theoretical model (Eqn. 2) adjusted to $k = 0.032\ d^{-1}$ at $K_{OC} = 10^5$ L kg^{-1} with $\varepsilon = 0.5$, $f_{OC} = 0.05$, and $\rho = 1.65$ g cm^{-3}. Dashed and dotted lines represent average k_{Fast} and k_{Slow} values, respectively.

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Examples heavy metals (1)

- Skei (1992)[4]*:*
  - Dissolved flux rates of heavy metals from contaminated sediment increased 2-128 fold after resuspension caused by hermit crabs (bioturbation);
    - > Hg 128x, Cu 28x, Pb 10x, Zn 2.2x, Cd 0.7x
  - Produced explanation:
    - > Release of pore water;
    - > Desorption of metals from resuspended particles;
  - Flux rates not proportional to metal content in sediment;
  - Conclusion: disturbance increases the risk of contaminant release;

4 Skei, J.M., 1992. A review of assessment and remediation for hot spot sediments. Hydrobiologia, vol. 223/236, pp. 629-638.

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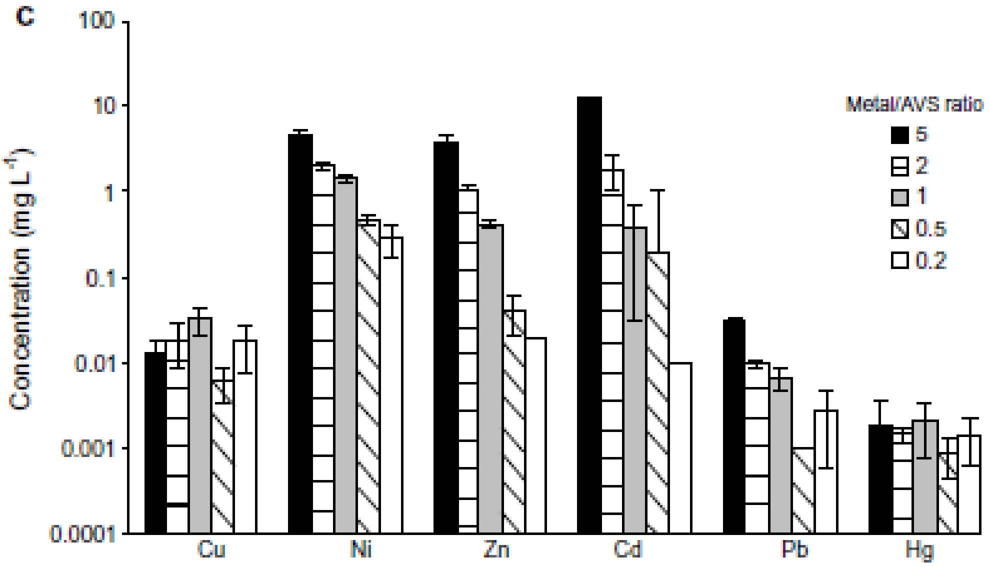
Examples heavy metals (2)

- <u>Cantwell *et al.* (2008)[5]*:*</u>
  - The release of heavy metals from spiked and field-aged sediments during resuspension depended on AVS > grain size > TOC;
  - Predictions of dissolved Cd, Ni and Pb concentrations from field aged sediments (based on • metal/AVS) overestimated measured concentrations with factors 2 – 50. Predicted Zn concentrations underestimated measured concentrations 2-10 times;
  - Conclusion: further work is necessary to better understand the role of water column conditions and other binding phases present in sediments which control metal partitioning during resuspension.

[5] Cantwell, M.G., R.M. Burgess and J.W. King, 2008.Resuspension of contaminated field and formulated reference sediments. Part I: Evaluation of metal release under controlled laboratory conditions. Chemosphere vol. 73, pp. 1824-1833.

From Cantwell *et al.* (2008)



Time averaged dissolved metal concentrations during resuspension of spiked sediments

Statement 3

- Although many factors have been identified that play a role in the desorption (kinetics) of contaminants from resuspended particles, there are still no reliable (generic) models to describe this process well enough.

  Will we ever be able to predict desorption accurately for any given resuspension event?

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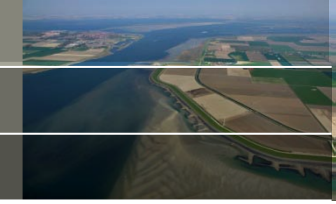
Recap statements



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- Resuspension of contaminated sediment can lead to much higher initial dissolved contaminant concentrations than predicted by equilibrium partitioning theory.

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