Sediment Quality - Ecotoxicology

Susanne Heise
Who am I?

1995: Biologist, PhD in Biological Oceanography, Institute for Marine Science, Kiel
2002 – 2008: Project leader, Consulting Centre for Integrated Sediment Management
Since 2008: Professor at Hamburg University of Applied Sciences
Aquatic sediment is aquatic particulate material with differing physical and chemical properties that can be biologically influenced. It is made up of layers of increasing solid content with depth and includes suspended material, fluid layer, unconsolidated and consolidated material, so all matter that could potentially comprise the suspension – sedimentation cycle (SedNet, 2002)
Aquatic sediment is aquatic particulate material with differing physical and chemical properties that can be biologically influenced. It is made up of layers of increasing solid content with depth and includes suspended material, fluid layer, unconsolidated and consolidated material, so all matter that could potentially comprise the suspension – sedimentation cycle (SedNet, 2002)

**Vertical processes**  
Resuspension accumulation

**Horizontal processes**  
Erosion, transport, mixing, dilution
Ecological Importance of Sediments: Habitat

<table>
<thead>
<tr>
<th>Taxon</th>
<th>Typical local species richness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Algae</td>
<td>0–1000</td>
</tr>
<tr>
<td>Fungi</td>
<td>50–300</td>
</tr>
<tr>
<td>Protozoa</td>
<td>20–800</td>
</tr>
<tr>
<td>Plants</td>
<td>0–100</td>
</tr>
<tr>
<td>Invertebrates</td>
<td>30–1500</td>
</tr>
<tr>
<td>Aschelminthes</td>
<td>5–500</td>
</tr>
<tr>
<td>Annelida</td>
<td>5–50</td>
</tr>
<tr>
<td>Mollusca</td>
<td>0–50</td>
</tr>
<tr>
<td>Acari</td>
<td>0–100</td>
</tr>
<tr>
<td>Crustacea</td>
<td>5–300</td>
</tr>
<tr>
<td>Insecta</td>
<td>5–400</td>
</tr>
</tbody>
</table>

[Palmer et al. 2000]

+ more than 100 000 bacteria species

(Foto: Dave Paterson)
Ecological importance of Sediments: Habitat

[from Fenchel et al. 1992]

(Foto: Dave Paterson)
"Ecotoxicity studies measure the effects of chemicals on fish, wildlife, plants, and other wild organisms" (US EPA, 2007)

Sediment ecotoxicology focuses on those contaminants that adsorb to fine particles, and on those organisms that either live in the sediment or are impacted by it and which are directly or indirectly exposed to adsorbed contaminants.
but by the way .... What exactly is “toxic”? 

“All substances are poisons; there is none which is not a poison. The right dose differentiates a poison from a remedy.”

Paracelsus (1493-1541)
Dose-response curves in toxicology

\[ \text{LD}_{50} = 40 \text{ mg/kg} \]
Dose-response curves in eco-toxicology

% effect (e.g. Inhibition)

Log concentration (mg/kg)

LC$_{50}$ = 40 mg/kg

NOEC

LOEC
but by the way …. What exactly is “toxic”?

“All substances are poisons; there is none which is not a poison. The right dose differentiates a poison from a remedy.”
Paracelsus (1493-1541)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Median lethal dose mg kg(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>10000</td>
</tr>
<tr>
<td>DDT</td>
<td>100</td>
</tr>
<tr>
<td>Nicotine</td>
<td>1</td>
</tr>
<tr>
<td>Tetrodotoxin</td>
<td>0.1</td>
</tr>
<tr>
<td>Dioxin</td>
<td>0.001</td>
</tr>
<tr>
<td>Botulinus toxin</td>
<td>0.00001</td>
</tr>
</tbody>
</table>
Currently, too little is known about:
- the number of potentially effective contaminants adsorbed to sediments
- their fate
- their bioavailability
- their exposure pathways
- their toxicodynamic and toxicokinetic
- their impact on physiological processes

to determine the toxicity of environmental matrices without on-site - ecotoxicological - investigations.
potentially effective contaminants adsorbed to sediments
What is monitored in sediments ..... 

Example Elbe River: e.g. ICPE / OSPAR / HABAK

Mostly:

- Heavy metals
- DDT et al.
- HCB
- HCH
- PAH
- PCB
- TBT

Historic contaminants
Historic sources
Why these substances?

They have a high tendency to adhere to sediments:

The $K_{ow}$ is an indicator of

- environmental transport
- sorption to organic matter
- uptake by organisms

$$K_{ow} = \frac{[A_{octanol}]}{[A_{water}]}$$
Sorption of organic substances: $K_{ow}$ and $K_{oc}$

Most important sorbant for organic contaminants:

Organic material e.g. humic substances, $C_{org}$

Partition coefficient $C_{org}/\text{water} : K_{oc}$

$K_{OC}$ has been empirically correlated to $K_{OW}$

$\rightarrow K_{OC} = 0,63 \times K_{OW}$ (Karickhoff et al, 1979)

Mostly $K_{OW}$ values are available rather than $K_{OC}$ values.
Affinity of contaminants to sediment and biota

<table>
<thead>
<tr>
<th>Affinity</th>
<th>Soil / sediment Log $K_{oc}$</th>
<th>Animals, membranes Log $K_{ow}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>High</td>
<td>&gt;5</td>
<td>&gt;5</td>
</tr>
<tr>
<td>Medium high</td>
<td>4 – 5</td>
<td>3.5 – 5</td>
</tr>
<tr>
<td>Medium</td>
<td>2 – 4</td>
<td>3 - 3.5</td>
</tr>
<tr>
<td>Medium low</td>
<td>1 – 2</td>
<td>1 – 3</td>
</tr>
<tr>
<td>Low</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

(UNEP training module 3 on Environmental Risk Assessment, mod.)

**Examples**

<table>
<thead>
<tr>
<th>Examples</th>
<th>Log $K_{ow}$</th>
<th>Examples</th>
<th>Log $K_{ow}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCB 153</td>
<td>6.8</td>
<td>HCB</td>
<td>5.31</td>
</tr>
<tr>
<td>PCB 52</td>
<td>5.79</td>
<td>2,3,7,8-TCDD</td>
<td>6.42</td>
</tr>
<tr>
<td>DDT</td>
<td>6.36</td>
<td>Naphthalene (PAH)</td>
<td>3.35</td>
</tr>
<tr>
<td>Benzo(a)pyrene (PAH)</td>
<td>6.35</td>
<td>γ-HCH</td>
<td>3.55</td>
</tr>
</tbody>
</table>
Most contaminants come from upstream!

Exception: TBT

(Heise et al. 2006)
Development of contamination of SPM along the Elbe catchment

Exceedance of target level for the protection of the aquatic community (SPM, 2000-2006)

(Heise et al. 2008)
Sediments as the memory of industrial history

Many European Rivers: **historic** contamination by mining and industrial emissions. **Recent** emission from resuspension of contaminated soil and sediments
Sediments as the memory of industrial history

Every persistent substance ever produced will sooner or later end up in sediments
BUT: How many substances are out there?

EINECS – European Inventory of Existing Commercial Chemical Substances: more than 100 200 chemicals that have been recorded as being commercially available between 1971 and 1981. Registered under the Dangerous Substances Directive (67/548/EEC)

Little information on toxicology and ecotoxicology of more than 90% of these substances
We only find what we are looking for ….

Analysis costs per sediment sample:

8 heavy metals (in < 20 µm fraction)  
PCB, HCB, PAH, DDT, DDD, DDE  

Ca. 250 – 500 €

1 dioxin analysis in sediment (estimation!):  250 – 750 €

Who wants to measure the rest?

Or are we on the safe site and those, that are commonly measured, the most toxic substances?
Emerging Substances (not exclusive)

Nanomaterials – in personal care products, could provide a vector for other substances to move through sediment
Pesticides - Although many are water soluble, some may end up and persist in sediments
Pharmaceuticals, like antibiotics, drugs, X-ray contrast media (iopromide, iopamidol)
Life-style compounds (e.g. caffeine, nicotine)
Products of Personal Care (PPC): Insect repellants, UV filters, fungistatic agents in cosmetics etc
Industrial activities and by-products – breakdown products of known substances
Water-treatment by-products
Flame retardants
Surfactants (PFOS, PFOA) – perfluorinated sulfonates and carboxylic acids
Hormones from contraceptives
Detection of emerging substances in water and sediment

USGS Work in Boulder Creek, Boulder Creek, CO

http://www.state.nj.us/dep/wmm/Buxton%20Emerging%20Contaminants%20For%20Posting.pdf
“Toxicologists know a great deal about a few chemicals, a little about many, and next to nothing about most.” (Rodricks, JV, 1992: 146)
Another problem: the bioavailability

Moderate concentrations are often not correlated with effect.
Why is the effect of sediment bound contaminants particularly difficult to predict?

(NRC, 2003)
Often no correlation between concentration of pollutants and biological effect

In many cases, there is little correlation between chemically measured concentrations in environmental samples and toxic effect. The bioavailability of substances changes with time, varies with substrate and organisms.
What to do?

- Too many chemicals to measure
- Mostly unknown toxic effects
- Little information on bioavailability
- Often unknown interaction of contaminants (synergic, additive effects?)

Measurement of ecotoxicity of sediments

To determine the impact of chemicals or mixture of chemicals on organisms with the aim to assess an impact on the environment.
Ecological evaluation of stressors in sediments

Benthic community structure:
- of ecological relevance
- important on the way to risk assessment

Bioassays:
- points out possible hazards
- effects on single species

Bioaccumulation:
- points to transfer in the food web
- effects otherwise unobserved
Time of exposure vs. test duration

- Biosensors
- Biotests
- Benthic Community Structure Analyses
- Bioaccumulation
- Ecological relevance

Expenditure of time

Time of exposure
How can ecotoxicological tests inform us about sediment quality?
Performance of ecotoxicity test

Environmental sample
Optimal growth medium
+ Test organisms
Incubation
„Endpoint“
+ Test organisms
Incubation
„Endpoint“

Comparison
e.g. % inhibition

Endpoints:
Growth
Mortality
Movement
Reproduction
Metabolic activity

Biotests with
Nematodes
Crustacea
Bacteria
Algae
Plants …..

Environmental sample:
Water
Sediment
Elutriate (water extract)

Standardizations acc. to ISO
Is application of one test enough? NO!

Sediments contain mixtures of contaminants
Different modes of action
Acting by different exposure pathways (water, direct contact etc)
Organisms are differently sensitive

Biotest combinations are necessary in order to detect all (?) potential effects
→ Often 3, better 5 bioassays
→ Different exposure pathways
→ Different sensitivities
→ Acute and chronic tests.
Application of a biotest-battery (Example)

Biotest battery

Sediment bacteria
- Bacillus cereus

Green algae
- Pseudokirchneriella subcapitata

Sediment Contact

Nematodes
- Caenorhabditis elegans

Elutriate
- Elutriate
- Elutriate and Methanol-extract

Fluorescing bacteria
- Vibrio fischeri
Tests and endpoints respond differently to the same environmental stress pattern → classification of results from a battery?
There is no uniform biotest classification

Single tests:

**Determination of the most sensitive organism**

Fixed thresholds: e.g. the first dilution step that results in a toxicity lower than 20%.

Test batteries:

- The most sensitive biotest indicates the toxicity

**Addition of inhibition values**

- Inhibition value of undiluted sample
- Adding up all inhibitions

**Integrative assessment of tests**

- Characterization of test responses
- On the basis of test characterization
- Combination of biotest results
- On the basis of pattern recognition
Evaluation of Ecotoxicological Data

Goal-oriented
- Monitoring
- Sediment management

Detection of patterns

Interpretation

absolute toxicities depending on issues
Changes with time: Hamburg Harbour


(Daten: TUHH)
Spatial variation: Elbe River

Increase of sediment toxicity

Ecotox
Ecology
Chemistry
Effects of the events e.g. Elbe-flood 2002 on brackish mudflats?

- **Elutriate and methanol extract**
  - **Solid phase tests**
    - **Bacterial Contact Assay**
      - *Arthrobacter globiformis*
      - Activity (dehydrogenase)/45mins
    - **Nematode Test**
      - *Caenohabditis elegans*
      - Growth, fertility, reproduction/96 hrs
  - **Elutriate tests**
    - **Algal Growth Inhibition Test**
      - *Pseudokirchneriella subkapitata*
      - Growth rate (fluorescence)/72hrs
    - **Bioluminescence Inhibition Test**
      - *Vibrio fischeri*
      - Activity (bioluminescence)/30mins
E.g. Impact of the Elbe flood 2002 before the flood

23/24.8.02

Positionen der GKSS-Proben

Scale: 1:366554 at Latitude 0°
E.g. Impact of the Elbe flood 2002 after the flood

30.9./2.10.02

Positionen der GKSS-Proben

Scale: 1:366554 at Latitude 0°

(Heise et al. 2003)
Other results?

Increased toxicity with algae (elutriate), bacteria and nematodes (sediment)

(Heise et al. 2003)

Ötken et al. 2005: No effects of estuarine sediments after the flood on *Chironomus riparius* (insecta) and *Potamopyrgus antipodarum* (gastropoda)

Einsporn et al. (2005): toxic effects in flatfish and mussels after the flood. Flatfish were most affected in the Elbe estuary and near Helgoland. High levels of organic contaminants in fish liver and mussels.
Lübeck Bight: Assessment of old dumping site/ or „Success of mitigation measures“

Lübeck Bight: Dumping site in the 60s

Mecklenburger Bight: Reference station
Heavy metals
In ppm

Sediment depth | Ni   | Zn   | Cu   | Pb   | Cd   | Hg   |
---             | ---  | ---  | ---  | ---  | ---  | ---  |
Surface        |      |      |      |      |      |      |
20 cm          | 200 ppm | 25000 ppm | 1250 ppm | 35 ppm | 35 ppm | 20000 ppm |

(Leipe et al. 2002)

Lead and Zn: up to 2 % of the sediment layers 3-18 cm
Effects measurements: Exposure pathways

- Increasing Toxicity
- Surface material (low toxicity) (0-2)
- Below surface (4-6)
- 16-18 cm depth

<table>
<thead>
<tr>
<th>Test Type</th>
<th>Surface Material</th>
<th>Below Surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact test, mar</td>
<td><img src="assets/yellow.png" alt="Yellow" /></td>
<td><img src="assets/red.png" alt="Red" /></td>
</tr>
<tr>
<td>Contact test, fw</td>
<td><img src="assets/blue.png" alt="Blue" /></td>
<td><img src="assets/green.png" alt="Green" /></td>
</tr>
<tr>
<td>Extract test</td>
<td><img src="assets/orange.png" alt="Orange" /></td>
<td><img src="assets/orange.png" alt="Orange" /></td>
</tr>
<tr>
<td>Elutriate test, mar</td>
<td><img src="assets/green.png" alt="Green" /></td>
<td><img src="assets/green.png" alt="Green" /></td>
</tr>
<tr>
<td>Elutriate test, fw</td>
<td><img src="assets/yellow.png" alt="Yellow" /></td>
<td><img src="assets/yellow.png" alt="Yellow" /></td>
</tr>
</tbody>
</table>
Investigation of the contaminated site in detail
Ocean Data View

Surface sediment

4-6 cm depth

Dumping of „clean“ material in the region as a capping measure

increasing Toxicity
Disadvantage of „only“ biotests

Lack of knowledge on relevant stressors!
No source control!
Transferability to other trophical levels / to the ecosystem?

Weight of evidence approaches and tiered approaches are necessary:
Combination of

- *in vitro*-biotests (on e.g. celluar level): → modes of action, fingerprinting
- *In vivo* biotests → exposure pathways, bioavailability
- Ecological community modelling → from organism level to population level
- and TIE – Toxicity Identification Profiling

are necessary for an efficient environmental assessment.
Risk Assessment: Application of a Sediment Triad

Chemical Contamination

- Sediment Quality Criteria
- Modelling of Biomagnification
- Ecosystem analysis (diversity of benthos organisms)

Ecotoxicological Test Systems

- Acute test
- Chronic test with Elutriates

Effects on the organisms

Bioaccumulation Potential

- Ecotoxicological Test Systems
- Acute test
- Chronic test with Elutriates

Sediment Quality Criteria

- Modelling of Biomagnification
- Ecosystem analysis (diversity of benthos organisms)
Thank you for your attention!

Prof. Dr. Susanne Heise
Aquatic Ecotoxicology
HAW-Hamburg

Susanne.heise@haw-hamburg.de
Bioconcentration: A process by which there is a net accumulation of a chemical directly from water into aquatic organisms resulting from simultaneous uptake (e.g., by gill or epithelial tissue) and elimination.

Bioaccumulation: accumulation of contaminants in tissue of organisms through any route, including respiration, ingestion, or direct contact with contaminated water, sediment, pore water, or dredged material.

Biomagnification: Tissue concentrations of bioaccumulated chemicals increase as the chemical passes up through two or more trophic levels.
(J.D. Buynak, 2011)
Contamination sources for sediments
# Ecotoxicology Versus Toxicology

<table>
<thead>
<tr>
<th>Toxicology</th>
<th>Ecotoxicology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protection of humans</td>
<td>Protection of the ecosystem</td>
</tr>
<tr>
<td>Target organism is well known</td>
<td>Often, sensitive species are not known</td>
</tr>
<tr>
<td>Models using mammals</td>
<td>Experiments with / direct studies of indicator species / test species</td>
</tr>
<tr>
<td>Model organisms are homeothermic</td>
<td>Many organisms are heterothermic, various physiologies</td>
</tr>
<tr>
<td>Exposure can be determined precisely (oral doses)</td>
<td>Identity of stressor, concentration and exposure time theoretically known, availability by various potential exposure pathways often is not.</td>
</tr>
<tr>
<td>Basic research: Understanding of processes</td>
<td>Basic research regarding availability, environmental exposure; also empirical studies to determine threshold levels for legislation</td>
</tr>
<tr>
<td>Methods are mostly established</td>
<td>Many methods are relatively new, often being in the process of standardization</td>
</tr>
</tbody>
</table>