

Sediment Quality - Ecotoxicology

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What is sediment?



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)







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Ecological Importance of Sediments: Habitat



Taxon	Typical local species richness	
Algae	0–1000	
Fungi	50–300	
Protozoa	20-800	
Plants	0–100	
Invertebrates	30-1500	
Aschelminthes	5–500	
Annelida	5–50	
Mollusca	0–50	
Acari	0–100	
Crustacea	5–300	
Insecta	5–400	

[Palmer et al. 2000]

+ more than 100 000 bacteria species



Ecological importance of Sediments: Habitat







(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



Dose-response curves in eco-toxicology



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Paracelsus (1493-1541)

Compound	Median lethal dose mg kg ⁻¹
Ethanol	10000
DDT	100
Nicotine	1
Tetrodotoxin	0.1
Dioxin	0.001
Botulinus toxin	0.00001

The reasoning for ecotoxicological studies

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 dermine 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

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Mostly:



Why these substances?

They have a high tendency to adhere to sediments:

The K_{ow} is an indicator of



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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}/water : K_{oc}

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

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

Mostly K_{OW} values are available rather than K_{OC} values.

Affinity of contaminants to sediment and biota



Affinity	Soil / sediment Log K _{oc}	Animals, membranes Log K _{ow}	
High	>5	>5	
Medium high	4 – 5	3.5 – 5	
Medium	2-4	3 - 3.5	
Medium low	1 – 2	1 – 3	
Low	<1	<1	

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

Examples	Log K _{ow}	Examples	Log K _{ow}
PCB 153	6.8	HCB	5.31
PCB 52	5.79	2,3,7,8-TCDD	6.42
DDT	6.36	Naphthalene (PAH)	3.35
Benzo(a)pyrene (PAH)	6.35	γ-HCH	3.55

Contaminant cocktails in sediments

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Most contaminants come from upstream!



Exception: TBT



Exceedance of target value



(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)

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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



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 μ m 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

The "Toxic Iceberg"





(slide: Vanderlinden, Toronto Public Health)

Another problem: the bioavailability



Conc. of contaminant in sediment Moderate concentrations are often not correlated with effect.

Effect on organisms

Why is the effect of sediment bound contaminants particularly difficult to predict?



Contaminant	Transport of	Passage across	Circulation within organism,
interactions	contaminants	physiological	accumulation in target organ,
between phases	to organism	membrane	toxicokinetics, and toxic effects

(NRC, 2003)

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Often no correlation between concentration of pollutants and biological effect

Bioavailable and bioaccessible in soil

This conceptual diagram illustrates the bioavailable and bioaccessible fractions of a contaminant in soil as defined by physical location. It also describes the relationship of soil-associated contaminant molecules in relation to bioaccessible fraction.



(Semple, 2004)



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





How can ecotoxicological tests inform us about sediment quality?





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

- \rightarrow Often 3, better 5 bioassays
- \rightarrow Different exposure pathways
- \rightarrow Different sensitivities
- \rightarrow Acute and chronic tests.

Application of a biotest-battery (Example)



Vibrio fischeri

Variation of test responses



Tests and endpoints respond differently to the same environmental stress pattern \rightarrow classification of results from a battery?

There is no uniform biotest classification

Single tests:

Test batteries:

Determination of the most sensitive organism

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

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



Changes with time: Hamburg Harbour



(Daten: TUHH)

Spatial variation: Elbe River





E.g. Impact of the Elbe flood 2002 before the flood

23/24.8.02





öko toxikologie



(Heise et al. 2003)

öko toxikologie

Other results?



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

ÛÛ

(Heise et al. 2003)

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



Mecklenburger Bight: Reference station

Chemical Analysis

Heavy metals In ppm



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

Effects measurements: Exposure pathways



Investigation of the contaminated site in detail





Dumping of "clean" material in the region as a capping measure

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

- \succ in vitro-biotests (on e.g. celluar level): \rightarrow modes of action, fingerprinting
- > In vivo biotests \rightarrow exposure pathways, bioavailability
- ➤ Ecological community modelling → from organism level to population level
- and TIE Toxicity Idenfitication Profiling

are necessary for an efficient environmental assessment.

Risk Assessment: Application of a Sediment Triad



Thank you for your attention!

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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.





Contamination sources for sediments





Ecotoxicology Versus Toxicology



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