

Emissions

The long-term memory of sediments

Theme 1 – Zero pollution

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Why this talk?

To improve the water quality, we need to look at contamination sources. Sediments are not a direct contamination source, but they can be a contaminant storage medium.

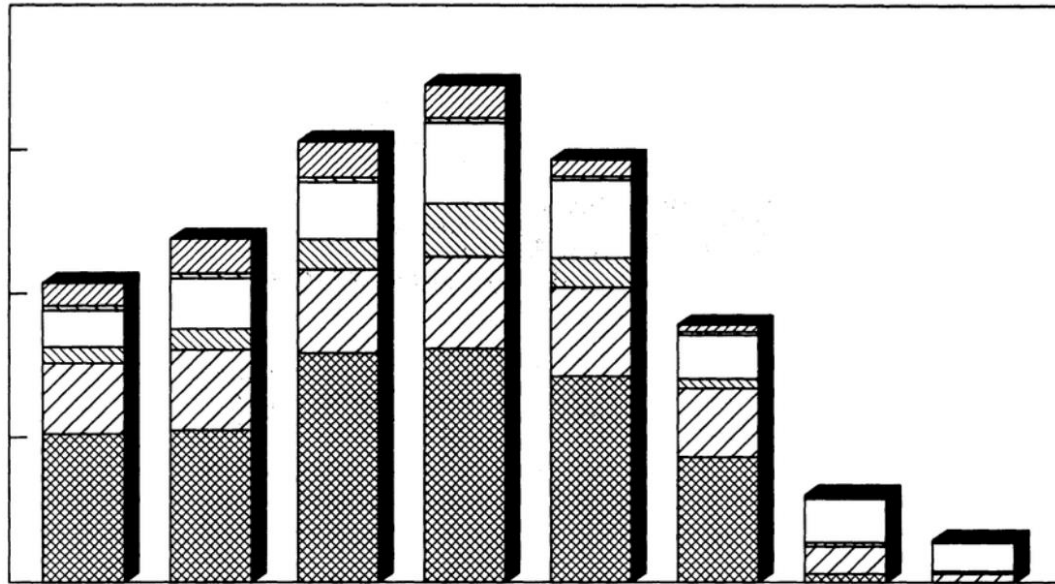
This talk is split in three parts:

- Introduction - The timescale for changes in the sediment quality,
 1. The timescale for historical contaminant fluxes, examples
 2. The impact of “clean” soils on the water quality.

Introduction

Intro – Timescales for changes in the sediment quality

To start on a positive note, during the hights of industrial spills (1950 -1980) sediments have improved the water quality.



Annual aqueous point source emissions of cadmium to the Rhine River from 1955 to 1988. Source: Stigliani et al., 1993c.

The downside is that some of those contaminants are now released to the water.

Intro – Timescales for changes in the sediment quality

Since the affinity for many contaminants for sediments is higher than for water, the uptake in sediment is significant.

This is reflected in the table on the right for metals in what is called 'total water'. The dissolved metal fraction declines with an increased turbidity. When this sediment settles the load in the surface water is reduced.

When sediments stay buried the impact on the surface water quality is limited. Meandering of rivers, storm surges or dredging can mobilize these buried sediments.

metals	Kp = (l/kg)	log(Kp)	Suspended solid concentration, fraction dissolved			
			1 mg/l	10 mg/l	25 mg/l	100 mg/l
cadmium cd	130000	5.1	88%	43%	24%	7%
mercury hg	170000	5.2	85%	37%	19%	6%
copper cu	170000	5.2	85%	37%	19%	6%
nickel ni	50000	4.7	95%	67%	44%	17%
lead pb	8000	3.9	99%	93%	83%	56%
zinc zn	640000	5.8	61%	14%	6%	2%
chromium cr	290000	5.5	78%	26%	12%	3%
arsenic as	10000	4.0	99%	91%	80%	50%
antimony sb	3700	3.6	100%	96%	92%	73%
barium ba	1350	3.1	100%	99%	97%	88%
beryllium be	850	2.9	100%	99%	98%	92%
cobalt co	3900	3.6	100%	96%	91%	72%
molybdenum mo	1120	3.0	100%	99%	97%	90%
selenium se	590	2.8	100%	99%	99%	94%
thallium tl	1500	3.2	100%	99%	96%	87%
tin sn	371500	5.6	73%	21%	10%	3%
vanadium v	5500	3.7	99%	95%	88%	65%

Intro – Timescales for changes in the sediment quality

So, *what timescales* do we talk about for significant changes in the sediment quality?

An example for soils: For soils this capacity to store contaminants in relation to land use has been evaluated and translated into standards (for metals) when applying soil improvers (like clippings and compost).



Impact of soil improvers on soil quality



dr.ir. Paul Romkens – WUR

Intro – Timescales for changes in the sediment quality

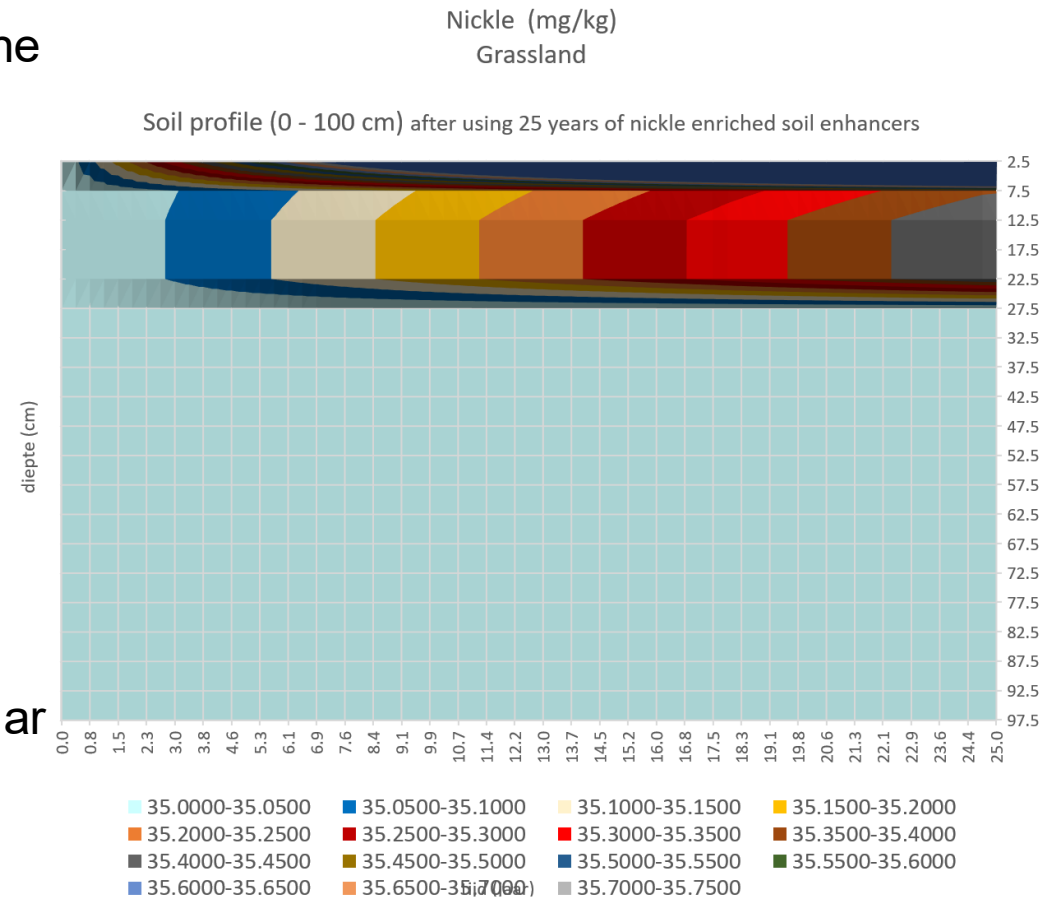
An example for Nickel concentrations in dry soils due to the use of clippings,

Soil background concentration:	35 mg/kg d.s.,
Nickel concentration in clippings:	45 mg/kg d.s.,
Use of dredged clippings over a period of	25 years,
<u>Dosing is 20 ton/ha.year =</u>	<u>2 cm a year</u>
Resulting in a Nickle increase of	+2%
in the top 25 cm soil over 25 years.	

Soil fertilisation ≠ sedimentation

... but the mass balance in input/output is somewhat similar

Take home message: *It takes decades to make an impression on soils or sediments.*



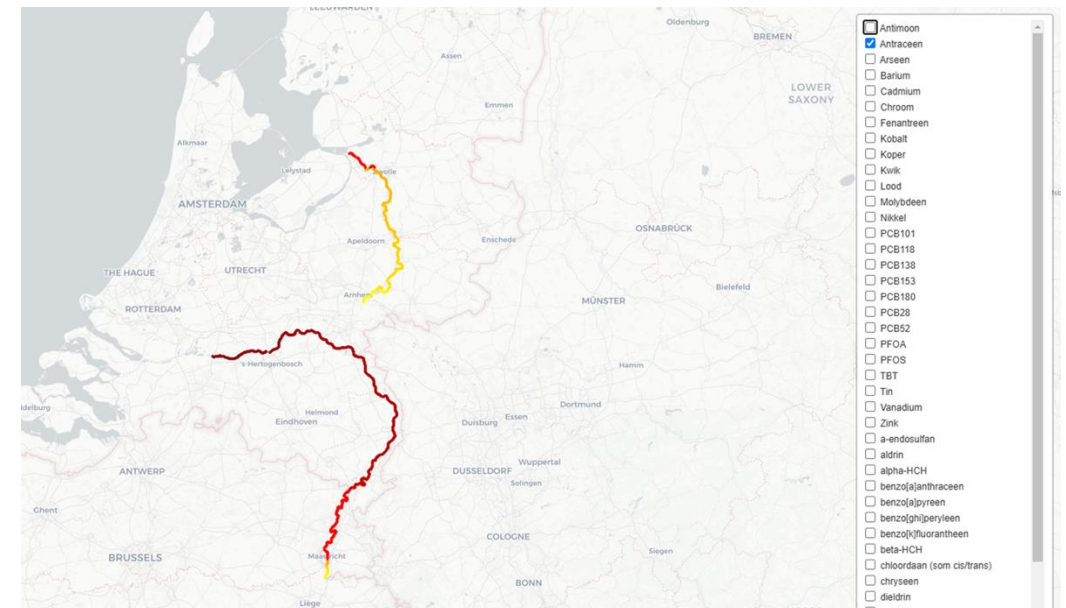
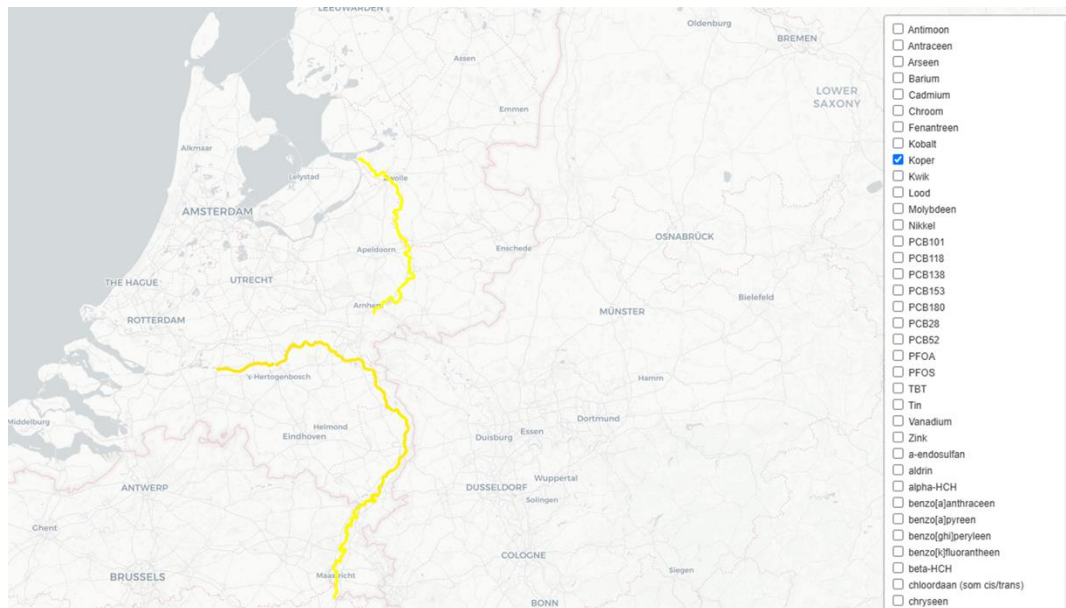
Part 1 - The timescale for historical contaminant fluxes

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The downside is that sediments, when polluted, can remain a source for recontamination for decades. Sediment emission can become the straw that breaks the camel's back for meeting the Water Framework Directive water quality goals.

An example for a moderately contaminated sediment in a river:

- On the **left (for copper)** the sediment emission does not exceed the WFD water quality criterium
- On the **right (anthracene)** the sediment emission does exceed the WFD water quality criterium



Part 1 – The timescale for historical contaminant fluxes

From model predictions to observations: An example for TBT in the Port of Hamburg.

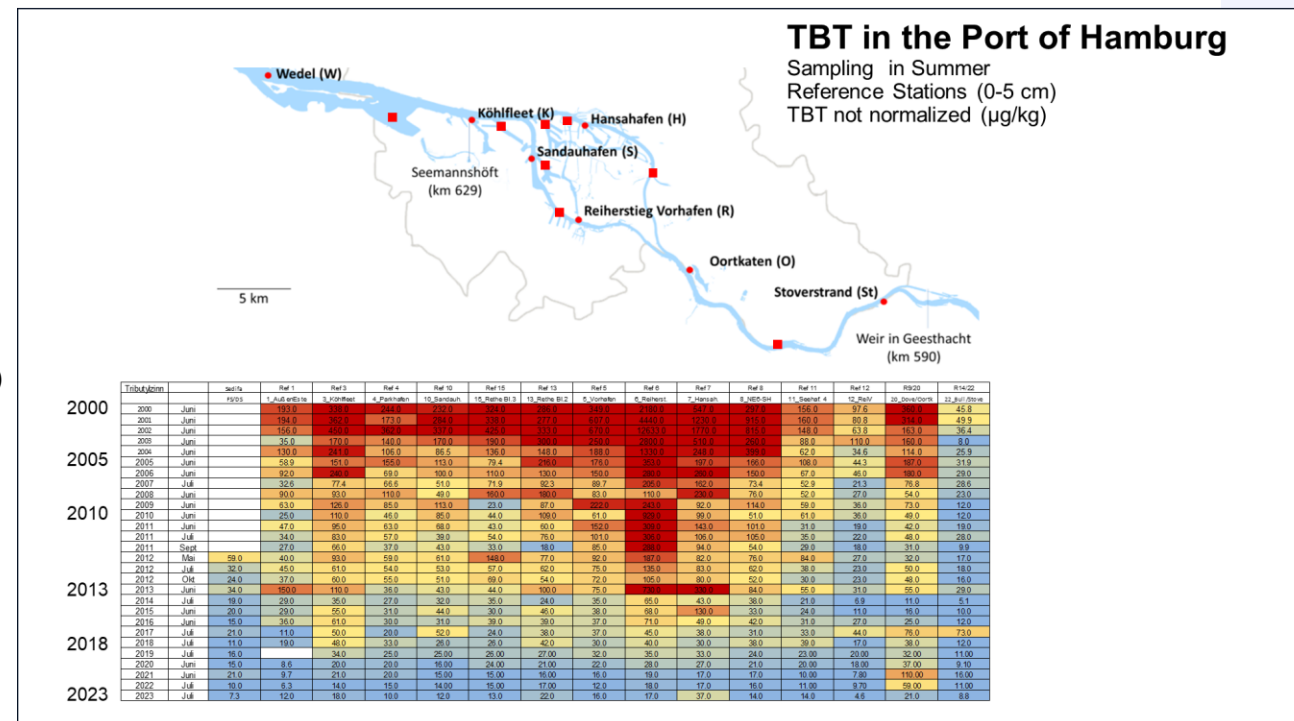
Since the ban on TBT in 2008 there are no point sources for TBT; TBT should only be in the sediments (not only in the port, but also up- and downstream).

Currently (2023 data) the TBT concentration in the port is roughly 10 - 20 µg/kg d.s.

The proposed EQS for TBT in sediment = 1,6 µg/kg d.s.⁽¹⁾

When will this EQS be met?

⁽¹⁾The impact of OC normalisation on the EQS for TBT will not be discussed in this presentation.



Part 1 – The timescale for historical contaminant fluxes

Looking at trends¹ it takes nearly 40 years to restore the sediment quality in the port.

Why so long? An indication:

- Yearly dredged volume: 3 to 4 million m³
 - Source: Terra et Aqua – Number 96 – September 2004⁽²⁾
- Up/downstream total suspended sediment: +/- 650,000 ton (= +/- 0,65 mln. m³ a year)
 - Source: International Commission for the Protection of the Elbe River - Information Sheet Sediment Management Concept - April 2015⁽²⁾

If we assume that the up/downstream sediment quality is clean⁽³⁾ and that the up/downstream sediments are diluting the concentration in the dredged sediment a trend fit results in the year 2030 to reach the EQS of 1,6 µg/kg d.s.

Even this over simplified model yields a timescale of more then two decades for reaching the EQS after stopping the TBT point sources.

¹ This is an oversimplification, lumping trends in boundary concentrations and assuming a continuation of the current sediment reallocation strategy.

² An oversimplification with a great yearly variation and some recent breaks in loads

³ Not true, currently the up/downstream TBT concentration = +/- 5,0 µg/kg d.s.

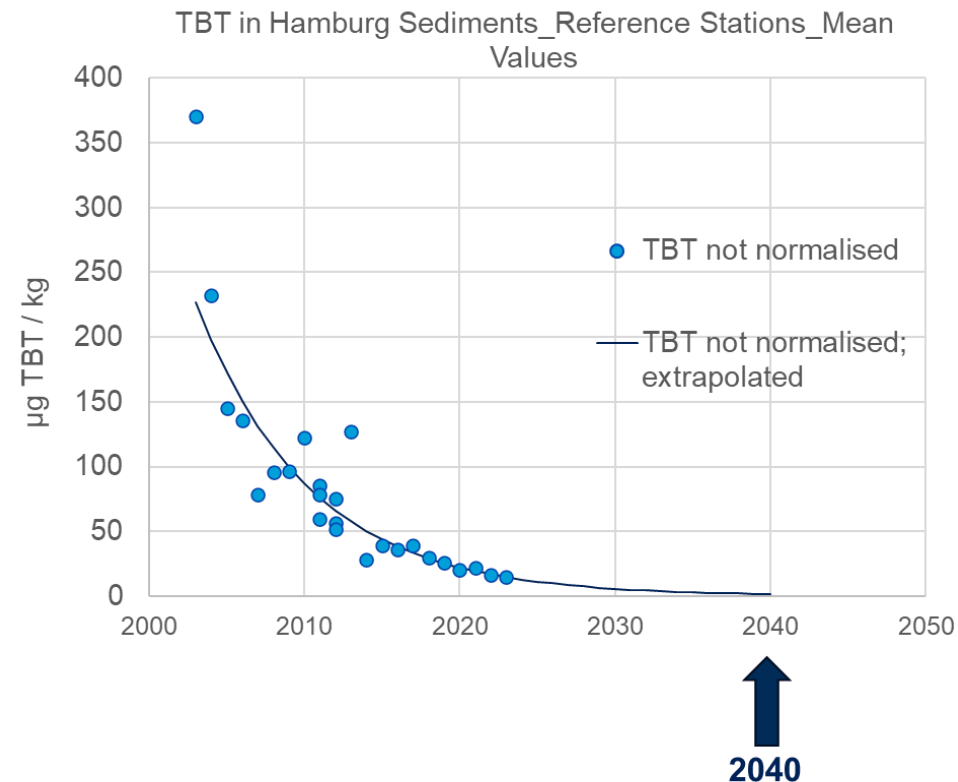


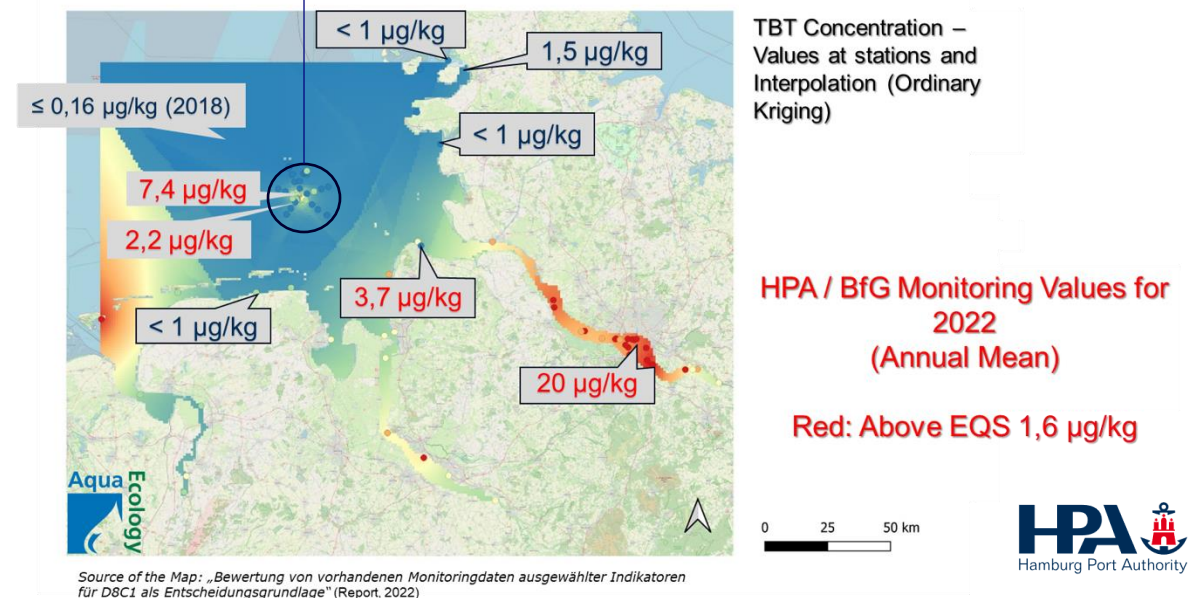
Figure - Extrapolation of the observed TBT concentrations in Hamburg sediments to the moment the EQS_{sediment} (proposal for directive on EQS, 2022) is reached (in 2040).

Part 1 – The timescale for historical contaminant fluxes

While the timescale might be long, the impact of contaminants in the sediment can be shorter.

Let's have a look at the Port of Hamburg sediment reallocation site in the North Sea.

2022 Observed sediment concentrations: TBT: Distribution in the German Bight and in the Elbe Estuary 2022



Part 1 – The timescale for historical contaminant fluxes

The impact of TBT on Common Whelp at the Port of Hamburg reallocation site in the North Sea.

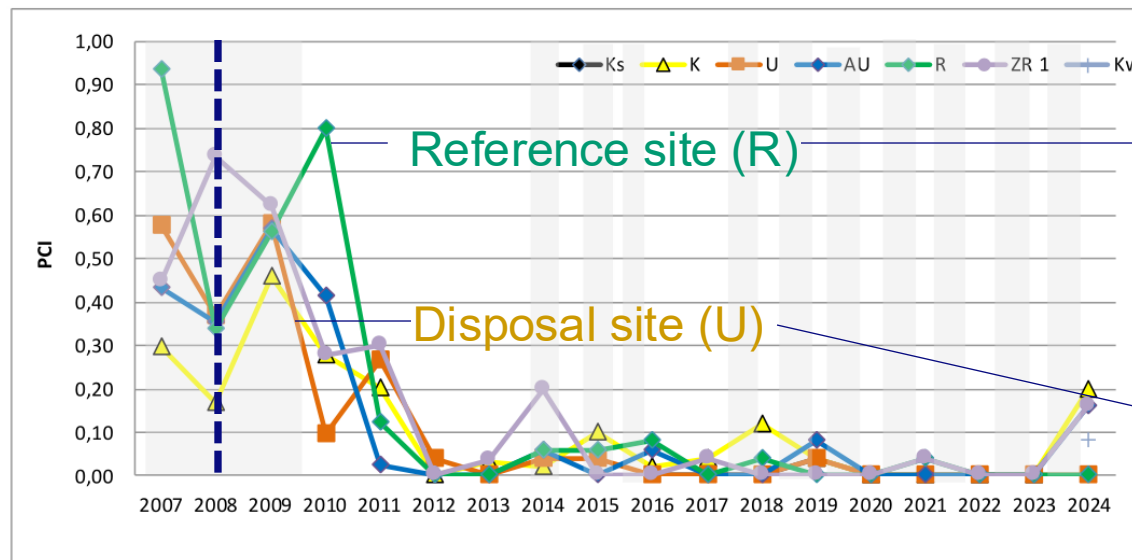


Abb. 19: Penis-Klassifizierungs-Index (PCI) der Wellhornschnecke in den einzelnen Teilgebieten in den Jahren 2007–2024, dargestellt sind die Jahresmittelwerte.

There is a recovery +/- 5 years after the TBT-ban.
(although with a relapse in 2024).

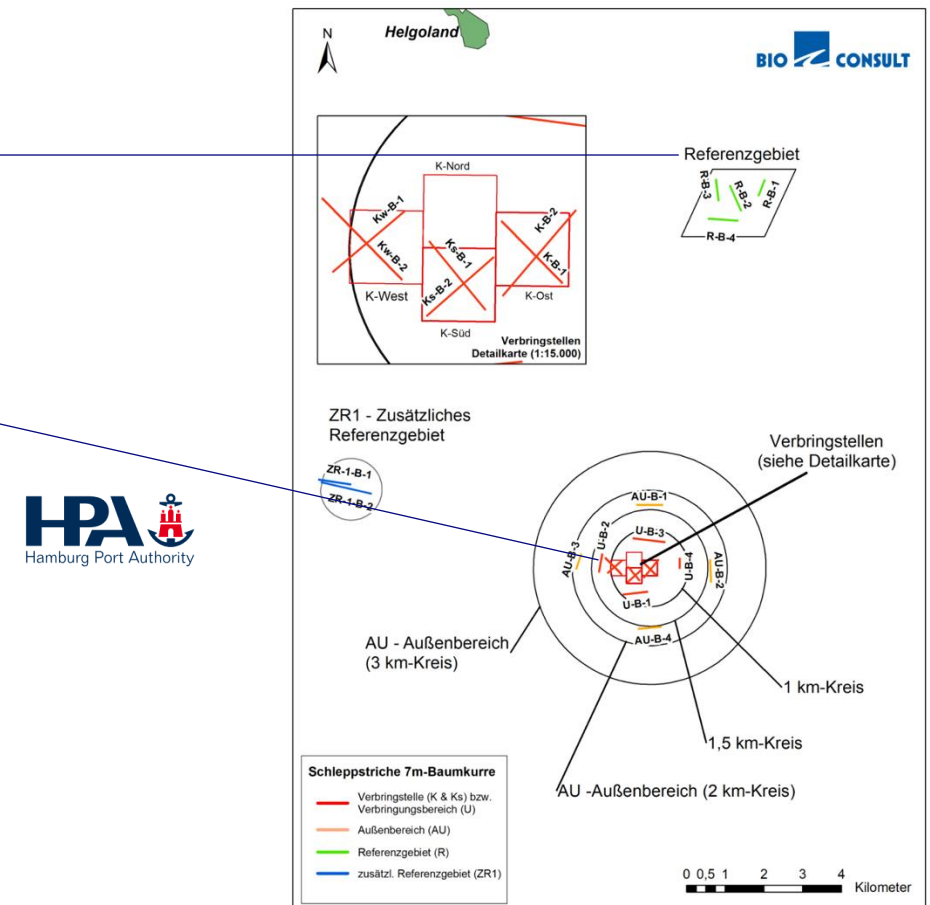


Abb. 7: Lage aller Schleppstrecken der 7 m-Baumkurre im Untersuchungsgebiet dargestellt für die Kampagne im Juni 2024.

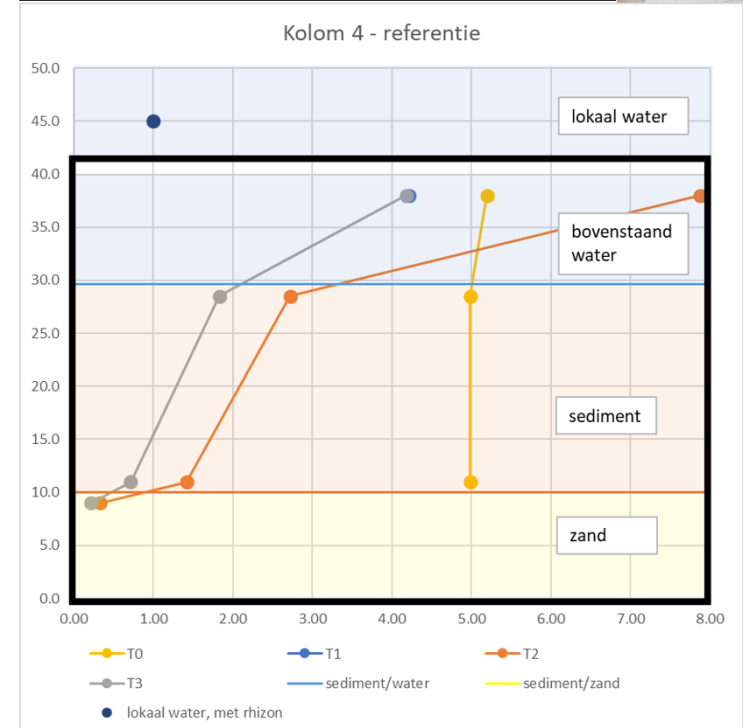
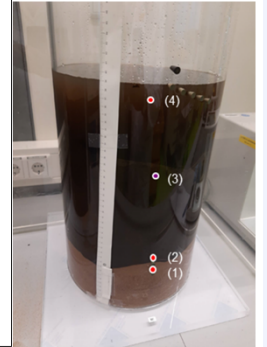
Part 1 – The timescale for historical contaminant fluxes

A decrease in impact (at TBT levels \gg EQS) can have multiple causes. One possible cause, a decline of the bio-available TBT fraction (aging) has been observed in the Netherlands.

On average the dissolved TBT concentration in pore water was 900 times lower than literature⁽¹⁾ predicted.

Tabel 8 Gemeten TBT concentraties scenario 4 (referentie, na correctie voor blanco's.

Posities beschrijving	cm	TBT (ng/l)				
		dagen	T0	T1	T2	T3
<i>grenslagen</i>						
sediment/water	29.6					
top water	39.0					
<i>monsterpunten</i>						
rhizon 4 opp. water	38.0		5.194	4.214	7.874	4.182
rhizon 3 top sediment	28.5		4.981		2.722	1.833
rhizon 2 bodem sediment	11.0		4.981		1.419	0.712
rhizon 1 zand	9.0				0.329	0.215
<i>Lokaal water Loosdrecht</i>						
lokaal lokaal water, met rhizon		0.948				
<i>blanco's</i>						
kraanwater		0.000				
kraanwater met rhizon		0.081				
UHQ		0.000				
UHQ met rhizon		0.000				



Figuur 20 TBT profielen in kolom 4 – referentie – op T0 (0 dagen) tot en met T3 (150 dagen).

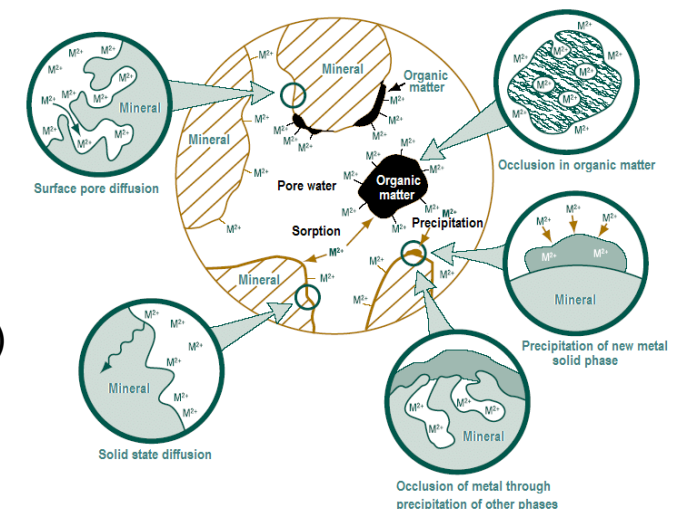
¹⁾ The partition behavior of tributyltin and prediction of environmental fate, persistence and toxicity in aquatic environments, S. Bangkedphol et al., Chemosphere 77 (2009) 1326–1333.

Part 1 – The timescale for historical contaminant fluxes

In conclusion:

- It can take decades for sediments to reach good chemical status for chemicals with historical contamination.
- The impact of contaminants can decrease over time (aging) by a decline in the bio-available concentration.
 - Aging has been observed for many organic pollutants like PAH's and PCB's
 - For metals mineralization, as an example due to reducing sulphates in sediments, can also limit the pore water concentration (somewhat similar impact as aging).

Using methods that give insight in sediment aging (like passive sampling or SEM/AVS) helps to quantify the potential role of sediments when taking measures to improve the water quality.



Chattopadhyay, Sandip. (2006). Management of Mercury Contaminated Sediments: Research, Observations, and Lessons Learned. 10.13140/RG.2.2.25968.46088.

Part 2 – The impact of “clean” soils on the water quality

In a country like the Netherlands the boundary between water and land can be fluid.

Soils are therefore also part of measures in relation to water management, like the backfilling of deep lakes (former quarries).

Soil quality standards and water quality standards have a different legal background. What could happen when soils are applied in a water body?



Part 2 – The impact of “clean” soils on the water quality

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Soils (or sediments) are often to some degree contaminated due to natural and anthropogenic sources. Since soils and sediments are not regulated in the WFD the levels of contamination for the application of soils and sediment (“clean” soils) is regulated by national soil laws.

The question: Can the application of “clean” soils in a waterbody⁽¹⁾ impact the WFD water quality?



⁽¹⁾ The application of soils (or sediment) can have beneficial impacts on ecological goals. The question addressed is limited to the impact on the chemical status of the waterbody according to the WFD.

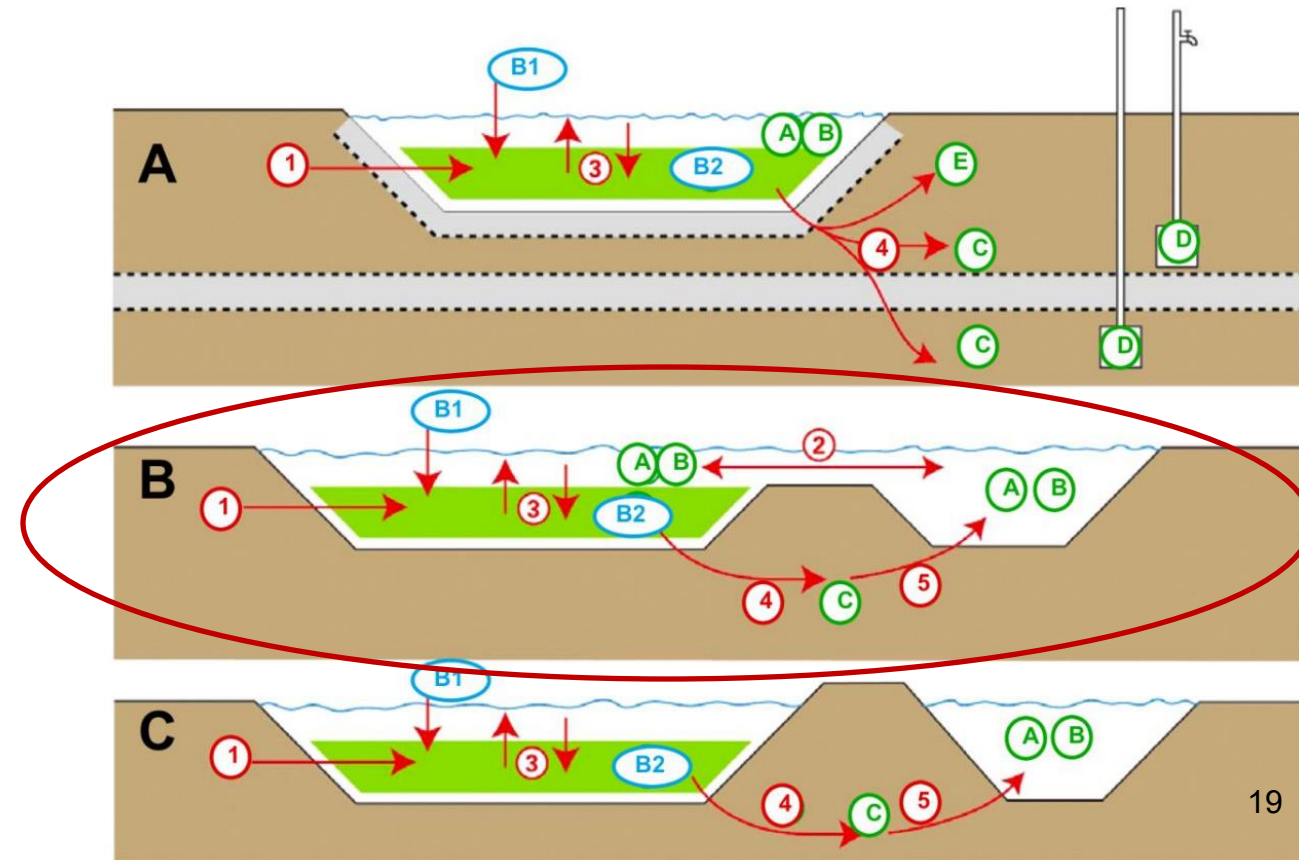
Part 2 – The impact of “clean” soils on the water quality

As a **collision test** the potential impact of backfilling deep lakes connected to a river with soil was investigated, based on the *maximum allowed concentration in soils*.

These fictional “clean” soils were applied for two deep lake locations in the Netherlands, considering:

- The background contaminant concentrations in the river,
- The lowest representative flow rate (less dilution) of the river,
- The exchange between the lake and the river,
- The impact of turbidity during allocation of the soil,
- Checked against the annual average concentration (AA-EQS)

derived from the Water Framework directive (WFD)



Part 2 – The impact of “clean” soils on the water quality

The outcome is for a collision test, in what can be considered as a worst-case condition.

For some metals, PAH's, pesticides and PFAS the application of “clean” soil can impact the water quality in the lake and on the river to a level above the WFD AA-EQS.

Background concentrations and residence time play an import role in the exceedance of the AA-EQS.

Conclusion: The results shows that it is not always advisable to “mix and match” between standards for different compartments (soil and water).

Tabel - Impression on the impact of backfilling on the water quality in the lake and bordering river.

	Does the emission from the soil/sediment meets the immission target (= have an acceptable WFD water quality impact)?			
	In the Lake		In the river	
	during backfilling	after backfilling	during backfilling	after backfilling
Metals				
antimony	ja	ja	ja	ja
arsenic	nee	ja	ja	ja
barium	ja	ja	ja	ja
cadmium	ja	ja	ja	ja
chromium	ja	ja	ja	ja
cobalt	nee	nee	ja	ja
copper	ja	ja	ja	ja
mercury	nee	nee	nee	ja
lead	ja	ja	ja	ja
molybdenum	ja	ja	ja	ja
nickel	ja	ja	ja	ja
tin	ja	ja	ja	ja
vanadium	ja	ja	ja	ja
zinc	ja	ja	ja	ja
PFAS				
PFOS	nee	nee	ja	ja
PFOA	ja	ja	ja	ja
Mefosaa	ja	ja	ja	ja
Etfosaa	ja	ja	ja	ja

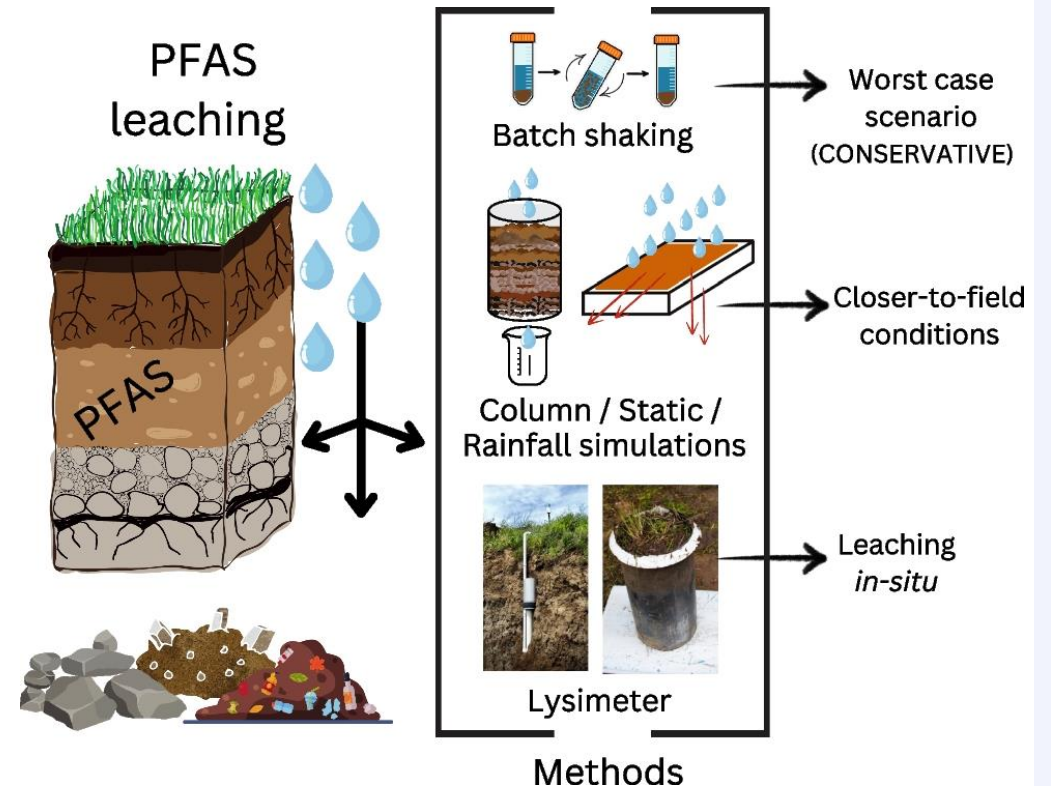
Linking part 1 and part 2

While the timescale for sediment recovery can not be accelerated (at least not for diffuse contaminants) and takes decades, the impact of contaminants can decline over time.

Generic parameters for contaminant behaviour are a starting point but are often conservative. Soil/sediment site specific measurements give a better picture.

There are internationally approved leaching tests for contaminants to evaluate worst case and closer to field conditions.

Advice: Further development and standardisation of these tests for in-situ sediment conditions ⁽¹⁾ helps to assess the site-specific ecological impact of sediments.



Navarro, D.A., Kabiri, S.S., Bowles, K. et al. Review on Methods for Assessing and Predicting Leaching of PFAS from Solid Matrices. *Curr Pollution Rep* 10, 628–647 (2024). <https://doi.org/10.1007/s40726-024-00326-6>

⁽¹⁾ As an example: <https://www.epa.gov/hw-sw846/leaching-environmental-assessment-framework-leaf-methods-and-guidance>