BIOKOL-BASERAD REAKTIV BARRIÄR FÖR TÄCKNING AV FÖRORENADE SEDIMENT

Christian Maurice – Luleå Tekniska Universitet
christian.maurice@ltu.se

Gabrielle Dublet-Adli – Norges Geotekniska Institut
gabrielle.dublet.adli@ngi.no

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Många inblandade

LTU

Christian Maurice

Wathiq Al Jabban

Emma Flodin

Nathalie Pantzare

Emma Heidrich

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Gabrielle Dublet-Adli

Gerard Cornelissen

Espen Eek

Erlend Sørmo

Caroline Berge-Hansen

Maren Valestrand Tjønneland

Skellefteå kommun

Christer Svensson

Swerock

Gunnar Wiklander

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Målet med projektet

Att visa att en tunn täckning av biokol/betonit effektivt kan hindra diffusion av Hg, metyl-Hg och PAH från bottensediment till vattenmassan.

Att skapa en täckning som minskar diffusion medan den naturliga sedimentationen bygger på barriären.

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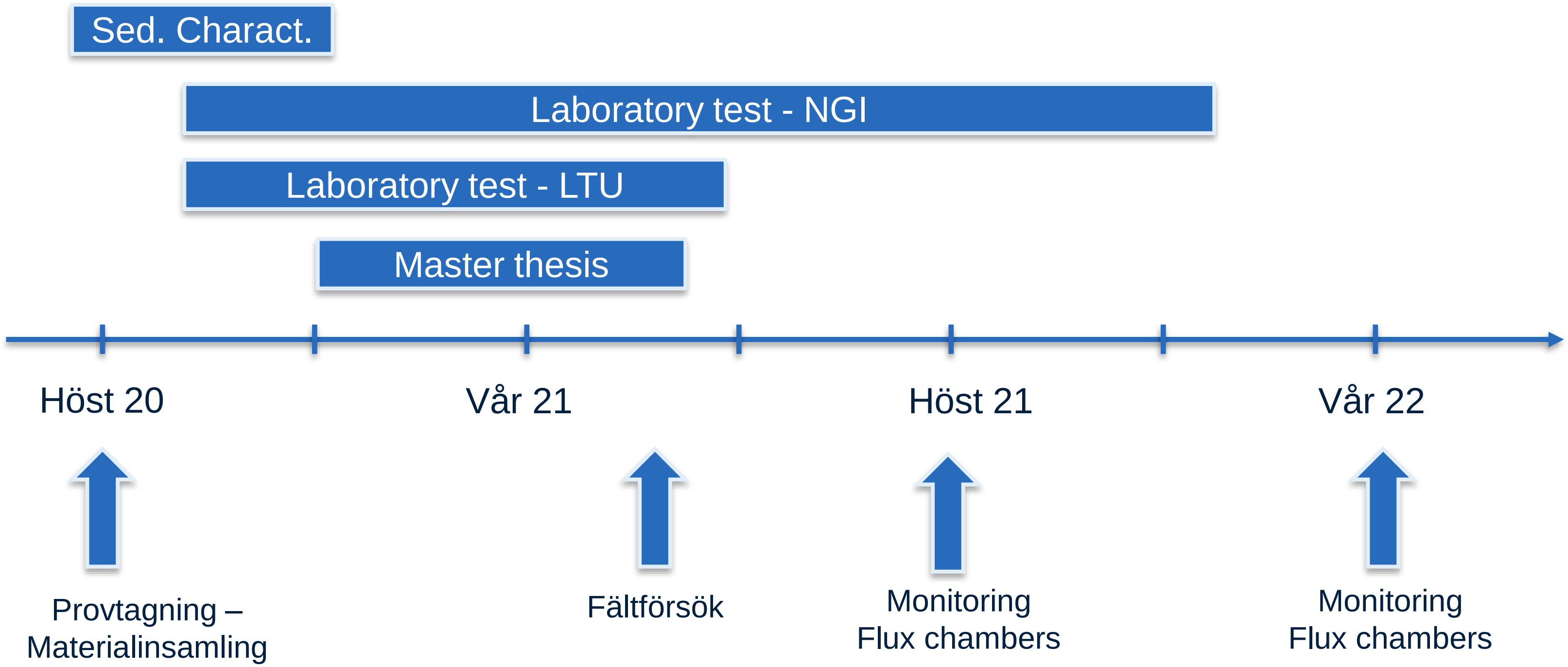
Projekt översikt



Bureå

Skellefteå

- Skellefteälvmynning
- Bure träsliperi och sågverk, verksamhet mellan 1928 och 1992.
- Mekanisk slipmassa, impregnerat med fenylkvicksilver mellan 1948 och 1964
- Spridning av fiberslam har skett från en sedimentationsbassäng till fjärden
- En fiberbank och förorenade omkringliggande sediment

Historik

Föroreningssituation

- Fibersediment
- Fiberbank
- Hg, PAH, As, Pb, Cu, Zn

Materialinsamling

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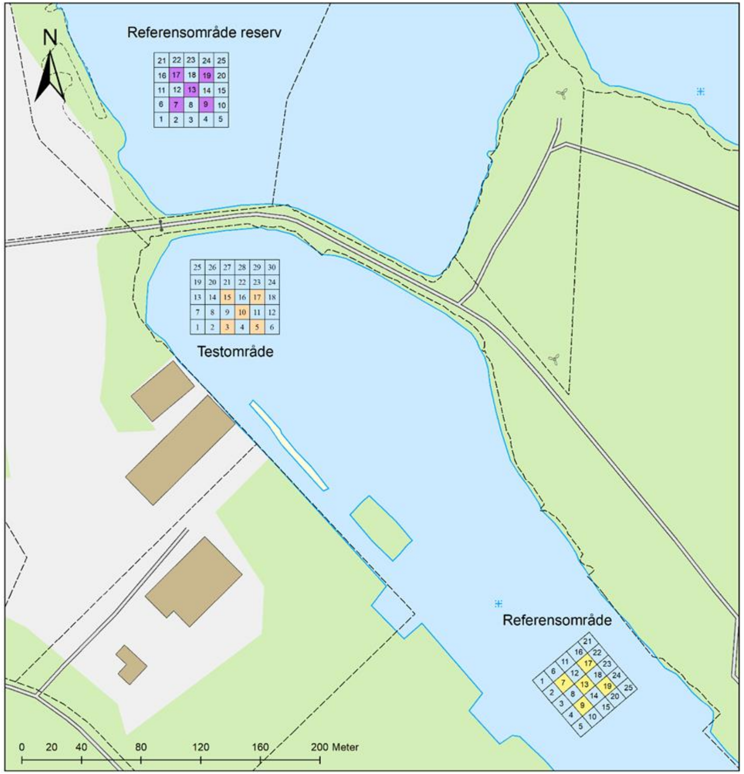
Föroreningssituation

5 replicate analyzed for trace elements and PAH

Halter i mg/kg TS

	Test	Referens
As	161-258	333-467
Cu	55-139	128-234
Hg	1,1-2,3	2,2-2,3
Pb	148-241	233-288
S	4 490-6 590	5 630-12 600
PAH_{16}	15-35	14-68



Capping remediation strategy: applicability to the Bureå sediments?

Frukostseminarium pilotprosjekt 2022

Gabrielle Dublet-Adli, Gerard Cornelissen, Espen Eek, Erlend Sørmo, Caroline Berge-Hansen, Maren Valestrand Tjønneland and Christian Maurice

Principle of sediment capping

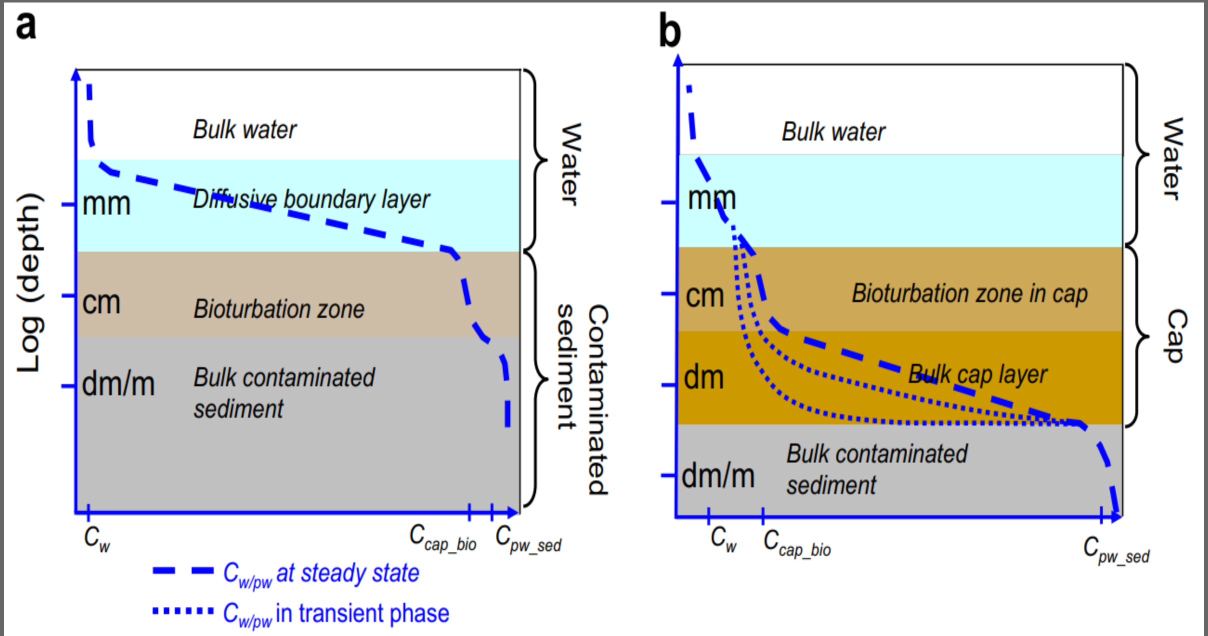


Figure from Eek et al., 2008

Boost natural attenuation, to:

- Isolate
- Limit suspension
- Limit diffusion

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Principle of sediment capping

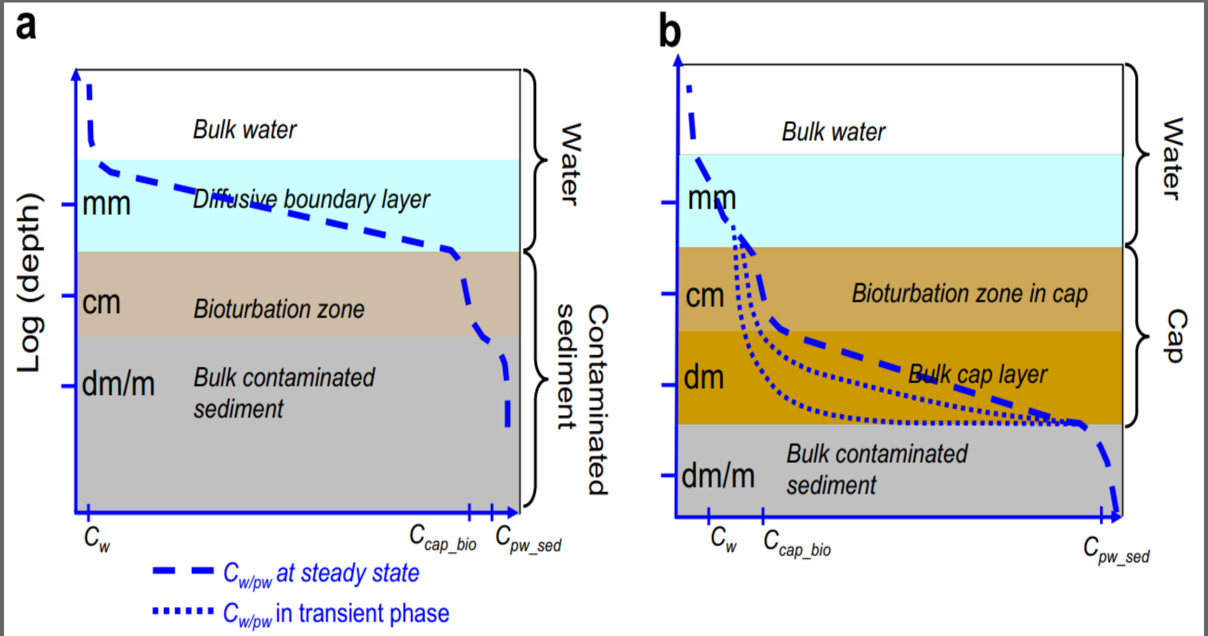

Figure from Eek et al., 2008

Boost natural attenuation, to:

- Isolate
- Limit suspension
- Limit diffusion

Thickness decided based on:

- Concentrations
- Material properties
- Bioturbation, erosion, slope, etc

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Sediment capping with activated sorbent

Capping Materials:

- Passive, e.g. sand, gravel – permeability
- Active, e.g. clay, biochar – sorption capacity

Effects of different active capping materials for different contaminants.

	cap material									
	sand		Organoclay		tires		Apatite		Activated carbon	
compound	CMC	CCC	CMC	CCC	CMC	CCC	CMC	CCC	CMC	CCC
Cd, pH 7	++/–	++/–	–/–	–/–	–/–	–/–	++/++	++/++	–/–	–/–
Cr, pH 7	+/–	+/–	–/–	–/–	–/–	–/–	–/–	–/–	–/–	–/–
Pb, pH 7	+++/–	++/–	+/–	–/–	+/–	+/–	++/++	++/++	–/–	–/–
Ag	+++/–	n.a.	–/–	n.a.	+/–	n.a.	–/–	n.a.	–/–	n.a.
As	+++/–	+++/–	–/–	–/–	–/–	–/–	–/–	–/–	–/–	–/–
Hg	+++/++	+++/+	++/+	++/+	+++/–	++/–	++/++	+/+	+/+	–/–
CH_3Hg	+++/–	+++/–	++/+	+/–	++/–	++/–	–/–	–/–	–/–	–/–
CN	–/–	–/–	–/–	–/–	–/–	–/–	–/–	–/–	–/–	–/–

[a] Symbols: – means cap complies with the USEPA CMC, or CCC after 100 yr within <50% CI; +, ++, and +++ mean cap complies with the CMC or CCC within mean, 75%, and 95% CI, respectively. First symbol means result for diffusion, second symbol means result for advection ($d_h/d_x = 0.05$). n.a. = there is no EPA CCC criteria for the compound.

from Viana et al., 2008

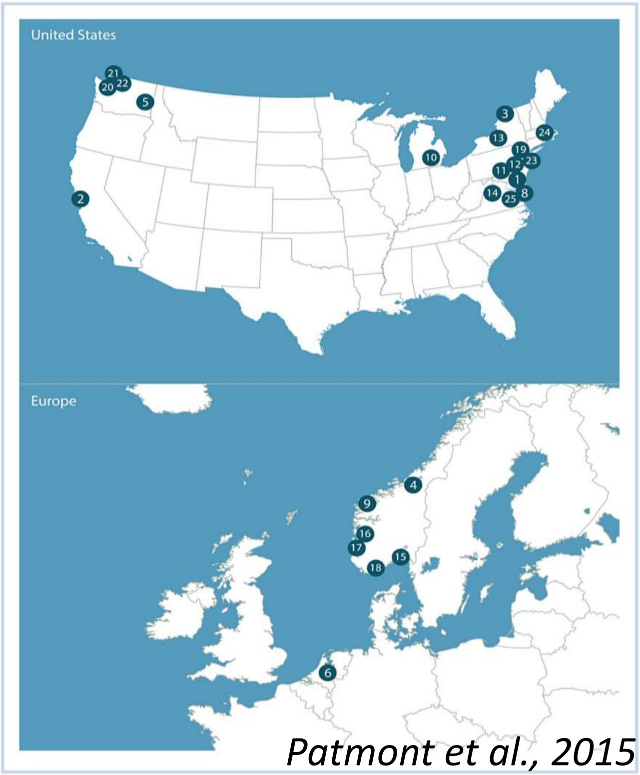
Examples of sediment capping in Norway

Sediment capping with activated carbon was used for remediation of:

- Dioxin-contaminated sediments
- Mercury-contaminated sediments
- PAH-contaminated sediments

In Norway:

- Capping combined with dredging
- So far, mostly passive cap or AC
- Activated biochar in the capping of Flekkefjord



In situ treatment field application sites involving capping with activated carbon or similar.

Patmont et al., 2015

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Advantages and limitations of sediment capping

Advantages of capping compared to dredging:

- Less invasive, less particle dispersion
- Faster
- Better environmental conditions in the decades after remediation
- Lower net environmental costs, especially in case of extended, moderate contamination levels.

But remediation results are sensitive to:

- Erosion,
- Stability issues and settlements,
- New contamination,
- Capping design (thickness, depth location of AC layer…),
- Choice of capping material (in case of AC: too fine particles are deleterious to benthic fauna, too large are inefficient for sorption)
- Multi-contamination

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Case of Bureå and cocktail of contaminants

Heavy metals, organometals & metalloids

Compound	Concentration in sediment (mg/kg)	Concentration in porewater (µg/L)	Concentration in the bay water (µg/L)
Fe	28 320	20	1100
Ba	463	46	11
→ **As**	**240**	**17**	**1,4**
→ **Pb**	**196**	<0,2	0,5
→ **Zn**	**183**	4,5	11
→ **Cu**	**93**	<1	2,6
V	37	0,2	0,3
Ni	17	1,8	2,5
Co	8,2	0,7	0,4
→ **Hg**	**1,7**	<0,02	<0,02
→ **Methyl-Hg**	**0,01**	ND	ND
Mn	0,43	**2120**	**58**

Mobile at high pH

Mobile at low pH

Produced under reducing conditions

PAHs

Compound	Sediment	Biochar	Bentonite
Naphthalene	0.72	0.09	< 0,05
Acenaphthylene	0.35	< 0,01	< 0,01
Acenaphthene	<0.10	< 0,01	< 0,01
Fluorene	0.26	< 0,02	< 0,01
Phenanthrene	1.3	0.07	< 0,02
Anthracene	0.63	< 0,01	< 0,01
Fluoranthene	2.72	0.05	< 0,01
Pyrene	2.2	0.04	< 0,01
Benz(a)anthracene	1.19	< 0,01	< 0,01
Chrysene	1.05	< 0,01	< 0,01
Benzo(b)fluoranthene	1.33	< 0,01	< 0,01
Benzo(k)fluoranthene	0.47	< 0,01	< 0,01
Benzo(a)pyrene	1.04	< 0,01	< 0,01
Dibenz(ah)anthracene	0.14	< 0,01	< 0,01
Benzo(ghi)perylene	0.61	< 0,01	< 0,01
Indeno(1,2,3-cd)pyrene	0.63	< 0,01	< 0,01
Sum PAH 16	**14.6**	**0.25**	**<LD**

$K_{ow} = 4$

$K_{ow} = 5$

$K_{ow} = 6$

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Can a sediment-capping improve the quality of Bureå benthic environment?

Main Hypothesis:
The upwards diffusion of PAH and Hg, will be limited by a capping and stopped by sorption on biochar

Question:
Will Arsenic be sorbed on biochar, and/or mobilised by locally higher pH?

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Experimental approach

Tests for Metal elements: finite sink (water)

Water
(NaCl 3g/L)
Capping
Sediment

→ As, Hg, etc

Concentration as a function of time (1,5h-96d)

Tests for PAHs: infinite sink (heptane)

Heptane
K_{ow} = 4,66*
Water
(NaCl 3g/L)
Capping
Sediment

→ 15 PAH

Concentration as a function of time (3d-400d)

Experimental approach

<u>5 recipes tested</u>

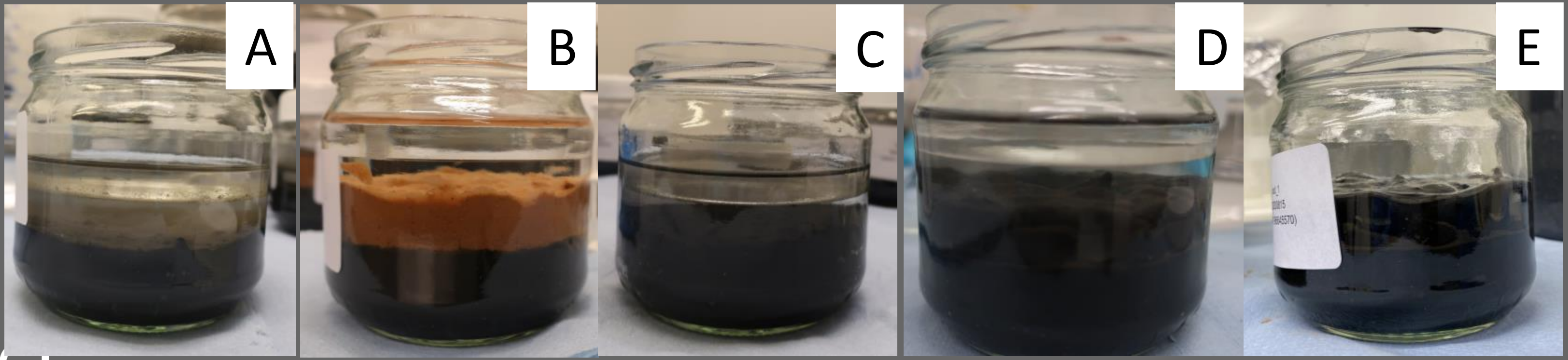
A. No treatment (control)

B. Only **bentonite** (2,6 ±0,4 kg/m^2) (~1.5 cm cap)

C. Only **biochar** (15 g/jar, i.e. 3 kg/m^2), mixed with the sediment

D. Biochar (0,7 ±0,1 kg/m^2) + **bentonite** (2,6 ±0,4 kg/m^2) (~1.5 cm cap)

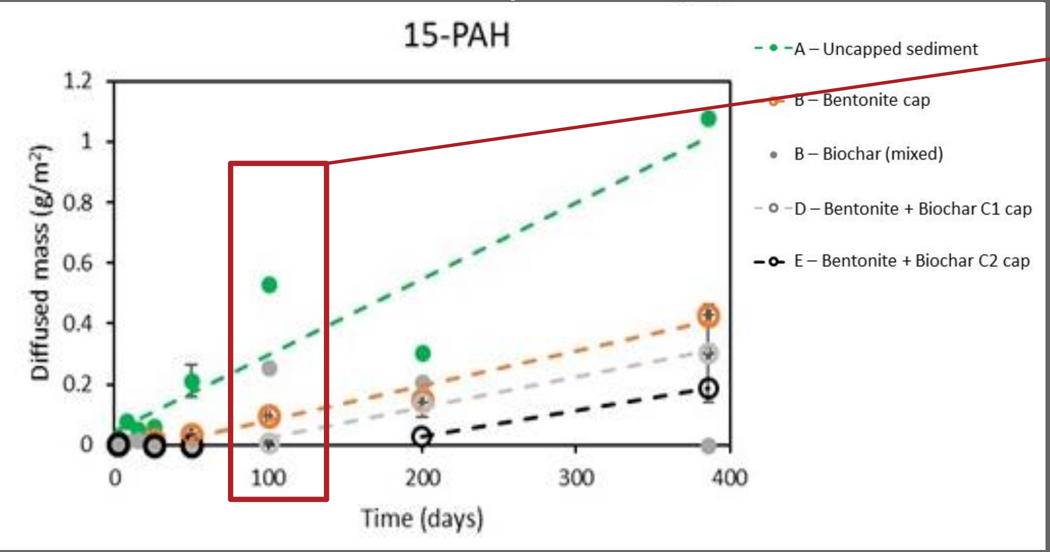
E. Biochar (1,8 ±0,1 kg/m^2) + **bentonite** (2,6 ±0,4 kg/m^2) (~1.5 cm cap)



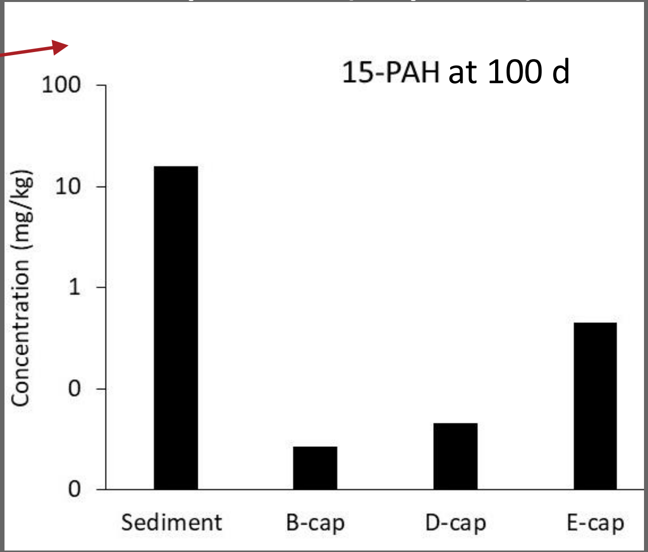
Results and discussion

- Positive effect of the capping: PAH diffusion limitation

Water phase



Solid phase (top cm)



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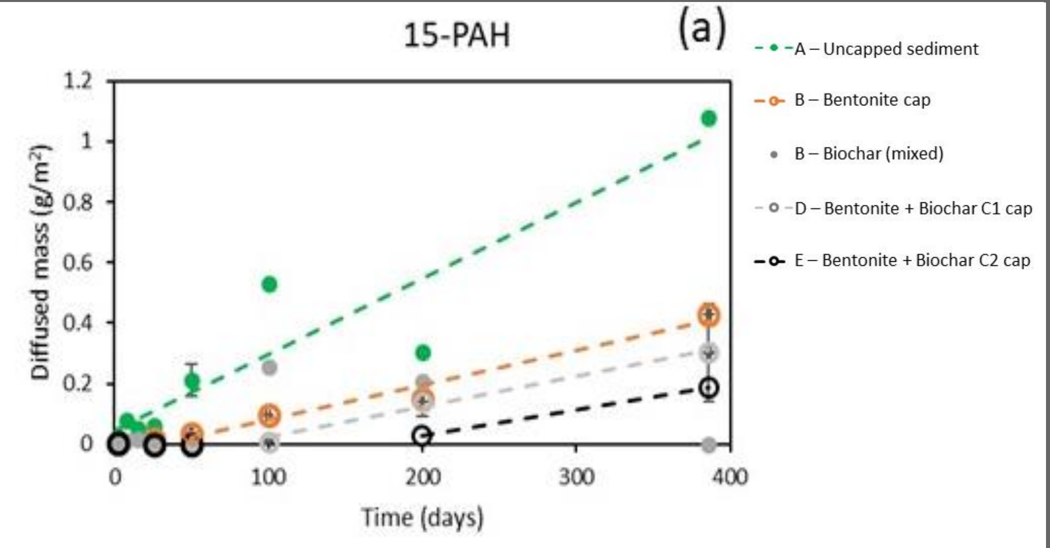
Results and discussion

- Positive effect of the capping: PAH diffusion limitation



Treatment	RE_B	RE_D	RE_E
15-PAH	56%	60%	65%
Acenaphtylene	0%	39%	92%
Fluoranthene	75%	95%	86%
Chrysene	79%	100%	100%

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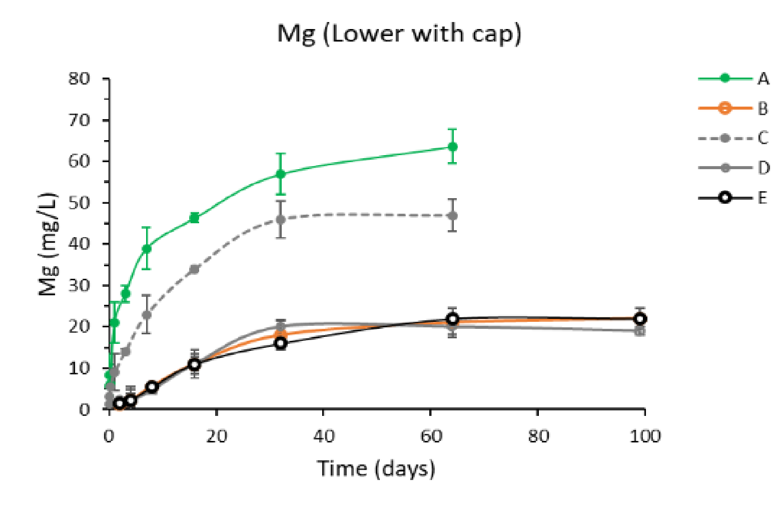
$RE = 1-(J_{cap}/J_{sed})$ (J is the flux from sediment to water, i.e. the slope after breakthrough as represented here with dashed lines)

Results and discussion

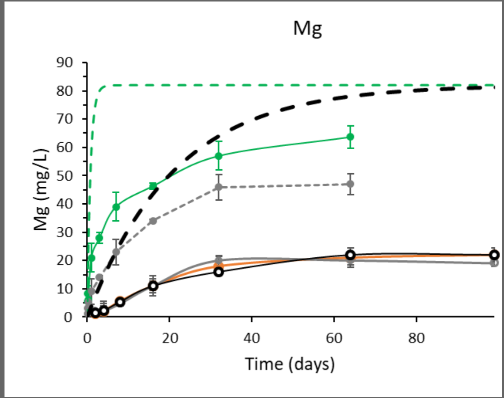
- Positive effect of the capping: metal diffusion limitation



$$J_{i\,\mathrm{sed}} = \frac{D_i}{\delta_{\mathrm{DBL}}}(C_{i\,\mathrm{pw}} - C_{i\,\mathrm{w}})$$

$$J_{i\,\mathrm{cap}} = \frac{\varepsilon \cdot D_i}{\tau \cdot (h_{\mathrm{cap}\,d} + \delta_{\mathrm{DBL}})}(C_{i\,\mathrm{pw}} - C_{i\,\mathrm{w}})$$

Eek et al., 2008



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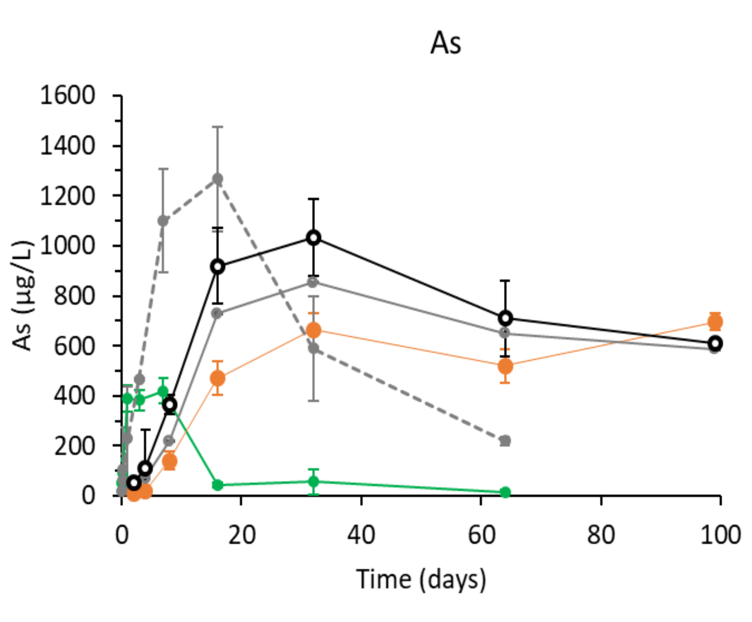
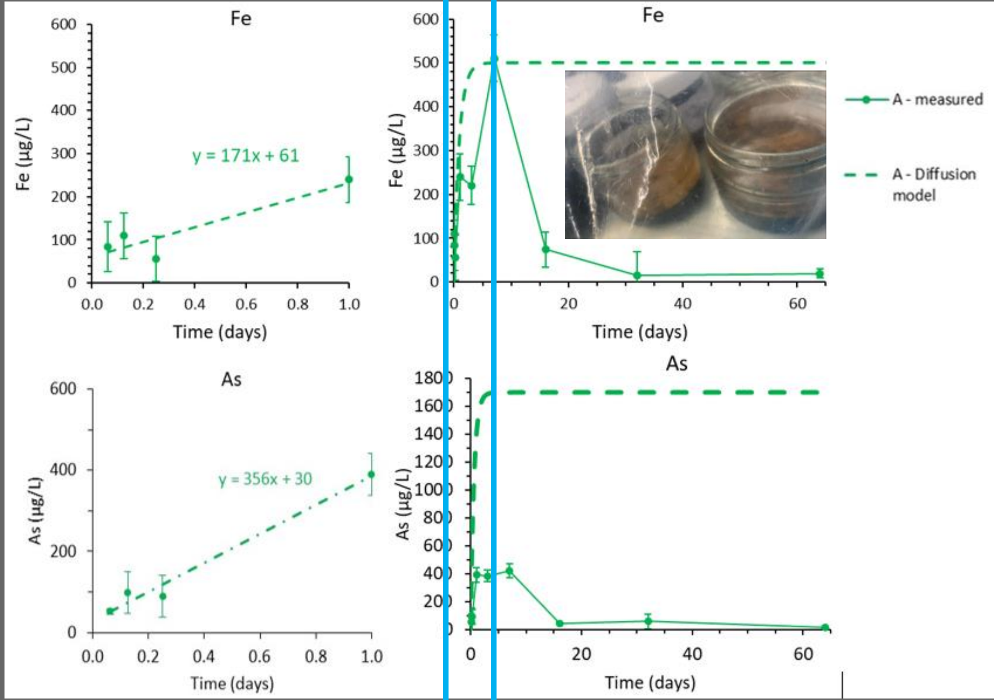
At Bureå, April 2021: 1 mg/L<O_2 < 2 mg/L

Results and discussion

O_2 < 1 mg/L

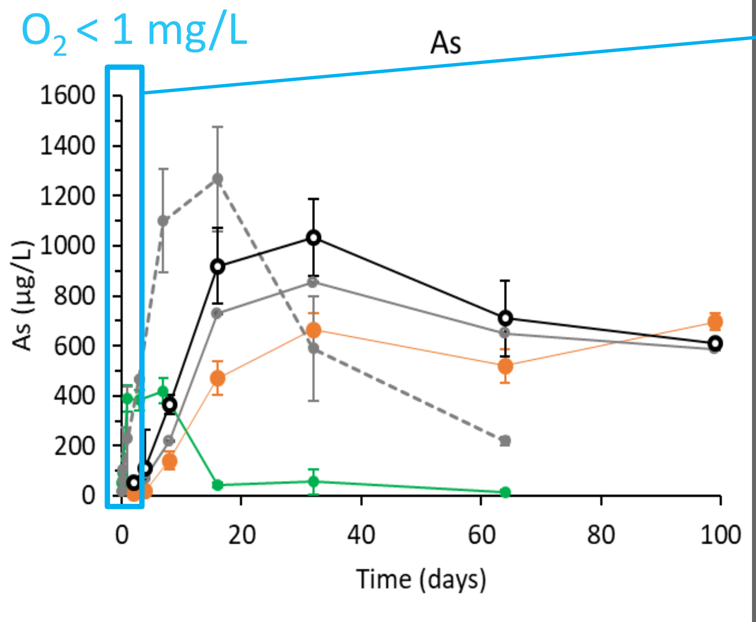
- Ambiguous effect of capping on As

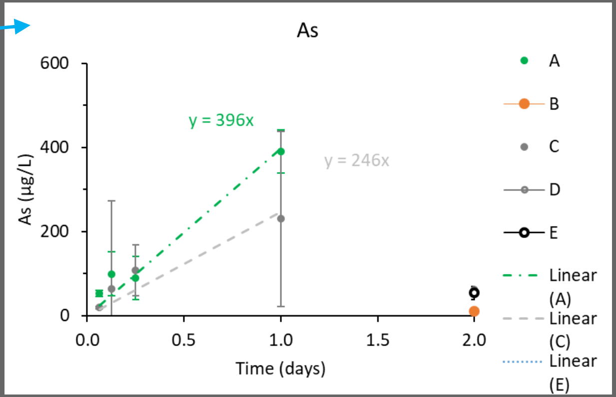




Ambiguous effects on As

- Positive effect of the capping: As diffusion limitation under anoxia





	A	B	D	E	Model sed	Model cap
As						
Initial flux (µg. $cm^{-2}.s^{-1}$)	1E+00	2E-02	9E-02	9E-02	3E+00	3E-01
RE (%)		100	100	100		88

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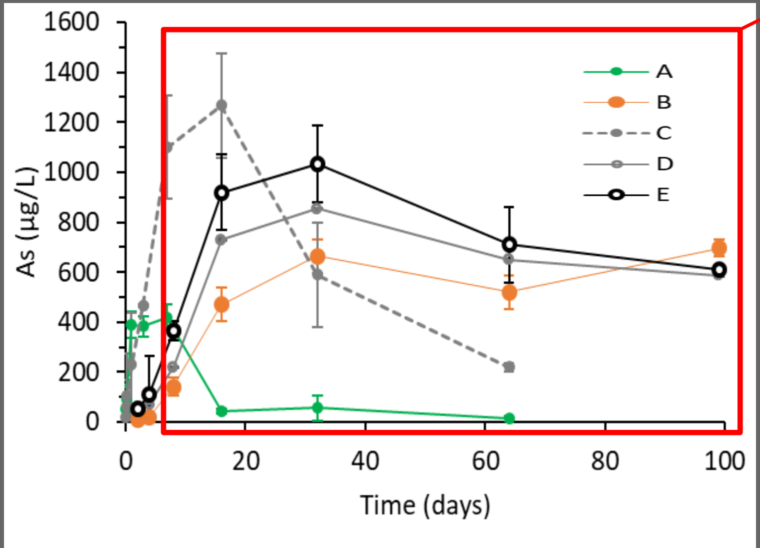
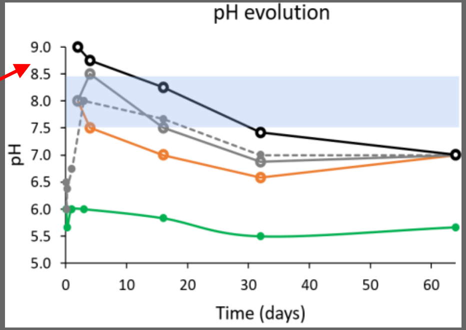
Ambiguous effects on As

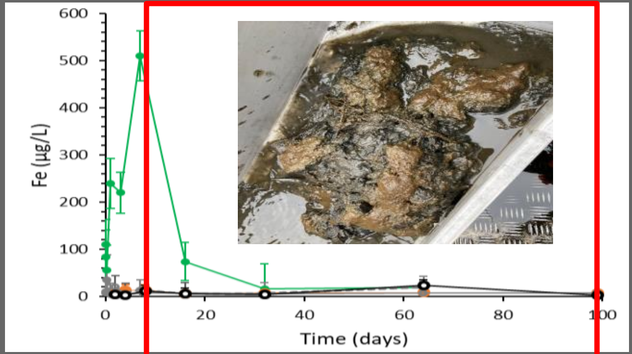
- Negative effect of the capping: As mobilisation at higher pH and lower redox

As

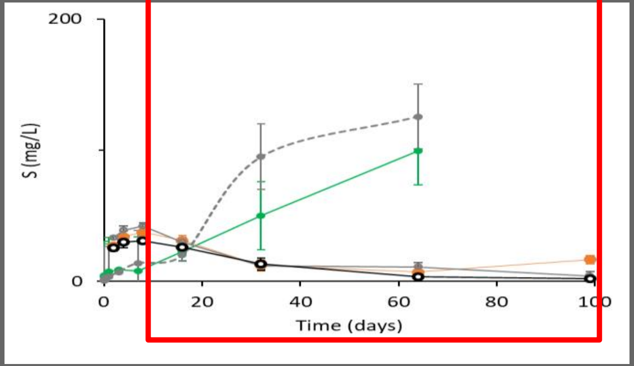




Fe

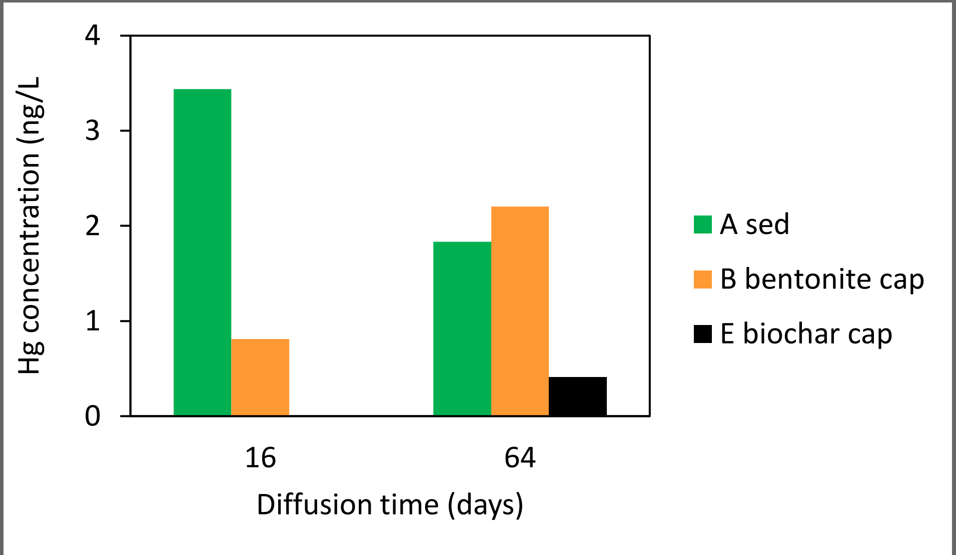


S



What about Hg?

- No Hg detected at NMBU (detection limit 0.04 µg/L)
- Fe, S, As results suggest that O_2 diffusion to sediment is limited by the capping -> methylation favored??



16d:

- capping limits Hg diffusion?
- Hg sorbs on biochar?

64 d:

- Confirms Hg sorbed on biochar?
- Why would Hg concentration decrease in A?
  - Hg sorbed on Fe oxides?
  - More data would be needed to confirm the significance

At NIVA: LOD 0.1 ng/L

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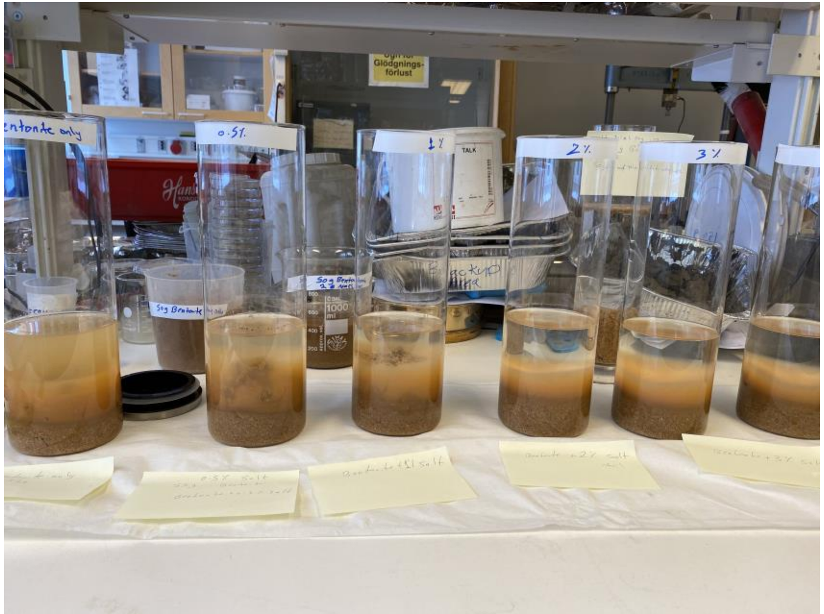
Laboratory test – recipe

- Amouts of biochar, bentonite, salt and the amout of water
- Expected thickness of the layer
- Mixing time
- Consistency of the mixture

- Recipe: Water/solid ratio: 7 ± 0,5
  - Bentonit: 6 000 kg
  - Biochar: 1 400 kg
  - Salt: 100 kg
  - Water: 45 000 kg



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Mixing at different scale and test application in aquarium

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Capping at the lab scale

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Capping at the pilot scale
Betongpump prolonged with a floating pipe

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Mixing and transport in a concrete truck

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Spreading of the capping

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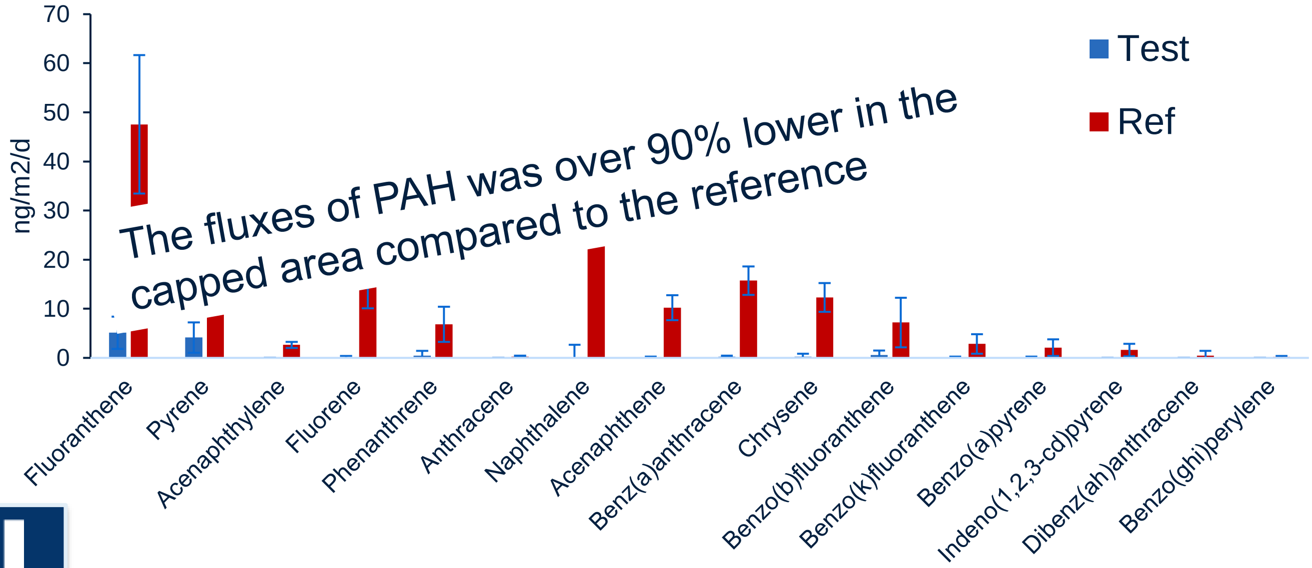
Application of the capping

Turbidity plume

SPMD membrane and flux chambers

- The PAH-fluxes were measured with flux chambers
- Test and reference area

Flux of PAH from the capped (Test) and the reference (Ref) area to the sea water, in ng/m²/d



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Discussion (The capping function)

- The mixture sank rapidly to the bottom
- No measurable excess turbidity (material loss)
- The capping was efficient to reduce PAH-diffusion
- The capping was still in place after one year but difficult to assess ocularly.

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Discussion (The pilot experiment)

- Minor issues with clogging – add water, salt, bentonite and biochar
- The logistic was not optimal
- Measuring the fluxes of redox sensitive trace elements in a relevant way is difficult

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Discussion (up-scaling)

- Up-scaling of the method
- Found a better structure material (sediment, stone dust, …)
- The figures from the pilot cannot be used to estimate the costs for field application
- E.g. mixing and pumping from a barge (Photo: example from a Norwegian case)

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Future work

- Assessing the effect on redox sensitive trace elements
- Replace bentonite with other structure material
- Long term efficiency
- Effect on bottom fauna

TACK FÖR UPPMÄRKSAMHETEN

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