

## Actual risk assessment and in-situ remediation of Norwegian harbour sediments

Gerard Cornelissen<sup>1,2</sup>, Dag Broman<sup>1</sup>, Kristoffer Næs<sup>3</sup>, Gijs Breedveld<sup>2</sup>, Amy M. P. Oen<sup>2</sup>, Anders Ruus<sup>3</sup>

<sup>1</sup> Department of Applied Environmental Science (ITM), Stockholm University, Sweden.

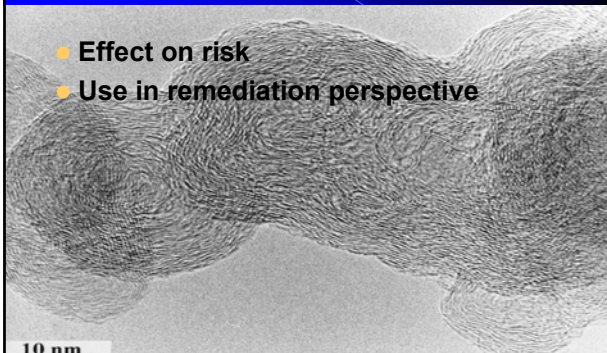
<sup>2</sup> Department of Environmental Engineering, Norwegian Geotechnical Institute (NGI), Norway

<sup>3</sup> Norwegian Institute for Water Research (NIVA), Norway.

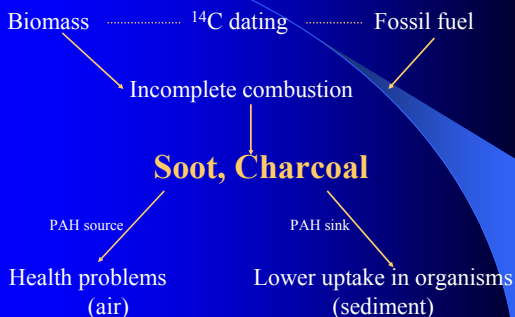


## Soot, coal and charcoal

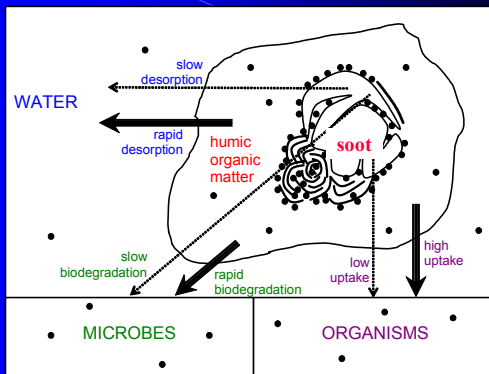
- Effect on risk
- Use in remediation perspective



## Soot and charcoal



## Strong binding to soot



Cornelissen Gustafsson Bucheli Jonker Koelmans Van Noort. critical review. Environ. Sci. Technol. 2005. 6881-6893

## How much soot do we find in sediments?

Sediment literature:

19 studies, 300 samples

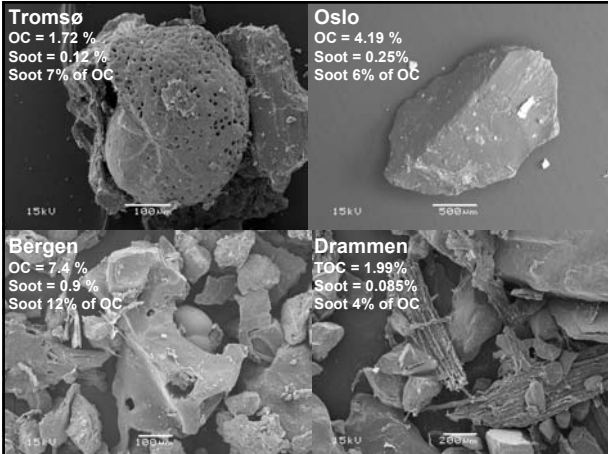
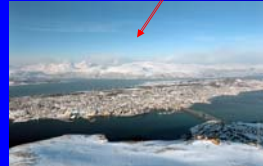
Median Soot/charcoal 10% of TOC, (2-30%)

Cornelissen Gustafsson Bucheli Jonker Koelmans Van Noort, critical review, Environ. Sci. Technol. 2005, 6881-6893

## Norwegian contaminated harbour sediments



Oslo (OS)  
Bergen (BG)  
Tromsø (TR)  
Drammen (DR)



Soot binds PAHs factor of 50-1000 stronger than humic organic matter!

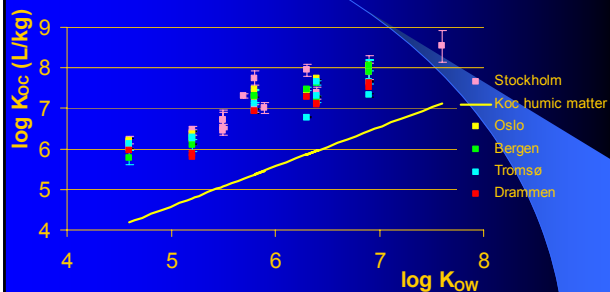
	Phe	BaP
OC-water distribution ratio:	$10^{4.2}$	$10^{5.7}$
Soot Oslo sediment	$10^{6.8}$	$10^{7.9}$
Soot Bergen sediment	$10^{6.3}$	$10^{7.8}$
Soot Tromsø sediment	$10^{6.8}$	$10^{7.1}$
Soot Drammen sediment	$10^{6.4}$	$10^{7.5}$

Cornelissen Breedveld Kalaitzidis Christianis Oen, Environ. Sci. Technol. 2006, 40, 1197-1203

## Strong binding to soot/charcoal (and to activated carbon!) for many compound classes

- PAHs (Jonker and Koelmans 2002; Bucheli and Gustafsson 2003; Cornelissen et al. 2004)
- (planar) PCBs (Jonker and Koelmans 2002; Bucheli and Gustafsson 2003; Cornelissen et al. 2004)
- PCDDs (Barrington et al. 2002)
- PCDFs (Barrington et al. 2002)
- PBDEs (Barrington et al. 2002)
- Chlorobenzenes (Kleimeidam et al. 2002; Ran et al. 2004; Braida et al. 2001; Chun et al. 2004)
- Chloroalkanes (Grathwohl 1990; Cornelissen et al. 2005)
- Diuron, butylate (Yang and Sheng 2003a,b; Cornelissen et al. 2005)

## Organic compounds in field: Binding 100 times stronger than humic materials!



Cornelissen Breedveld Kalaitzidis Christianis Oen, Environ. Sci. Technol. 2006, 40, 1197-1203

## Measured uptake in worms and snails (BSAF for 16 PAHs)

	Worms	Snails
Oslo	0.004	0.01
Bergen	0.009	0.01
Tromsø	0.01	0.009

$BSAF = C_{lipid}/C_{OC}$   
BSAF = 1 for humic organic matter!

Cornelissen Breedveld Næs Oen Ruus, Environ. Toxicol. Chem. 2006, 25, 2349-2355

## Measured uptake in worms and snails (BSAF for 16 PAHs)

	Worms	Snails
Oslo	0.004	0.01
Bergen	0.009	0.01
Tromsø	0.01	0.009

$BSAF = C_{lipid}/C_{OC}$   
BSAF = 1 for humic organic matter!

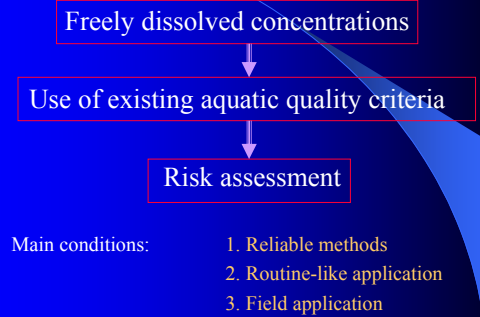

Uptake from sediments factor of 100 lower than uptake from humic organic matter!

Cornelissen Breedveld Næs Oen Ruus, Environ. Toxicol. Chem. 2006, 25, 2349-2355

### Implications for risk assessment: Effect of strong binding to soot on actual risk

Binding stronger than assumed (factor 100)  
 ↓  
 Freely dissolved porewater concentrations lower  
 ↓  
 Uptake in organisms lower (factor 100)  
 ↓  
 Actual risk factor 100 lower

### Improved chemical risk assessment

### Risk assessment for sediment: total sediment contents

	Sediment Quality Guideline (µg/kg)	Sediment Content (µg/kg)
<b>Phenanthrene</b>	543	
Oslo		570
Drammen		70
Bergen		4,600
Tromsø		770
<b>Benzo[a]pyrene</b>	33	
Oslo		1,450
Drammen		200
Bergen		5,000
Tromsø		570

### Risk assessment for sediment: free porewater concentrations

Sediment	Water Quality Guideline (ng/l)	Free concentration in porewater (ng/l)
<b>Phenanthrene</b>	3,200	
Oslo		16.8
Drammen		3.8
Bergen		128
Tromsø		59
<b>Benzo[a]pyrene</b>	5	
Oslo		3.3
Drammen		0.33
Bergen		3.8
Tromsø		2.8

## Measuring free concentrations in sediment and water

- In **sediment porewater**:  
easy, take sediment to the lab and shake with passive sampler
- In **overlying water**:  
more difficult, has to be done in the field



## Risk assessment of overlying water



POM 500  $\mu\text{m}^{\text{a}}$

POM 55  $\mu\text{m}$

SPMDs: no equilibrium!

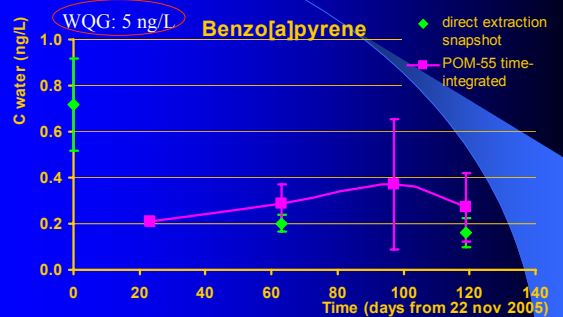
<sup>a</sup> Polyoxymethylene, Jonker and Koelmans, Environ. Sci. Technol 2001, 3742

## Deployment in field (Oslo harbour)



- Deployed 22 november until now
- Measured  $C_{\text{water}}$  (total extraction) at several times
- 1 m over bottom, depth 9-65 m, current 2-10 cm/sec

## Deployment in field: POM 55 $\mu\text{m}$



## Advantages of equilibrium passive samplers

- Time-integrated measurements
- Equilibrium in 3-6 weeks in the field
- Free concentrations
- Low detection limits (< 0.1 pg/L)
- No pumping for e.g. PCBs, dioxins

## Advantages of equilibrium passive samplers

- Time-integrated measurements
- Equilibrium in 3-6 weeks in the field
- Free concentrations
- Low detection limits (< 0.1 pg/L)
- No pumping for e.g. PCBs, dioxins

Expose 10 g  
passive sampler

## Advantages of equilibrium passive samplers

- Time-integrated measurements
- Equilibrium in 3-6 weeks in the field
- Free concentrations
- Low detection limits (< 0.1 pg/L)
- No pumping for e.g. PCBs, dioxins

Expose 10 g  
passive sampler

OR

## Advantages of equilibrium passive samplers

- Time-integrated measurements
- Equilibrium in 3-6 weeks in the field
- Free concentrations
- Low detection limits (< 0.1 pg/L)
- No pumping for e.g. PCBs, dioxins

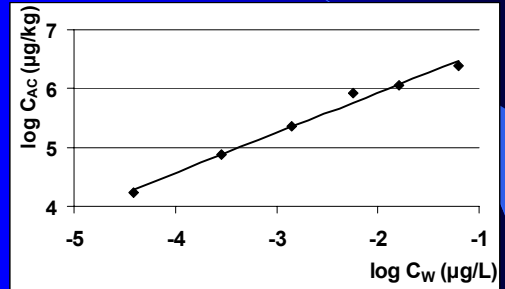
Expose 10 g  
passive sampler

OR

Extract 10.000-  
100.000 L water

## Remediation perspective of charcoal: Activated Carbon (AC) amendment

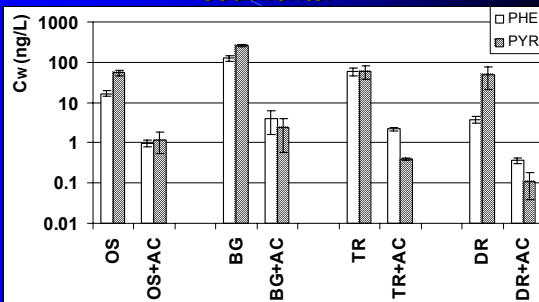
## How strong is the binding to AC?



$K_{AC} 10^{8.08}$  at 1 ng/L ( $K_{SOOT} 10^7$ ,  $K_{OC} 10^4$ ) (phenanthrene)

Cornelissen Breedveld Kalaitzidis Christianis Oen, Environ. Sci. Technol. 2006, 40, 1197.

## 2% AC very effective for Norwegian sediments!



Free concentrations in water reduced by 95-99.5%!

## AC does not influence habitat quality

	Lipid contents (%)			
	No AC		AC 2 %	
	Worms	Snails	Worms	Snails
Clean sed.	0.7	0.8		
Oslo	1.3	1.3	0.5	1.2
Bergen	0.7	1.2	1.0	1.2
Tromsø	0.8	1.3	0.6	1.6
	<b>No AC: 1.1 ± 0.3 %</b>		<b>AC: 1.0 ± 0.4 %</b>	

Cornelissen Breedveld Næs Oen Raus, Environ. Toxicol. Chem. 2006, 25, 2349-2355

## Effect of AC on uptake

Reduction in PAH uptake

	Worms	Snails
Oslo	85%	30%
Bergen	20%	10%
Tromsø	83%	~ 0%

- AC less effective than expected!
- Possible explanation: AC in foldings in snail skin (tested now)
- Promising technique for all other compound groups that sorb strongly to soot and coal

Thank you!!

