

# ERMS Workshop May 3-4th

## Task 1 "Toxicity"

### PNEC approaches for toxicity in the water column and the sediments

Toxicity task members

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# Outline

- Topics covered in the Task 1 “Toxicity”
- Selection of drilling constituents for inclusion in the EIF drilling discharges ( $EIF_{DD}$ )
- Conclusion sediment toxicity review
- Selected PNEC approaches for the water column
- Selected PNEC approaches for the sediments

# Topics - Task 1

- Selection of constituents for inclusion in EIF drilling discharges
- Sediment toxicity literature review and quality on selected metals and PAHs
- Literature review: Determination of partition coefficients ( $\log K_p$ ) for metals in barite in seawater and in sediments for calculation of PEC of metals for the water column and the sediments
- Selection of approach for calculation of PNEC in the water column and in the sediment compartment
- Validation of toxicity threshold values derived from literature data versus field data

# Selection of constituents for inclusion in EIF<sub>DD</sub>

- **Three categories of chemicals:**
  - Metals (as ingredients of added chemicals og cuttings)
  - Natural organic compounds (PAHs, aliphatic hydrocarbons etc.)
  - Added chemicals (drilling fluid chemicals e.g. non-PLONOR, PLONOR chemicals etc.)
- **Selection criteria:**
  - The total amount used/discharged (PLONOR)
  - Bioavailability and toxicity potential
  - Potential for non-toxic disturbances (O<sub>2</sub> depletion, burial etc.)

# Selected metals for inclusion in EIF<sub>DD</sub> sediments

Metal	Abundant in Mud/Cuttings?	Potentially bioavailable?	Potential toxic?	Include in EIF <sub>DD</sub> ?
Arsenic	No	No	Yes	No
Barium	Yes	No	No	No
Cadmium	Yes	Yes	Yes	Yes
Chromium	No	Yes	Yes	Yes
Copper	No	Doubtful	Yes	Yes <sup>a</sup>
Lead	Yes	Yes	Yes	Yes
Mercury	Yes	Doubtful	Yes	Yes <sup>a</sup>
Nickel	No	Doubtful	Yes	No
Zinc	Yes	Yes	Yes	Yes

a. Cu and Hg is of concern because of its high toxicity

# Selected metals for inclusion in EIF<sub>DD</sub> water column

- Main source of heavy metals (NCS):
  - Weighting agents (barite, ilmenite)
  - Clays

Metal	Include in EIF <sub>DD</sub> ?
Arsenic	No
Barium	No
Cadmium	Yes
Nickel	Yes
Copper	Yes
Lead	Yes
Mercury	Yes
Chromium	No
Zinc	Yes

# Selected natural organic compounds for inclusion in $EIF_{DD}$ of the sediments

- Organic compounds with  $\log Kow > 3$
- Assumed attached to cutting cuttings/mud particles – deposition down on the sea floor
- Inclusion in  $EIF_{DD}$  calculation of the sediments:
  - PAHs
  - Aliphatic hydrocarbons
- Not assumed to contribute to the environmental risk in the water column

# Selected "added chemicals" for inclusion in EIF<sub>DD</sub>

- All non-PLONOR chemicals
- Selected PLONOR chemicals or green chemicals  
NCS: Selected the 6 out of 17 most discharged PLONOR chemicals for Hydro, Total and Statoil in 2003)
- Inclusion in EIF<sub>DD</sub> water column:
  - Chemical substances with  $\log Kow/Koc < 3$  (non-PLONOR)
  - Suspended particulate matter (weighting agents: barite, ilmenite etc.)
- Inclusion in EIF<sub>DD</sub> sediments:
  - Chemical substances with  $\log Kow/Koc > 3$  (non-PLONOR)
  - Weighting agents: barite, ilmenite etc.
  - Bentonite clay and quarts etc.



# Sediment toxicity literature review

- Natural occurring components:
  - Metals (Cd, Cu, Zn, Pb, Hg and Cr)
  - PAHs
- 6 PLONOR chemicals
- Species and life-stages living in close contact with the sediment
- Controlled spiked sediment exposures with single elements

# Conclusion toxicity literature review - metals

- Lack of toxicity endpoint data from long-term studies (few chronic data)
- Limited number of species/taxonomic groups
- For all metals the number of species is too low to define a reliable SSD plot (needed to define the PEC/PNEC to the risk relationship in the model)
- Toxicity related to total sediment concentration of metals is poorly supported by several studies (DiToro et al. 1992)



- PNEC derivation based on quality assured sediment toxicity data for metals and PAHs (TGD approach) was concluded insufficient due to lack of reliable toxicity data

# Conclusion sediment toxicity literature review PLONOR chemicals

- PLONOR: Sediment toxicity data are poorly available (old studies, on freshwater species)

# Selected PNEC approach - EIF water column

## Heavy metals

PNEC approach	Components included	Input to $PNEC_{water}$ derivation
<ul style="list-style-type: none"> <li>- Dutch Guideline (Crommentuin et al., 1997)</li> <li>- Application of water toxicity data using the SSD approach</li> </ul>	Cu, Pb, Zn, Hg, Cd, Ni (weighting agents)	<p><b>Option 1:</b> <math>MPA_{water}</math> (<math>PNEC_{water}</math> excl. background conc.)*</p> <p><b>Option 2:</b> <math>MPC_{water}</math> (<math>PNEC_{water}</math> incl. regional/local background conc.)*</p>

\*Will be replaced by updated PNEC values (OLF project) for metals (EIF produced water) by using the SSD approach recommended by the TGD (2003).

# PNEC heavy metals – water column

- Calculation  $MPC_{\text{water}}$  – Dutch guidance (Crommentuijn et al., 1997):

$$MPC_{\text{water}} = MPA_{\text{water}} (+ Cb_{\text{water}})$$

in which:

$MPC_{\text{water}}$  = Maximum Permissible Concentration in the surface water ( $\mu\text{g/l}$ )

$MPA_{\text{water}}$  = Maximum Permissible Addition in the surface water ( $\mu\text{g/l}$ )

$Cb_{\text{water}}$  = background concentration in the surface water ( $\mu\text{g/l}$ )

$$MPA_{\text{water}} \sim PNEC_{\text{water}}$$

$$Kp_{\text{sediment-water}} \sim Kp_{\text{barite-water}}$$

- Application of water toxicity data using the SSD approach

# PNEC values – water column

## Heavy metals

Heavy metals	$PNEC_{\text{water}} \sim MPA_{\text{water}}^*$
Cadmium	0,34
Mercury	0,01
Lead	11
Zinc	6,6
Chromium	8,5
Copper	1,1

\* Dutch guidance, Crommentuijn et al., 1997

# Selected PNEC approach - EIF water column

## Natural organic substances

PNEC approach	Components included	Input to PNEC <sub>water</sub> derivation
PAHs, naphthalenes, aliphatic hydrocarbons etc.	Not included in the risk calculation of the water column; <b>log Kow/Koc &gt; 3</b>	<b>None</b>

# Selected PNEC approach - EIF water column

## Added chemicals

PNEC approach	Components included	Input to PNEC <sub>water</sub> derivation
<ul style="list-style-type: none"> <li>- TGD (1996/2003)</li> <li>- Application of assessment factors</li> </ul>	Chemicals on product level or preferably on substance level with <b>log Kow/Koc &lt; 3</b>	<ul style="list-style-type: none"> <li>- <b>PNEC<sub>water</sub></b> derived from available toxicity data (preferably on substance level)</li> <li>- Intermittent release (lowered AF by a factor of 10)</li> <li>- Acute data: Application of an AF of 100*</li> </ul>

•TGD definition "Intermittent release": Discharge occurring infrequently: less than once per month and for no more than 24 hours

\* Cementing chemicals, BOP chemicals, weighting agents etc.



# Selected PNEC approach - EIF sediment

## Heavy metals

PNEC approach	Components included	Input to $PNEC_{\text{sediment}}$ calculation
<p><b>Equilibrium Partitioning Method (EqP)</b></p> <ul style="list-style-type: none"> <li>- Dutch Guideline</li> <li>- Based on water toxicity data (<math>MPA_{\text{water}}</math>)</li> </ul>	<p>Cu, Pb, Zn, Cr, Hg, Cd</p>	<p><b>Option 1:</b> <math>MPC_{\text{sediment}} (MPA_{\text{water}} \times Kp_{\text{sediment-water}} + Cb_{\text{sediment}})</math></p> <ul style="list-style-type: none"> <li>- includes sediment background conc. (<math>Cb_{\text{sediment}}</math>)</li> </ul> <p><b>Option 2:</b> <math>MPC_{\text{sediment}} (MPA_{\text{water}} \times Kp_{\text{sediment-water}} + Cb_{\text{sediment}})</math></p> <ul style="list-style-type: none"> <li>- excludes sediment background conc. (<math>Cb_{\text{sediment}}</math>)</li> </ul>

# Selected PNEC approach for metals in sediments

## Equilibrium Partitioning Method (EqP)

- Dutch Guidance - Crommentuijn et al., 1997, 2000:

$$MPC_{\text{sediment}} = MPA_{\text{water}} \times Kp_{\text{sediment-water}} + Cb_{\text{sediment}}$$

In which:

$MPC_{\text{sediment}}$  = Maximum Permissible Concentration in marine sediment [mg/kg]

$Kp_{\text{sediment}}$  = partition coefficient sediment and water [m<sup>3</sup>/m<sup>3</sup>]

$MPC_{\text{water}}$  = Maximum Permissible Concentration in the surface water

$Cb_{\text{sediment}}$  = background concentration in the sediment (mg/kg)

$$PNEC_{\text{sediment}} = PNEC_{\text{water}} \times Kp_{\text{barite-water}} + Cb_{\text{sediment}}$$

# PNEC values – sediments

## Heavy metals

Metals	Log $K_p$ <sub>barite-water</sub> **	$K_p$ <sub>barite-water</sub> **	PNEC <sub>sediment</sub> (MPA <sub>sediment</sub> ) *	Background conc. (Cb) ***	PNEC <sub>sediment Cb</sub> (MPC <sub>sediment</sub> )
	L/kg	L/kg	mg/kg	mg/kg	mg/kg
Cadmium	1,46	29	0,01	0,037	0,047
Mercury (methyl)	4,79	61660	0,62	0,021	0,638
Lead	1,9	79	0,87	10,7	11,57
Zinc	1,84	69	0,46	20,7	21,16
Chromium	3,24	1738	14,77	14,6	29,37
Copper	1,64	44	0,05	4,1	4,148

\* Dutch guidance, Crommentuijn et al., 1997

\*\*Trefry et al. 2005 (applied to sediments)

\*\*\* Mean background sediment concentration for the NCS

# Selected PNEC approach - EIF sediment

## Natural organic substances

PNEC approach	Components included	Input to PNEC <sub>sediment</sub> calculation
<b>Equilibrium Partitioning Method (EqP)</b>	Naphthalenes, PAHs 2-3 ring, PAH 4+, aliphatic hydrocarbons <b>(log Kow/Koc &gt; 3)</b>	$\text{PNEC}_{\text{produced water}} * Kp_{\text{sediment}}$

# Selected PNEC approach - EIF sediment compartment

## "Added" chemicals

PNEC approach	Components included	Input to PNEC <sub>sediment</sub> calculation
<b>Equilibrium Partitioning Method (EqP)</b>	Drilling fluid chemicals on product level or preferably on substance level with  <b>log Kow/Koc &gt; 3</b>	<b>Kp<sub>sediment</sub></b> and <b>PNEC<sub>produced water</sub></b> derived from HOCNF data

# Selected PNEC approach for organic substances in sediments

## Equilibrium Partitioning Method (EqP)

- US-EPA, 1997, 2003

$$SQC = WQC * Kp_{\text{sediment}}$$

$$PNEC_{\text{sediment}} = PNEC_{\text{water}} \times Kp_{\text{sediment-water}}$$

in which:

SQC = Sediment Quality Criteria (mg/kg) or  $PNEC_{\text{sediment}}$

$Kp_{\text{sediment}}$  = partition coefficient between sediment and water (l/kg)

WQC = Water Quality Criteria (mg/l)

# PNEC values – sediments

## Natural organic substances

PAHs	Log K <sub>ow</sub>	Log K <sub>oc</sub>	K <sub>oc</sub>	Kp	PNEC <sub>water</sub> (mg/L)	PNEC <sub>sediment</sub> (µg/g dry wt) 1%	PNEC <sub>sediment</sub> (µg/g oc)
C0-C3 naphthalenes	4,064	3,9953	9891	297	0,021	2,05	205,46
2-3 ring PAHs	4,9555	4,8717	74416	2233	0,00015	0,11	11,16
4+ ring PAHs	5,9998	5,8981	790861	23726	0,00005	0,40	39,54
Aliphatic hydrocarbons	?	?	?		0,040		





# Selected PNEC approach in sediments – metals

## Equilibrium Partitioning Method (EqP)

- Based on Crommentuijn et al., 1997 – Dutch guidance

$$\text{MPA}_{\text{sediment}} = \text{MPA}_{\text{water}} \times K_{p \text{ sediment-water}}$$

- **MPA<sub>sediment</sub>**: Maximum Permissible Additon for the sediment compart.
- **MPA<sub>water</sub>** : Maximum Permissible Additon for the water compart.
  - defined as the maximum concentration of a metal allowed to be added to background concentration in water
  - derived from laboratory toxicity data (NOECs) using SSD approach
- **K<sub>p sediment-water</sub>**: Partition coefficient between sediment and water based on Dutch monitoring data (K<sub>p barite-water</sub> from E. Crecelius)

# Equilibrium Partitioning Method (EqP) - metals

$$MPA_{\text{sediment}} \sim PNEC_{\text{sediment}}$$

$$MPA_{\text{water}} \sim PNEC_{\text{water}}$$

$$Kp_{\text{sediment-water}} \sim Kd_{\text{barite-water}}$$

- $Kp_{\text{sediment-water}}$  replaced by  $Kd_{\text{barite-water}}$  for the sediment (Trefry et al., 2005)

$$PNEC_{\text{sediment}} = PNEC_{\text{water}} \times Kd_{\text{barite-water}}$$

## Equilibrium Partitioning Method (EqP) - metals

- **MPC<sub>sediment</sub>** = Maximum Permissible Concentration is the concentration of metals in sediment above which risk for the ecosystem is considered unacceptable, taking the natural background concentration into account

$$\text{MPC}_{\text{sediment}} = \text{MPA}_{\text{sediment}} + \text{Cb}_{\text{sediment}}$$

$$\text{MPC}_{\text{sediment}} \sim \text{PNEC}_{\text{sediment}} \text{ Cb}$$

$$\text{PNEC}_{\text{sediment}} \text{ Cb}^* = \text{PNEC}_{\text{sediment}} + \text{Cb}_{\text{sediment}}$$

\*  $\text{PNEC}_{\text{sediment}} \text{ Cb}$  adjusted for regional background concentration

# PNEC<sub>sediment</sub> approaches – Validation

Approach	Components included	Input to PNEC <sub>sed</sub> calculation	Input PEC model calculation
<b>MOD</b>	Cu, Pb, Zn, Cr, Hg, Cd and Naphthalenes, PAHs 2-3 ring, PAH 4+, THC	PNEC <sub>ssd</sub> from field data	Total sediment extraction /concentration
<b>ERL etc.</b>	Cu, Pb, Zn, Cr, Hg, Cd and Naphthalenes, PAHs 2-3 ring, PAH 4+, THC	ERL (10 percentile)	Total sediment extraction /concentration

# Background concentrations – North Sea

(Bjørgesæter, 2005)

Background concentrations (mg/kg)		Cd	Cr	Cu	Hg	Pb	Zn	Decalins	NPD	PAH	PAH & 3-6 aro	THC	Grain size	TOM
<b>Mean</b>		0,05	13,65	4,06	0,03	10,49	20,28	0,04	0,06	0,13	0,10	4,86	3,84	2,96
<b>Min</b>		0,003	2,5800	0,3	0,003	1,9220	0,4200	0	0,0003	0,0038	0,0004	0,50	0,35	0,36
<b>Max</b>		0,82	39,20	17,18	0,40	46,48	83,74	0,16	1,37	0,67	0,67	29,85	9,84	12,40
<b>SD</b>		0,07	11,32	4,37	0,06	9,81	21,63	0,04	0,15	0,16	0,12	3,88	1,58	3,03
<b>N</b>		185	68	186	148	187	188	85	121	57	116	190	190	171

## MPA<sub>water</sub> is derived as follows:

1. Laboratory toxicity data selected from a data set on a number of species and are based on concentrations excluding background. Based on pooled for fresh and marine data if no difference in sensitivity
2. If NOECs for species of more than four taxonomic groups are available, the MPA is calculated using statistical extrapolation – SSD approach
3. If fewer NOECs or only acute data are available, a modified EPA-method is used to derive the MPA

# Selected PNEC approach metals in sediments

## Equilibrium Partitioning Method (EqP)

- Based on Crommentuijn et al., 1997 – Dutch guidance – RIVM

$$\text{MPA}_{\text{sediment}} = \text{MPA}_{\text{water}} \times K_{p \text{ sediment-water}}$$

- **MPA<sub>sediment</sub>**: Maximum Permissible Additon for the sediment compart.
- **MPA<sub>water</sub>** : Maximum Permissible Additon for the water compart.
  - defined as the maximum concentration of a metal allowed to be added to background concentration in water
  - derived from laboratory toxicity data (NOECs) using statistical extrapolation (SSD approach)
- **K<sub>p sediment-water</sub>**: Partition coefficient between sediment and water based on Dutch monitoring data (Kpbarite-water from E. Crecelius)