report

ERMS

Environmental Risk Management System

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RTD0602 Open
Date: 01.05.2006

ERMS Report no. 14A

# Field Validation part II: Comparing the results from the two approaches SSD and MWM including operational implications

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# MEMO

TITLE

## Field Validation part II;-
**Comparing the results from the two approaches; Species Sensitivity Distribution and the Mowing Window Approach including operational implications.**

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CLIENT

ERMS project / Ivar Singsas, SINTEF

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|---|---|---|---|
| Rapport nr.<br>RTD0602 | Klassifikasion<br>Open | CLIENTS REF.<br>Project no.: 66136730 /ref.no.:04-0013 | |
| | ISBN | Prosiekt nr.<br>RTD05/03 | Pages/appendices<br>12/0 |
| Elektronisk adresse for rapport<br>G:/DATA/RAPPORTER/RTD0602.DOC | | Project manager (navn/sign.)<br>Frode Brakstad | Checked by (navn/sign.)<br>Morten Raaholt / |
| | DAT0<br>2006-01-05 | Accepted by (name, position, signature)<br>F.Brakstad, Managing Director | |

**Summary**
Field data has been analyzed to find toxical values for selected chemical stressors to benthic fauna. The data has been extracted from the Norwegian MOD (Miljø Overvåking Databasen), and includes the grain size (as µm), the level of selected chemical components in sediments (ppm or ppb) and the benthic fauna. Two data analytical approaches have been selected, namely the “Mowing Window Modelling” (MWM) and the Species Sensitivity Distribution (SSD) approach. MWM is a new methodology proposed by MUST and Akvaplan niva, on the scope of the ERMS multiclient project, in order to identify the concentration of an individual substance that once in the field, among different other substances, has no evidence to cause effects on the abundance of a main group of species from the macrofauna community. This concentration is a field threshold effect level (f-TEL) that is supposed to not be influenced by the other contaminants present in the field, although there is a clear correlation to grain size. The SSD approach was used to define the field PNEC (f-PNEC) (the concentration of a substance in the field that together with other substances, is not expected to cause effects on the macrofauna abundance for more than 5% of the species. We may therefore expect the impacts values from the SSD approach to be higher than the ones calculated from the MWM approach. The SSD approach has not been able to verify the outcome from the MWM analysis regarding the relation between the grain size and the contributions from the single chemical stressors. From literature such a relation may be expected, as the availability is a function of interstitial water of the sediments. Both approaches have been reported separately, while this memo discuss the comparison of the approaches and the operational implications. There is an overall very good agreement between the average results from the two approaches of revealing toxic environmental levels from field data. When it comes to the trace elements, i.e. the f-PNEC values are as a rule of thumb some higher than the FTV values *as expected*.

Both methods have their limitations when it comes to decalines and THC, as these components are rapidly weathered and biodegraded at the seafloor. All data on the organic chemicals in MOD are probably considerably lower than the concentration at the time for exposure and impacting the benthic fauna. As the MWM method delivers pure FTV values, i.e. isolated FTV values for individual chemical toxic stressors, the problem of degrading of decaline and THC becomes pronounced, resulting in too low values. The SSD delivers f-PNEC values that are influenced by the presence of a combination of organic stressors and different ranges of pollution. As a consequence the rapid degrading of THC and decaline, becomes less pronounced and evident in the f-PNEC estimates from the SSD method. This may explain a less good agreement between the pure FTV and the f-PNEC for the THC and decalines. The degrading of NPD and PAH is less rapid, resulting in a better agreement between the two methods.
By comparing the results from the field validation with the values derived from literature according to the Equilibrium Partitioning Method (EqP) (task 1), there is a fair agreement with only Mercury and Chromium as exceptions. The PNECs from field data are recommended used as model input for Mercury and Chromium.

**CONTENT**

# 1. Introduction

This memo compares and discusses the results from the two different approaches used in the field validation of the literature values. The f-SSD method shows the response of all the sensitive species (macro fauna) to the given contaminant in the presence of other contaminants. Thus, the f-SSDs account for both possible interacting and synergetic effects along with correlations, and thus do not separate the effect of single substances. The f-SSD method reports f-PNECs, i.e. values below which benthic organisms in the sediment are unlikely (5 % risk) to be affected.
The Moving Window Modeling approach is a new methodology proposed by MUST and Akvaplan niva. It aim to identify the concentration of an individual substance that once in the field, among different other substances, has no evidence to cause effects on the abundance of a main group of species from the macrofauna community. This concentration is a field threshold effect level (f-TEL) that is supposed to not be influenced by the other contaminants present in the field, although there is a clear correlation to grain size. The FTV value of a chemical stressor is simply *the highest measured level of the specific stressors where no effect has been observed on the macrofauna community*. In this memo FTV and f-PNECs are termed TELs (threshold effect levels).

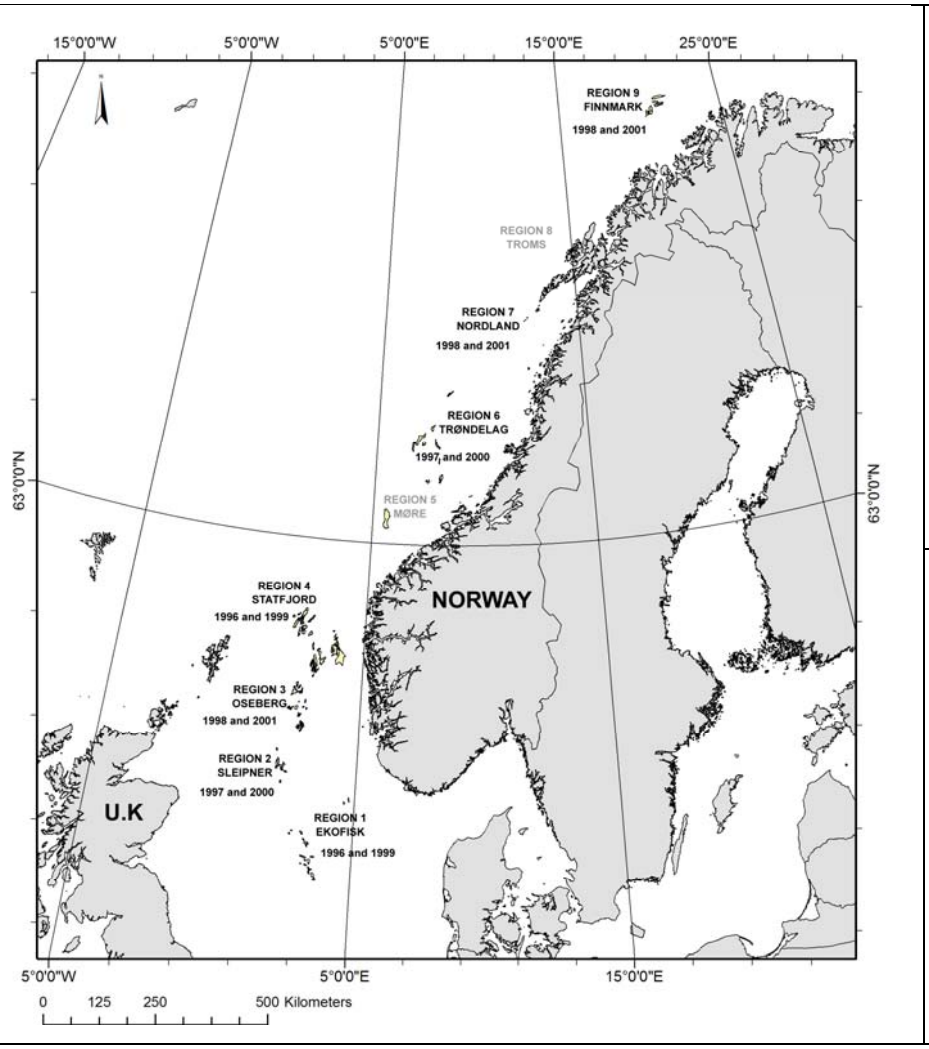
Both methods have been applied to the same data, i.e. 2258 samples containing chemical and biological analyses along with sediment characteristics. Data was extracted from the Norwegian database MOD; a database developed by the Norwegian Oil Association (OLF) and maintained by Det Norske Veritas. The extent of the Norwegian continental shelf with the 7 regularly sampled regions is evident from Figure 1.

The methods have been described in detail in separate reports [1, 2].

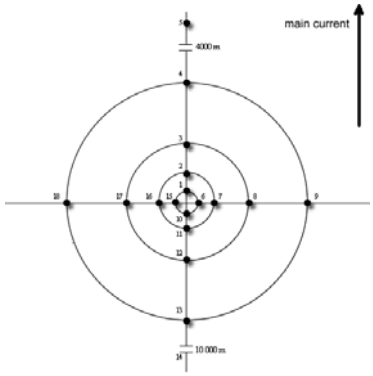
# 2. Methods

Although the two approaches have used the same MOD data, they have collected the samples into different grain size intervals. Thus some simplifications are necessary in order to compare the TELs from the MWM and SSD method. The MWM TELs have been “averaged” by calculating the average for each of the 6 grain size intervals weighted by the number of

stations, while the SSDs TELs have been averaged over 3 grain size intervals (Table 1). Note that these are values for comparison of the TELs from the two methods only.




*Sampling design:*




*Taxa (1990 – 2001):*

| Phylum | Percent |
|---|---|
| Annelida | 40 % |
| Arthropoda | 29 % |
| Mollusca | 21 % |
| Echinodermata | 5 % |
| Other | 5 % |

*Fig. 1: Norwegian continental shelf with the 7 sampling regions which are sampled regularly through the Norwegian offshore monitoring programme.*

## 3. Comparison of field TELs

The threshold values, i.e. the FTVs from Mowing Window modelling approach and the f-PNECs from the Species Sensitivity Distribution approaches have been copied from the separate reports [1,2] into Table 1.

The degree of match is expressed by the ratio percentage, where identical values are expressed as ratio% equal 100. As the f-PNECs is the level where the element is supposed to affect 5% of the population and the FTV is the highest observed value where **no** effect has been observed, the f-PNEC values should be expected to be some higher than the FTV values. As a consequence we may expect the ratio% ideally to be lower than 100%.

Chromium is the element with most similar TEL, yielding a ratio% of 104. A ratio% higher than 100% express the FTV has been found to be higher than the f-PNEC. This may happen if the discharge of Chromium at that specific sample (i.e. the sample that yield Cr at 10,47 ppm and at same time where no observed effect on the benthic fauna appear) has taken place close before the sampling period. A too short time interval of exposure may result in that the benthic fauna not yet has responded.

*Table 1: Comparison of FTV values from MWM (weighted average from the grain size intervals, see method description) with f-PNECs from the SSD. The ratio% values have been calculated as the ratio of MWM value to the SSD value (percentage). The relative toxicity is based on relative FTV (from the MWM) value as compared to Barium.*

| *All data as mg/kg dried sediment* | **MWM** FTV | **f-SSD** PNEC | **Ratio %** (FTV/f-PNEC) | **Relative "FTV in field"** (relative to MWM-Ba) |
|---|---|---|---|---|
| **Ba and trace elements** | | | | |
| **Ba** | **848** | 2286 | 37 % | **1** |
| **Zn** | **19,15** | 30,97 | 62 % | **44** |
| **Cr** | **10,47** | 10,08 | 104 % | **81** |
| **Pb** | **9,93** | 14,65 | 68 % | **85** |
| **Cu** | **3,23** | 6,46 | 50 % | **263** |
| **Cd** | **0,030** | 0,062 | 48 % | **28267** |
| **Hg** | **0,020** | 0,104 | 19 % | **42400** |
| | | | | |
| **Organics** | | | | |
| **THC** | **9,83** | 100,3 | 10 % | **86** |
| **Decalins** | **0,040** | 15,67 | 0,3 % | **21200** |
| **NPD** | **0,030** | 0,183 | 16 % | **28267** |
| **PAH** | **0,030** | 0,158 | 19 % | **28267** |

In overall there seem to be a very good agreement between the two methods SSD and MWM for the trace elements, where the FTV values fall in the interval 37%-104% of the f-PNEC values. The Mercury is the element with largest discrepancy. Still the FTV value is 19% of the f-SSD value. Again, bear in mind that we expect the FTV values to be at some lower level than the f-PNECs. A ratio% of 50-80% thus seems reasonable.

For the organics there seem to be a poor match between the TELs derived from the two methods. Possible explanations are presented in the discussion part. The last column is simply a comparison of relative FTV extracted from the MOD. The interpretation will be that Lead may be presented at sea level at a 1/85 times lower level than Lead without any observable effect on the macro fauna.

# 4. Discussion

## *4.1 Barium and the trace elements*

There is a fairly good agreement between the average FTV and the f-PNEC values for the metals. As expected the FTV values calculated by the MWM approach are lower than the f-PNECs calculated from the SSD approach (on average 2.3 times lower in the range of 19 % for Hg to 104 % for Cr; Table 1). One exception is the Chromium where the f-PNEC and FTV values are almost the same (104%). Taking into account the inherent analytical variation[1] in the MOD and the uncertainties in estimating TELs (two quite different approaches), the agreement between the MWM and the SSD approaches for the trace elements may be considered to be fairly good as the relative ratio are on same level (19%-104%).

## *4.2 The organic compounds*

There is less good agreement between the average FTV and the f-PNEC values for organics than for metals (Table 1). On average the FTVs from the MWM approach are 5 – 10 times (average 7.7 times) lower than the f-PNEC estimated from the f-SSD approach. A large discrepancy is found between the FTV and f-PNECs for decalins where the FTVs are almost 400 times lower than the f-PNEC.

The larger differences between the TELs for organic compounds than for metals may be partly explained by the uncertainties introduced by the time delay between the discharges to the sea floor and the sampling. Sampling takes place every three years, while the discharges to the sea floor from drilling operations and accidental spill (over time 12 % of the discharges all together) and produced water (88 %) may happen during the whole lifespan of an oil field [3]. The effect on the benthic macro communities are accumulated over all these years. Weathering and biodegradation of the organic compounds starts as soon as they are discharged. Within some days as much as 90% of the THC may be weathered (e.g. Grahl-Nielsen and Brakstad, 1986 [4]). Thus, at the time of sampling the concentration in the

[1] In analytical data as the ones in MOD there will always be some sources of errors from sampling, sample work-up and instrumental analysis that sums up to a certain error. This error may vary between consultant companies, between different chemical stressors, and from time to time due to sampling. The classification of macro fauna may also vary to a certain level from consultant to consultant.

sediments of the organic compounds may be much lower than originally, however, their negative impact of the fauna may still be registered. This is illustrated in Figure 2:

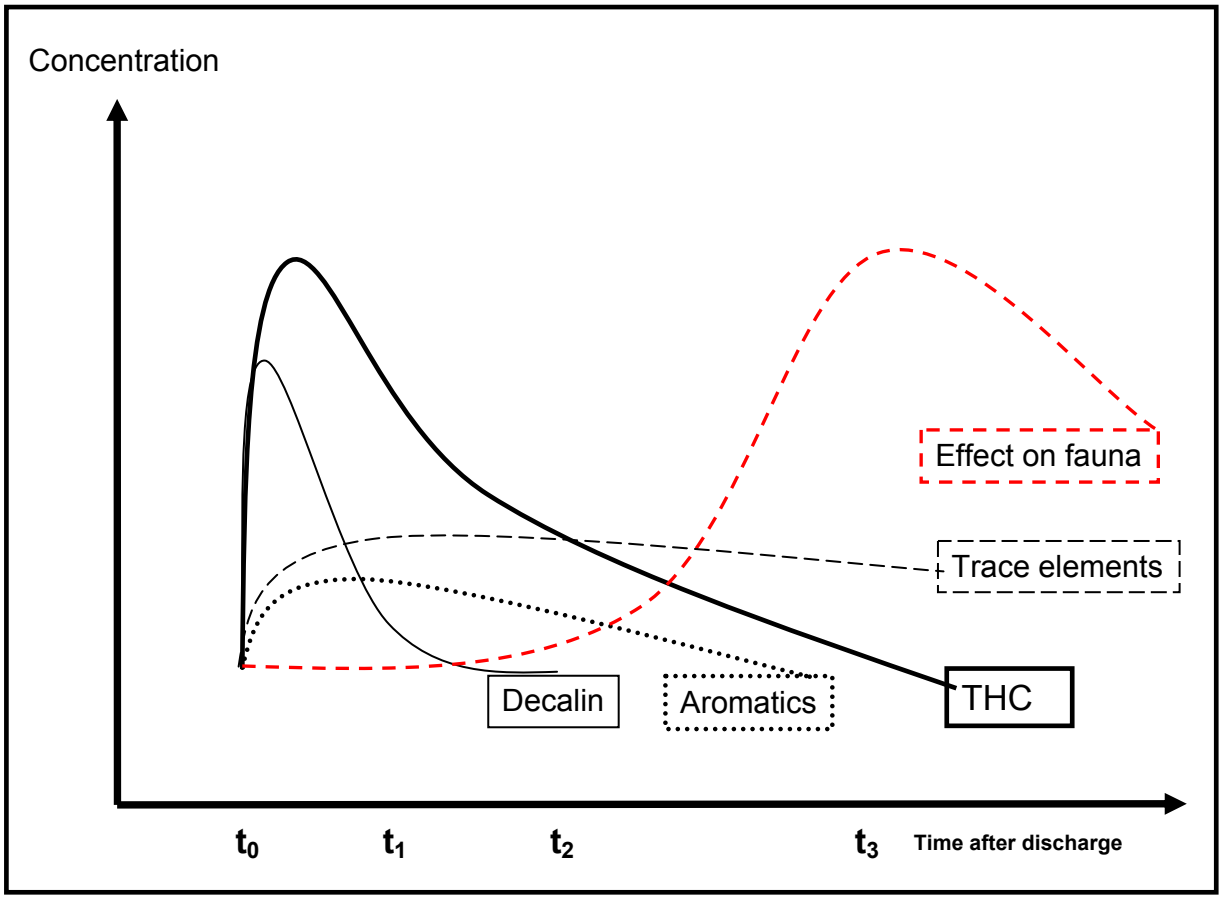



*Figure 2:* *Illustration of the effect of time span between discharges of rapid degradable organics as THC and decaline and sampling time, while comparing concentrations in sediments and impacts on the benthic fauna.*

As illustrated in Figure 2, the initial concentration of organic toxic stressors will soon after the discharge be degraded by a number of physical, chemical and biological processes. The result is that their concentrations in sediment are reduced over time. Some of the compounds discharged through the oil activities are rapidly degradable, some less rapid. The effect on the benthic fauna will however not appear before after some time. As an example, decaline may have a relatively high concentration at the time of discharge ($t_0$), and thus it may initiate a change in the benthic community. The actual response in the benthic fauna (measured as a change in the structure of the benthic community) may not be evident before after some time, e.g. as shown in Figure at $\mathbf{t_2}$ and $t_3$. However, sampling may take place at any time during this time delay: $\mathbf{t_0}$ to $t_3$. With a sampling frequency every third year, the normal situation revealed

during the monitoring study is the one with a rather large time delay (i.e. time delay from discharge to sampling > 2 weeks). In such situation, only a fraction of the decaline will be present while the benthic community still hasn't recovered.

Both methods have their clear limitation as they tend to correlate the concentration level of a specific organic compound (decalins) or group or organic compounds (THC, NPD and PAH) *at sampling time to a certain level at exposure time* i.e. there is a time delay between the decrease in chemical concentrations and the restitution time of the biological community. This suggests that most or all of the data on concentrations of organic compounds in sediments in MOD are lower than initially, and that the benthic fauna has been exposed to higher concentration of stressors than are measured at the time of sampling. As a result, our calculations from the SSD and the MWM will give too low TELs for the organics.

## *4.3 Comparison with literature and EqP values (task 1)*

Task 1of the ERMS project recommends that the sediment PNECs (PNECsed) of the hydrocarbons are to be derived from the PNECs derived for the water column multiplied with the equilibrium constants for sediment –water. As the FTVs of the hydrocarbons derived from the field data most probably are too low (see discussion above), the validation should be that the PNECsed should at least be higher than the one reported as FTV values. Furthermore, the possible influence from variation of grain size on the hydrocarbon and chemical PNECs should be discussed and clarified. Most probably the PNECsed should be increased when average grain size decrease below 80 μm, as evident for all FTV found in the Moving Window approach. The scientific explanation for the observed correlation between decreasing FTV values is outlined in the MWM report (ref.2).

The PNECsediments for the metals have been derived in a similar way using:

toxicity x equilibrium constants

resulting in the values as reported in Table 2.

*Table 2: Background concentrations of metals in sediment, PNEC values derived from literature data and field derived PNEC values (from Task 1, Toxicity report Draft Version rev 070406)*

| Metals | World sediments* | North Sea sediments** | PNEC sediments EqP▪ | F-TEL◊ | FTV◊◊ | ER-L b | TEL d |
|---|---|---|---|---|---|---|---|
| Ba | 1 – 2000 | 4.6 – 554 (mean 131) | - | 2286 | 848 | | |
| Cd | 0,1 – 0,6 | 0,003 – 0,130 (mean 0,037) | 0,05 | 0,062 | 0,030 | 1,2 | 0,68 |
| Cr | 36 – 110 | 2,58 – 39,2 (mean 14,6) | 29,37 | 10,08 | 10,47 | 81 | 52,3 |
| Cu | 7 – 33 | 0,3 – 17,2 (mean 4,10) | 4,15 | 6,46 | 3,23 | 34 | 18,7 |
| Hg (inorganic) | | 0,003 – 0,100 (mean0,021)*** | 14,18 | 0,104*** | 0,020*** | 0,15 | |
| Hg (methyl) | | | | | | | 0,13 |
| Pb | 10 – 33 | 1,92 – 46,5 (mean 10,7) | 11,57 | 14,65 | 9,93 | 46,7 | 30,2 |
| Zn | 27 – 88 | 0,42 – 83,7 (mean 20,7) | 21,16 | 30,97 | 19,15 | 150 | 124 |

* World background concentrations

** Ranges of NCS (Norwegian Continental Shelf) background concentrations based on samples from about 150 reference stations (extraction with nitric acid)

*** Based on total concentration of Hg

▪ Calculated from mean background concentrations from NCS

◊ Data from A. Bjørgesæter 2006

◊◊ Data from B. Grung et al 2006

b ER-L (Effects Range-Low) and ER-M (Effects Range-Median) from Long et.al. 1995. Incidence of Adverse Biological Effects Within Ranges of Chemical Concentrations in Marine and Estuarine Sediments. *Env. Management* 19:81-97

d TEL (Threshold Effect Level) and PEL (Probable Effect level) from MacDonald *et al*., 1996; FDEP, 1994
TEL is a concentration which adverse effects to sediment-dwelling fauna would be observed infrequently. PELs represent concentrations above which adverse effects are likely to occur.

As evident by comparing the PNEC sediments in Table 2 with the one derived from field data, it is a very good agreement between the field validation and the values as derived from task 1, with Mercury and Chromium as exceptions. The numbers of samples containing Mercury are rather low, and thus less accuracy may be expected. However, the difference between EqP value of 14,20 ppm and the field threshold effect levels (i.e. the SSD and MWM approaches) are too large to be explained by sampling size.

Thus we recommend that the field data for Mercury and Chromium to be used as PNECs for sediment, instead of the reported values from task 1. When discrepancies are as large as the ones for Chromium and Mercury, we suggest to trust the field data more than the theoretical

ones. We could also argue that because both the methods gave more or less the same values, this is underlying the credibility of the field values.
Thus our recommendations for PNEC sediments are the one as reported below (operational implications).

## 5. Operational implications

For the chemicals and the hydrocarbons we recommend to use the PNECs as presented in Task 1, i.e. PNECs for water column corrected for sediment –water equilibrium constants. In addition we suggest to take into account the bioavailability as influenced by variation in grain size. This may be done by increasing the PNECs when average grain size (µm) decreases from 80 µm. As evident from these equations, the PNEC for a specific stressor is more or less constant and independent of grain size variation at grains size > 80 µm. The equations as reported in the Moving Window Modeling report may be thus used, or alternatively, the correction may be derived on theoretical basis using the volumes of interstitial water of the sediment (interstitial volumes may be theoretically derived from average grain size).

When it comes to the suggested PNECs for the metals we recommend using the ones as given in Table 3. All the recommended PNECs from the metals are from Task 1, except the one for Mercury and Chromium. For these two, the difference of the Task 1 value are too large as compared to the ones derived from field data. Thus we suggest to use the two f-PNEC as reported from the SSD approach. In general the influence from other toxic stressors on the f-PNECs in the SSD study is not known, and restricts their use as PNECs. But for Mercury and Chromium we may expect the f -PNECS to be close to the "true" TEL as they are on the same level og slightly higher than the respective reported FTVs. Again, we suggest correcting the PNECS in Table 3 according to grain size. More specific, the PNECs for the metals should be increased according to grain size decreasing from 80 µm. Again, the equations from the FTV work may be used, or a theoretical function may be found.

*Table 3: Recommended sediment PNECs for the metals*

| Metal | Sediment PNEC (ppm) |
|---|---|
| Cd (task 1) | 0,05 |
| Cr (task 5) | 10,08* |
| Cu (task 1) | 4,15 |
| Hg (task 5) | 0,104** |
| Pb (task 1) | 11,57 |
| Zn (task 1) | 21,16 |

* Value suggested from the f-PNEC work. Probably somewhat too low and thus conservative as the FTV is reported to 10.47 ppm. The value is the average of f-PNECx of the three grain size (from F-PNEC report n.15)

** Value suggested from the f-PNEC work. The f-PNEC is a factor of 5 higher thean the FTV, and that seems reasonalble. The value is the average of f-PNECx of the two grain size (<63 μm and 63-94 μm). (from F-PNEC report n.15)

## 6. Conclusion

For the trace elements there is an overall fairly good agreement between the average results from the two methods (SSD and MWM). The f-PNEC values calculated from the SSD approach are some higher than the FTV values from the MWM approach, which is as expected.

The outcome from the MWM analysis showed that the FTV values vary with grain size. This observation was not observed by the SSD approach for the f-PNECs, but may be supported from literature. Task 1 has also concluded that availability of toxic stressors adsorbed on sediment particles is dependent on fraction of water available[2].

Both methods have their limitations when it comes to decalines and THC, as these stressors are rapidly degraded. All concentration data on organic compounds in MOD represent the concentration at sampling time, and are probably considerably lower than the concentration at the time of discharge. The registered observed impacts on the benthic fauna from the hydrocarbons will in most samples correspond to significant higher values than the one registered in the MOD database.

As the MWM approach delivers “pure” FTV values , e.g. isolated FTV values for individual chemical toxic stressors (derived independent on the other chemical stressors), the rapid degrading of decaline and THC results in too low values. The SSD delivers f-PNEC values

that are influenced by the presence of a number of other compounds, possibly being stressors. As a consequence the rapid degrading of THC and decaline becomes les pronounced and evident in the f-PNEC estimates from the SSD method. This may explain a less good agreement between the pure FTV and the f-PNEC for the THC and decalines. The degrading of NPD and PAH is less rapid than the ones for THC and decalines [4], resulting in a better agreement between the two methods.

As a result of the degradation of organic compounds, the FTV values from the MWM approach will be too conservative. The effect on the quality of the f-PNEC values is not so simple to estimate, but these values will also probably be too conservative as an estimate related to 5% risk.
Consequently, we recommend to use the estimated PNECs from Task 1 as input to the EIF sediment model for *i*) hydrocarbons[3], *ii*) chemicals and *ii*) trace elements with the exception of Mercury and Chromium.

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[2] "*Bioavailability of metals in sediments and hence toxicity is related to chemical activity in the sediment-pore-water system, and can therefore better be expressed by toxicity in the pore-water*", from pp presentation Task 1
[3] *When values for organic components are provided through Task 1. We do not recommend that the field PNEC for the hydrocarbons are used as input to the EIF sediment model.*

## 7. References


1. Anders Bjørgesæter (**2005**) *Field Based Predicted No Effect Concentrations (F-PNECs) for macro benthos on the Norwegian Continental Shelf*, ERMS Report, UiO.

2. Frode Brakstad, Bjørn Grung, Sten-Richard Birkely (**2005**), *FTV Field Validation part II;- the Mowing Window Approach*, ERMS report, MUST RTD05_05.

3. Anon. (**2002**) *Utslipp fra olje og gassvirksomhet i 2001;* Årsrapport for OLF utarbeidet av Novatech a.s. pp 48. In Norwegian.

4. F. Brakstad and O. Grahl-Nielsen, (1988) "Identification of Weathered Oils", *Marine Pollution Bulletin*, Vol.19, no.7., 319-24.

5. Breuer, J. A. Howe, G. B. Shimmield, D. Cummings & J. Carroll J. A. Howe, G. B. Shimmield, D. Cummings & J. Carroll, (**1999**) *Contaminant Leaching from Drill Cuttings Piles of the Northern and Central North Sea: A Review. pp 55.*