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CHARM Sensitivity and Uncertainty Analysis for Drilling Chemicals and for Completion and other Chemicals

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Summary

The aim of the study reported here was to assess the sensitivity of the CHARM model for variations in input parameters and the uncertainty associated with the calculated results when using the model for two different groups of offshore chemicals. The first group of chemicals studied is that of drilling chemicals. The second group consists of mixwater, spacer fluids, completion, workover and cleaning chemicals. The results of this study complement an earlier study, which analyzed the sensitivity and uncertainty of the CHARM model for production chemicals (Karman and Schobben, 1996).

The sensitivity has been studied by varying each input parameter by $\pm 10\%$, where a resulting spread of less than 20% indicates low sensitivity and a spread of more than 20% indicates high sensitivity.

For the drilling chemicals it is found that the model is sensitive for the following input parameters:

- dw28 (fraction of substance degraded in 28 days time)
- Pow (log Pow is usually reported, and quantifies the partitioning of a substance between octanol and water)

For the other group of chemicals (completion etc.) the model is not sensitive for any of the input parameters.

The uncertainty analysis has been performed using a Monte-Carlo scheme. This means that for each input parameter a large number of values were randomly drawn from a statistical distribution. The characteristics of the distribution used for each input parameter has been determined before starting the analysis. This Monte-Carlo scheme yields a large number random combination of inputs. These combinations are used to calculate results. These results are analysed and presented.

As in the previous study (Karman and Schobben, 1996) the final results that are presented disregard the uncertainty associated with the dosage (or initial concentration) of the chemicals.

For drilling chemicals the 90% confidence interval for the Hazard Quotient for the water-compartment (HQ_{water}) is [0.33 .. 3]. For the sediment-compartment (HQ_{sediment}) this 90% confidence interval is [0.2 .. 5], provided the PNEC_{sediment} is based on ecotoxicological test data. If this Predicted No Effect Concentration for the sediment is derived by extrapolating from the PNEC_{water} by using either the Pow or the Koc a wider confidence interval is the result.

For mixwater, spacer fluids, completion, workover and cleaning chemicals the 90% confidence interval for HQ_{water} is [0.33 .. 3].

These confidence intervals are in good agreement with the results from the uncertainty analysis for production chemicals (Karman and Schobben, 1996).

The confidence limits presented for Hazard Quotients can also be applied to Risk Quotients, provided that the Risk Analysis calculations for all substances under consideration at an installation are performed without changing inputs parameters, except those that describe substance characteristics.

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1. Introduction

In this report the results are presented of a study of the sensitivity and uncertainties of the CHARM (Chemical Hazard Assessment and Risk Management) model. The study evaluates the properties of the model when performing calculations on the environmental risk of the use and discharge into the marine environment of chemicals used to drill oil and gas production wells.

The CHARM model is part of the Harmonized Mandatory Control System (HMCS) as ordained by OSPAR (*OSPAR 2000a*). The CHARM model is therefore used in all OSPAR countries (those countries bordering the North Sea) when evaluating chemicals used in the offshore industry.

In a previous report (verslag) as well as in the CHARM manual (Thatcher *et al.*, 2001) information is available on the sensitivity and uncertainties surrounding the CHARM calculations when evaluating production chemicals. The results in this report focus on the sensitivity and uncertainties when modelling two different groups of chemicals: drilling chemicals, and completion (including workover and cementing) chemicals.

Drilling chemicals are used in the offshore industry when a well is made (drilled) either for exploration or production of fossil fuels (oil and gas). Their purpose is to ensure that a borehole can be drilled successfully. They therefore require diverse properties of: lubrication, density, viscosity, crack filling, cooling and corrosion inhibition. The complete combination of chemicals used is often referred to as mud. A drilling mud can be based on water (Water Base Mud or WBM) or oily substances (Oil Based Mud or OBM). OBM in general pose a large risk to the environment and are therefore not released to the environment. This type of mud and the associated drill cuttings are shipped to shore for treatment and/or controlled disposal.

The completion chemicals form a group that is subdivided as follows: mixwater, spacer fluids, cleaning chemicals (surface and well), other completion and workover chemicals. Each of these subgroups is used with a different purpose and at different times. Mixwater is released as a leftover of operations on a well where piping is cemented into place using a cement-slurry. Spacer fluids are used to ensure separation between different types of other fluids, e.g. between a drilling mud and cement-slurry. Cleaning chemicals are used to clean either the platform (including topside production facilities) or the borehole. Other completion and workover chemicals are used at the start of production to e.g. aid in the flow of oil or gas or during maintenance to keep production levels up.

Completion chemicals are released batchwise when a drilled well needs to be completed or when maintenance is done on an existing well. Each subgroup is used for a specific purpose.

Mixwater is released following operations downhole where production piping needs to be cemented into a fixed position with a cement-slurry.

Spacer fluid is used to make certain that when a switch is made between different types of fluids down the well unwanted contamination is avoided. An example could be the use of spacer fluid in between a WBM and a cement-slurry when a section of drilling has been completed.

Surface and well-cleaning chemicals are released into the environment when the well hole (or the surface of the platform) needs to be cleaned. An example where cleaning could be needed is prior to cementing in order to remove greasy and oily deposits that may result in the cement otherwise not being able to do its work properly.

Completion and workover chemicals are compounds that are sent downhole to e.g. help in starting or improving production from a well.

2. CHARM model

The CHARM model consists of a number of calculation rules. With these rules a Predicted Environmental Concentration (PEC) is calculated. Other rules are available to decide on a Predicted No Effect Concentration (PNEC) based on results of ecotoxicity testing. As defined by OSPAR these test results should be available for an algae (usually *Skeletonema costatum*), a crustacean (usually *Acartia tonsa*) and a fish (*Scophthalmus maximus*, juvenile). When a compound is likely to have an effect on organisms living in the sediment, a test result for a sediment reworker (usually *Corophium volutator*) is also mandatory (OSPAR, 2000c; OIC, 2002).

When performing calculations for hazard assessment many default values are used. These defaults mainly define the physical environment. Their use allows for the comparison of different compounds on an equal footing. In this report the calculations have been made as if performing an hazard assessment. The default values have also been taken into account when analysing the sensitivity and the uncertainty.

When performing calculations for Risk Analysis the defaults values – used in Hazard Assessment – are replaced with actual numbers defining the location of the installation being studied and the precise chemical composition of the mud in use there. At this time some uncertainty will be added, as for example current velocities vary. However the values entered for Risk Analysis are expected to better reflect the situation at the site than the default values of Hazard Assessment do.

2.1 Default values for drilling chemicals

The default values used by the CHARM model define a realistic worst case for use in Hazard Assessment. The following tables present the default used when calculating PEC and PNEC for drilling chemicals.

Table 1: Characteristic conditions of the reference platforms (realistic worst case) used in Hazard Assessment

| Parameter | North Sea Oil Prod. plfm | North Sea Gas Prod. plfm | Units |
|---------------------------------|-----------------------------|-----------------------------|-------|
| water depth | 150 | 40 | m |
| sediment organic carbon content | 0.04 | 0.04 | - |

Table 2: Default values for calculating the PEC for drilling chemicals (both continuous and batchwise discharge)

| Parameter | Value | Unit |
|---------------------------|-------------|------------------|
| platform density | 0.1 | km ⁻² |
| drilling time per section | 16 | d |
| water depth | 150 | m |
| refreshment rate | 0.24 | d ⁻¹ |
| batchwise dilution factor | 7.69231E-05 | - |

Table 3: Default data related to the drilling of the various sections

| Section drilled | Length drilled (m) | Mud density (kg.m-3) | Volume continuous discharge (m3) | Volume batchwise discharge (m3) |
|-----------------|--------------------|----------------------|----------------------------------|---------------------------------|
| 36" | 100 | - | * | - |
| 24" | 400 | - | * | - |
| 17.5" | 1500 | 1400 | 600 | - |
| 12.25" | 1500 | 1600 | 450 | 375 |
| 8.5" | 1000 | 1600 | 250 | 280 |

Note: * Only PLONOR-listed chemicals are used in the drilling of the 36" and 24" sections.

The PLONOR-list is a list of chemicals/substances maintained by OSPAR. It lists substances that Pose Little Or NO Risk to the marine environment. The use of substances on this list is generally regarded as environmentally safe.

Table 4: Terms as used in the previous tables and their definitions

| Term | Definition |
|---------------------------------|--|
| platform density | number of platforms per square kilometre |
| water depth | average water depth around the platform in meters |
| refreshment rate | fraction of sea water refreshed in the area around the platform per day |
| sediment organic carbon content | organic carbon in sediment, expressed as fraction of dry weight |
| dilution at 500 m. | dilution factor at a distance of 500 metres away from the platform |
| drilling time per section | time needed to drill a section of a well in days |
| batchwise dilution factor | dilution factor for batchwise discharges |
| section drilled | a section is a part of the drilling process, and is identified by its diameter (in inches). Deeper sections have a smaller diameter. |
| length drilled | length of a section in meters |
| mud density | density of the discharged mud in kg/m ³ |
| volume continuous discharge | volume of mud in cubic metres when continuously discharging to the environment |
| volume batchwise discharge | volume of mud in cubic metres when discharging per batch |

2.2 PEC Calculations for drilling chemicals

The PEC for drilling chemicals takes three different forms.

1. PEC for continuous discharge
2. PEC for batchwise discharge
3. PEC for the sediment

The PEC_{water} for continuous discharge is calculated using the following inputs:

- M or dosage (kg)
- Platform density (km⁻²) (default)
- Water depth (m) (default)
- T or time (d) (default)
- r or refreshment rate (d⁻¹) (default)

The PEC_{water} for batchwise discharge is calculated using the following inputs:

- M or dosage (kg)
- V_m or the Volume of mud discharged per section (m³) (default)
- D_{batch} or the dilution factor for batchwise discharges (default)

The PEC_{sediment} is calculated by extrapolating from the PEC_{water} for continuous discharge. The extrapolation uses the following inputs, besides the PEC_{water,cont.}:

- f_{oc} or sediment organic carbon content (fraction of dry weight) (default)
- Pow (actually $\log(Pow)$) or n-octanol/water partition coefficient
- Koc or experimental partition coefficient to sediment organic carbon
- F_{test} the fraction organic carbon of the test sediment used in determining the Koc (fraction of dry weight)
- $Dw28$ or degradation in 28 days

Further details of the calculation method can be found in *Thatcher et al.* (2001)

2.3 PNEC calculation for drilling chemicals

The PNEC is determined from the available toxicity data according to the scheme in Table 5, by applying a safety factor.

Table 5: Decision scheme for Safety factor to apply to toxicity test results to arrive at a PNEC

| | EC50 | | |
|---|------------------------------------|---|----------------|
| NOEC | <i>all 3 biota groups</i> | <i>2 biota groups (algae & crustacean incl. sed.reworker)</i> | <i>No Data</i> |
| <i>all 3 biota groups</i> | Min(NOEC)/10 | Min(NOEC/10) | Min(NOEC)/10 |
| <i>2 biota groups (algae & crustacean incl. sed.reworker)</i> | Min(min(NOEC)/10 or min(EC50)/100) | Min(min(NOEC)/10 or min(EC50)/1000) | not calculated |
| <i>No Data</i> | Min(EC50)/100 | Min(EC50)/1000 | not calculated |

Note on extrapolation factors:

PNEC_{pelagic} extrapolation factor 10,100,1000
 PNEC_{pelagic,acute} (batchwise discharges!) extrapolation factor 1,10,100
 (chronic value from table and as mentioned above divided by 10)

The method for calculating a PNEC is generic for all applications of CHARM.

Please note that there are different methods to arrive at a PNEC_{benthic}. The preferred method is to use relevant ecotoxicity data. If however such data is unavailable an estimation can be made by using the sediment/water partition coefficient. In the CHARM manual there are two ways to calculate this value, one based on the $\log(Pow)$ and one using the measured Koc (which is mostly relevant in cases were the chemical is surface-active). Thus there are three possible ways of arriving at a PNEC_{benthic}.

2.4 Default values for completion and other chemicals

The default values used by the CHARM model define a realistic worst case for use in Hazard Assessment. The following tables present the default used when calculating PEC and PNEC for completion chemicals. As can be seen in the tables presented here the terminology used to refer to these chemicals is not fully standardised.

Table 6: Default values to be used for Hazard Assessment of cementing chemicals being discharged with spacer fluid or mixwater

| Parameter | Spacer fluid | Mixwater |
|-------------------|--------------|-------------|
| dilution at 500m. | 1.23457E-05 | 2.22222E-05 |

Table 7: Default values to be used for completion and workover chemicals (specified as 'cleaning chemicals' and 'other chemicals')

| Parameter | Cleaning chemicals | Other chemicals |
|-------------------|--------------------|-----------------|
| fraction released | not relevant | 0.1 |
| dilution at 500m. | 7.69231E-05 | 7.14286E-05 |

2.5 PEC Calculations for completion and other chemicals

The PEC for drilling chemicals takes only one form.

1. PEC_{water} for batchwise discharge

The PEC_{water} is calculated using the following inputs, besides the $PEC_{\text{water,cont.}}$:

- C_i or initial concentration (mg.l^{-1})
- $D_{\text{batch,x}}$ or batchwise dilution factor where x can take the following values: mixwater, spacerfluid, cleaning chemicals, other chemicals
- f_r or fraction released of the chemical

The fraction released (f_r) is only used in the calculation for other (completion) chemicals. For the remaining group it is not included in the calculations, which in effect equals a fraction released of one.

Further details of the calculation method can be found in *Thatcher et al.* (2001)

2.6 PNEC calculation for completion chemicals

The method for calculating a PNEC is the same as that described in 2.3. The rules are almost the same for all applications of CHARM. In the case of completion chemicals which are only discharged at certain times, and not too closely together, there are two differences.

First as the discharges are only short-lived and infrequent these chemicals are thought to have only short-term environmental impacts. When calculating a PNEC the safety factor used is one order of ten smaller than for drilling (and production) chemicals, which are released over a much longer period of time and are much more likely to have long term influences on the environment. This PNEC is referred to as the $PNEC_{\text{pelagic,acute}}$.

Secondly no $PNEC_{\text{benthic}}$ is calculated. The characteristics of these discharges are such that the amounts and the time over which these chemicals are present in the environment are too low and short to have a long-term impact on benthic organisms.

3. Sensitivity Analysis

In this chapter the results of the uncertainty analysis for drilling chemicals and for completion chemicals are presented. To test the sensitivity of the results for varying input values, the inputs have been varied up- and downward by 10% relative to their (default or chosen) value. When the resulting spread (in absolute terms) was found to be 20% or less, the model is not very sensitive for this parameter. Alternatively it can be said that the parameter has a low influence on the outcome of the model calculations.

3.1 Sensitivity Analysis for drilling chemicals

For the sensitivity analysis CHARM calculations were performed for all three PECs. These calculated PECs were combined with PNECs based on (artificial) ecotoxicological data for three compounds. This resulted in the calculation of Hazard Quotients (PEC:PNEC-ratio's). For all possible parameters the sensitivity for the results for changes in the input was determined by adjusting the default (or initially chosen) value up- and downwards by 10%.

Table 8: Summary of sensitivity analysis results for the water compartment

| Parameter varied | Spread | Influence |
|------------------------------------|--------|-----------|
| M [#] | 20% | Low |
| platform density | 20% | Low |
| water depth | -20% | Low |
| T | -20% | Low |
| V _{m, batch} [#] | -20% | Low |
| r | -20% | Low |
| D _{batch} [#] | 20% | Low |
| PNEC | -20% | Low |

[#] Used in the calculation for batchwise discharge.

Table 9: Summary of sensitivity analysis results for the sediment compartment

| Parameter varied | Spread | Influence |
|------------------|--------|-----------|
| PEC water | 20% | Low |
| foc | 20% | Low |
| Pow (log) | 95% | High |
| Koc | 20% | Low |
| Ftest | -20% | Low |
| dw28 | -39% | High |
| PNEC | -20% | Low |

In the final results the spread of the resulting HQs nearly always was 20%, which is exactly the amount expected (Table 8, Table 9).

The exceptions to this are both involved with the calculation of the PEC_{sediment} (Table 9). The Pow (log Pow to be accurate) is very influential and care should be taken when using Pow in this calculation. The strong influence can be explained by the fact that it is used in an inverse log-operation – 10^{Pow} . The fact that measured Koc and Ftest values are preferred inputs for this calculation is therefore with good reason. These inputs do not have such a large influence in the outcome of the calculations. The determination of the Pow is known to be prone to variation (Karman and Schobben, 1996, Vik and Bakke 1996). A $\pm 10\%$ change in Pow gives a spread of 95% in the resulting HQs. On the other hand the process of determining a Koc is also prone to fairly large uncertainties (this study). When the Pow were to be varied by $\pm 10\%$ without log-transformation it has an influence of 20%. The choice to vary Pow on a log-scale instead of untransformed is based on the fact that this parameter is usually reported as a logarithm. Following the same reasoning the Koc has been varied untransformed. This parameter is however in some cases reported as a logarithm.

The dw28 is the second influential parameter. As with the log Pow, an inverse log-operation can be pointed to as the numerical cause of the observed influence. As there is no alternative to this input parameter, it is clear that carefully determined biodegradation values are important for a reliable estimation of the HQ of a substance.

3.2 Sensitivity Analysis for completion and other chemicals

For the sensitivity analysis PEC calculations were performed for all four chemical types in this group. In no case there was evidence of the calculations being extremely sensitive to the inputs. A linear relation exists between any input in these calculations and the outcome ($\pm 10\%$ change in input, results in a spread of 20%).

Table 10: Summary of sensitivity analysis results for the sediment compartment

| Parameter | | |
|-------------------|--------|-----------|
| Varied | Spread | Influence |
| Ci,x | 20% | Low |
| Dbatch,mixwater | 20% | Low |
| Dbatch,spacer | 20% | Low |
| Dbatch,cleaning | 20% | Low |
| Dbatch,completion | 20% | Low |
| fr | 20% | Low |

4. Uncertainty Analysis

Here the results are presented for the uncertainty analysis for drilling chemicals and for the uncertainty analysis for completion and other chemicals.

The uncertainty analysis is performed using a Monte-Carlo scheme. This means that a large number of calculations are made where the input parameters are randomly chosen from a (statistical) distribution. This is done in such a way that each parameter varies independently from the others. For each varied parameter one thousand separate values have been generated, resulting in one thousand results per calculated endpoint. The distribution characteristics of the results are then examined to arrive at e.g. a 95% confidence interval.

The way in which these calculations have been performed is identical to the approach used in the uncertainty analysis for production chemicals (Karman and Schobben, 1996).

4.1 Uncertainty analysis for drilling chemicals

The uncertainty of the CHARM calculations for drilling chemicals was investigated using a Monte-Carlo scheme. Results (HQs) were generated by randomly sampling each input parameter from a distribution. The type of distribution and with what characteristics it is defined depends upon the parameter.

As much of the work with CHARM is for hazard assessment purposes and the fact that the sensitivity analysis has shown that most parameters only have a linear influence on the end result, not all parameters have been used in the Monte-Carlo scheme.

The following parameters have been randomised for the Monte-Carlo scheme:

- M (PECwater, continuous; PECwater, batch)
- Pow, Koc, dw28 (PECsediment)
- Ecotoxicity data – algae, crustacean, fish, sediment reworker (PNEC)

Randomisation of Ftest has been deemed to be of no interest as it only serves to recalculate the Koc to fit with either the default foc (0.04) in Hazard Assessment or the actual foc of the sediment at the site under investigation in Risk Analysis.

In Table 11 the distribution type and other characteristics needed for the randomisation of the parameters are listed. For the variables M, Pow, dw28 and PNECs the distribution characteristics have been taken from Karman and Schobben (1996). This holds true particularly for the type of distribution used and the spread. The values for the mean/median have been taken from the spreadsheet used in preparing the document and represent a dosage and ecotoxicity of one of the

products used in that study. These values have been reused for this study as they were judged to be representative of the type of product being investigated.

Table 11: *Randomisation characteristics of the drilling chemicals calculation for the Monte-Carlo scheme*

| Variable | Distribution | min | max | mean/median | spread |
|-------------|----------------|--------|--------|-------------|--------|
| M | lognormal | | | 3.75 | 1.72 |
| Pow (log) | normal | | | 3.7 | 0.24 |
| Koc (log) | normal | | | 3.5 | 0.37 |
| Ftest | not randomised | | | | |
| dw28 | uniform | 0.1125 | 0.4125 | 0.2625 | |
| PNECpelagic | lognormal | | | 6.30E-02 | 0.7 |
| PNECbenthic | lognormal | | | 1.00E-02 | 0.5 |

For the Koc no data was available from a previous study. In the evaluation that has been made here the following observations have been made. The OSPAR documents, which determine how data on offshore chemicals is reported and determined, refer to Karickhoff *et al.* (1979) for a procedure to determine the Koc of a substance. This reference however does not give any indication of the uncertainty or spread in the resulting data. It does however provide a regression formula from which the Koc can be estimated if the log Pow is known for a substance. A similar estimation procedure was taken from Minnich (1993) who refers to Hasset and Banwart (1989) as the original source. From this it is concluded that it is most likely that the type of distribution that characterizes the Koc is a lognormal distribution. If it is possible to estimate the Koc based on the Log Pow, which is lognormally distributed it stands to reason that the Koc is lognormally distributed as well.

As for determining a value for the mean to be used as input, it turns out that both regression formulae estimated a log Koc very close to 3.5 when a log Pow value of 3.7 was entered.

The estimation formula in Minnich (1993) is accompanied by a graph in which a 95% confidence interval is indicated. The formula and the graph are based on a diverse set of 34 non-ionic organic contaminants. Using the calculated mean 3.5 and the limits of the confidence interval as read from this graph a (ln-transformed) standard deviation of 0.37 was estimated.

Besides the previously mentioned source OECD Guideline 106 (OECD, 2000) has also been referenced. In Annex 3 to this guideline attention is given to accuracy of both analytical method and concentration change. When a test is done to determine the Koc of a chemical and the amount of chemical adsorbed is low, resulting in a low concentration change (around 10% drop in water concentration), a small error in the analytical method (e.g. 5%) can result in a large error (over 50%) in the end

result. This however only serves to illustrate the fact that care must be taken when determining the Koc of a substance.

4.2 Uncertainty results for Drilling Chemicals

In the calculation method for drilling chemicals there are two dichotomies resulting in several sets of results. The dichotomies are:

- continuous or batchwise discharge and
- use of Pow or Koc for the PEC-calculations.

For the PNECbenthic there are three possible routes:

- estimation based on ecotoxicological test data for sediment reworkers;
- estimation using PNECpelagic and the Pow or
- estimation using PNECpelagic and Koc.

All possible combinations are listed in Table 12. As can be seen a choice has been made not to calculate all combinations. The Koc based calculations are e.g. especially relevant when a substance is surface-active. A decision was made that in practice it would be highly unlikely that a PECsediment would be calculated using a Pow-based calculation while calculating the PNECbenthic based on Koc-data or vice versa. The PNECbenthic calculations are made using separate Monte-Carlo results. This adds extra variation into the calculations, which is representative of actual CHARM-calculations where in many cases Pow and/or Koc are given as a range. From this range the lower limit is used in water-oriented calculations, while the upper limit is used for sediment-oriented calculations. In this way calculated concentrations are maximized which fits with the ‘realistic worst case’-approach.

Table 12: Possible routes towards CHARM calculations for drilling chemicals, showing which options have and have not been calculated. See text for further explanation. The Roman numerals are used to refer to a combination of calculation options.

| | | Continuous | Batchwise |
|--------------------|--------------------|------------|------------|
| PECsediment | PNECbenthic | | |
| <i>Pow</i> | <i>Ecotox.</i> | Yes / I | Yes / II |
| | <i>Pow</i> | Yes / III | Yes / IV |
| | <i>Koc</i> | No | No |
| PECsediment | PNECbenthic | | |
| <i>Koc</i> | <i>Ecotox.</i> | Yes / V | Yes / VI |
| | <i>Pow</i> | No | No |
| | <i>Koc</i> | Yes / VII | Yes / VIII |

The calculated PEC, PNEC and HQ values have been analysed. It turns out that, not unsurprisingly when the inputs have been randomised based on either a normal or lognormal distribution that the results also follow a lognormal distribution. Performing t-tests (two-tailed, homoscedastic –equal variances) gives p-values of 0.98 or higher in all cases.

Combination I

For the purpose of judging the uncertainty in the CHARM results a 5-95% confidence interval is presented in Table 13 where the mean of the distribution has been shifted to one. In this way all uncertainty intervals are centred on one and can be compared directly. Table 13 lists the calculated values. The results in Table 13 are based on calculations for a North Sea oil platform and using the Pow as input in the PNECbenthic.

Table 13: Confidence interval for PEC, PNEC and HQ for a (lognormal) distribution with a mean of one as calculated for drilling chemicals (Combination I: North Sea oil platform, continuous discharge, PECsed from Pow, PNECbenthic from ecotox)

| Confidence intervals | 5% | 95% |
|----------------------|------|-------|
| PECwater | 0.06 | 16.25 |
| PECsediment | 0.05 | 18.28 |
| PNECpelagic | 0.33 | 3.00 |
| PNECbenthic | 0.44 | 2.25 |
| Hqwater | 0.05 | 21.13 |
| Hqsediment | 0.05 | 18.25 |
| Hqecosystem | 0.05 | 18.21 |

As can be seen from Table 13 above the uncertainty in the PEC is generally from 0.05 to 20. A lower uncertainty is associated with the calculated PNEC (0.33 – 3.0). The uncertainty from the PEC dominates the HQ (PEC:PNEC-ratio) which again has a 90% confidence interval with limits of 0.05 and 20.

Combination II

The results for combination II (North Sea oil platform, batchwise discharge, PECsed from Pow, PNEC benthic from ecotox) are listed in Table 14. The results are identical with those from combination I.

Table 14: Confidence interval for PEC, PNEC and HQ for a (lognormal) distribution with a mean of one as calculated for drilling chemicals (Combination II: North Sea oil platform, batchwise discharge, PECsed from Pow, PNECbenthic from ecotox)

| Confidence intervals | 5% | 95% |
|-----------------------------|-----------|------------|
| PECwater | 0.06 | 16.25 |
| PECsediment | 0.05 | 18.28 |
| PNECpelagic | 0.33 | 3.00 |
| PNECbenthic | 0.44 | 2.25 |
| HQwater | 0.05 | 21.13 |
| HQsediment | 0.05 | 20.05 |
| HQecosystem | 0.05 | 19.07 |

Combination III

The results for combination III (North Sea oil platform, continuous discharge, PECsed from POW, PNECbenthic from Pow) are listed in Table 15. There are two noticeable differences in comparison with combinations I and II. First the uncertainty in the calculated PNECbenthic is larger (0.25-4.0 as opposed to 0.33-3.0). This higher uncertainty is also reflected in the HQsediment which is calculated using the PNECbenthic, with a range of 0.04-25.0 (0.05-20.0 for combinations I-II).

Table 15: Confidence interval for PEC, PNEC and HQ for a (lognormal) distribution with a mean of one as calculated for drilling chemicals (Combination III: North Sea oil platform, continuous discharge, PECsed from Pow, PNECbenthic from Pow)

| Confidence intervals | 5% | 95% |
|-----------------------------|-----------|------------|
| PECwater | 0.06 | 16.25 |
| PECsediment | 0.05 | 18.28 |
| PNECpelagic | 0.33 | 3.00 |
| PNECbenthic | 0.23 | 4.34 |
| HQwater | 0.05 | 21.13 |
| HQsediment | 0.04 | 25.11 |
| HQecosystem | 0.05 | 21.13 |

Combination IV

The results for combination IV (North Sea oil platform, batchwise discharge, PECsed from Pow, PNECbenthic from Pow) are listed in Table 16. The results are very similar to those of combination III.

Table 16: Confidence interval for PEC, PNEC and HQ for a (lognormal) distribution with a mean of one as calculated for drilling chemicals (Combination IV: North Sea oil platform, batchwise discharge, PECsed from Pow, PNECbenthic from Pow)

| Confidence intervals | 5% | 95% |
|-----------------------------|-----------|------------|
| PECwater | 0.06 | 16.25 |
| PECsediment | 0.05 | 18.28 |
| PNECpelagic | 0.33 | 3.00 |
| PNECbenthic | 0.23 | 4.34 |
| HQwater | 0.05 | 21.13 |
| HQsediment | 0.04 | 26.92 |
| HQecosystem | 0.05 | 21.13 |

Combination V

The results for combination V (North Sea oil platform, continuous discharge, PECsed from Koc, PNECbenthic from ecotox) are listed in Table 17. In comparison with the Pow based PECsediment (as used in combinations I through IV) the Koc based variety has a larger 95% confidence interval ranging from 0.04 to 25.0 (as opposed to [0.05 .. 20] when based on Pow). Results from this calculation are less certain. This higher uncertainty in PECsediment is however not reflected in the HQsediment.

Table 17: Confidence interval for PEC, PNEC and HQ for a (lognormal) distribution with a mean of one as calculated for drilling chemicals (Combination V: North Sea oil platform, continuous discharge, PECsed from Koc, PNECbenthic from ecotox)

| Confidence intervals | 5% | 95% |
|-----------------------------|-----------|------------|
| PECwater | 0.06 | 16.25 |
| PECsediment | 0.04 | 23.90 |
| PNECpelagic | 0.33 | 3.00 |
| PNECbenthic | 0.44 | 2.25 |
| Hqwater | 0.05 | 21.13 |
| Hqsediment | 0.05 | 18.59 |
| Hqecosystem | 0.05 | 18.55 |

Combination VI

The results for combination VI (North Sea oil platform, batchwise discharge, PECsed from Koc, PNECbenthic from ecotox) are listed in Table 18. In comparison with combinations I through IV the differences are very similar to those of combination VI. There are two exceptions to this similarity. The larger uncertainty associated with the PECsediment based on Koc is reflected in the HQsediment and as well in the HQecosystem. For both the 95% confidence interval widens from [0.5 ... 20.0] to [0.04 ... 25.0].

Table 18: Confidence interval for PEC, PNEC and HQ for a (lognormal) distribution with a mean of one as calculated for drilling chemicals (Combination VI: North Sea oil platform, batchwise discharge, PECsed from Koc, PNECbenthic from ecotox)

| Confidence intervals | 5% | 95% |
|-----------------------------|-----------|------------|
| PECwater | 0.06 | 16.25 |
| PECsediment | 0.04 | 23.90 |
| PNECpelagic | 0.33 | 3.00 |
| PNECbenthic | 0.44 | 2.25 |
| HQwater | 0.05 | 21.13 |
| HQsediment | 0.04 | 26.20 |
| HQecosystem | 0.04 | 25.85 |

Combination VII

The results for combination VII are listed Table 19. The most notable difference with all previous combinations is that here the PNECbenthic, which is calculated using the Koc to extrapolate from the PNECpelagic (instead of using ecotoxicity data for benthic organisms or extrapolating from the PNECpelagic using Pow), has a larger 95% confidence interval. This larger uncertainty is reflected in the HQsediment as well. It is however not reflected in the HQecosystem in this case.

Table 19: Confidence interval for PEC, PNEC and HQ for a (lognormal) distribution with a mean of one as calculated for drilling chemicals (Combination VII: North Sea oil platform, continuous discharge, PECsed from Koc, PNECbenthic from Koc)

| Confidence intervals | 5% | 95% |
|-----------------------------|-----------|------------|
| PECwater | 0.06 | 16.25 |
| PECsediment | 0.04 | 23.90 |
| PNECpelagic | 0.33 | 3.00 |
| PNECbenthic | 0.17 | 5.87 |
| HQwater | 0.05 | 21.13 |
| HQsediment | 0.04 | 28.68 |
| HQecosystem | 0.05 | 21.13 |

Combination VIII

The results for combination VIII are listed in Table 19. Although similar to the results from combination VII the larger uncertainty in the PECsediment is in this case not reflected in the HQsediment.

Table 20: Confidence interval for PEC, PNEC and HQ for a (lognormal) distribution with a mean of one as calculated for drilling chemicals (Combination VIII: North Sea oil platform, batchwise discharge, PECsed from Koc, PNECbenthic from Koc)

| Confidence intervals | 5% | 95% |
|----------------------|------|-------|
| PECwater | 0.06 | 16.25 |
| PECsediment | 0.04 | 23.90 |
| PNECpelagic | 0.33 | 3.00 |
| PNECbenthic | 0.17 | 5.87 |
| HQwater | 0.05 | 21.13 |
| HQsediment | 0.05 | 21.56 |
| HQecosystem | 0.05 | 21.13 |

4.3 Uncertainty results for Drilling Chemicals, disregarding uncertainty in Dosage

The data used in the previous paragraph on M (dosage) has been taken from Karman and Schobben (1996). In the final results presented in that report the uncertainty in dosage has been disregarded. The reason given for this is that the uncertainty of the dosage is based on a very weak data set. Since the available data on this aspect has not been improved upon it is seen as justifiable to present results in this report as well while disregarding the uncertainty in dosage. This also makes the results of this uncertainty analysis more comparable with the previous uncertainty analysis.

The summarized results of this analysis are given in Table 21. The obvious result is that PECwater also has no more uncertainty associated with it. The dosage is the only variable in its calculation. The uncertainty in both possible estimates for PECsediment is also reduced. As both are based on PECwater this is what is to be expected. The PNECs are not influenced as the dosage is not used in their calculation. The uncertainty in all Hazard Quotients is reduced, resulting from the reduced uncertainty in the calculated PECs.

To decide which confidence limits to apply to the HQecosystem, it is best to use the values for the environmental compartment which is the most sensitive. This means using the HQwater limits if the pelagic community is the most sensitive and the HQsediment limits if the benthic community is the most sensitive. In the case of HQsediment the confidence limits are not the same for all available estimators (ecotox, Pow or Koc) and the appropriate limits should be used.

Table 21: Summary table for CHARM uncertainty analysis for Drilling chemicals, disregarding uncertainty in dosage (M). * Please refer to the text.

| Confidence interval | 5% | 95% | estimator |
|---------------------|------|------|-----------|
| PECwater | - | - | |
| PECsediment | 0.40 | 2.5 | Pow |
| PECsediment | 0.22 | 4.5 | Koc |
| PNECpelagic | 0.33 | 3.0 | |
| PNECbenthic | 0.45 | 2.2 | ecotox. |
| PNECbenthic | 0.25 | 4.0 | Pow |
| PNECbenthic | 0.17 | 6.0 | Koc |
| HQwater | 0.33 | 3.0 | |
| HQsediment | 0.20 | 5.0 | ecotox. |
| HQsediment | 0.17 | 6.0 | Pow |
| HQsediment | 0.09 | 11.0 | Koc |
| HQecosystem | * | * | |

When these results are presented graphically the broader confidence interval for HQsediment than for HQwater is clear in

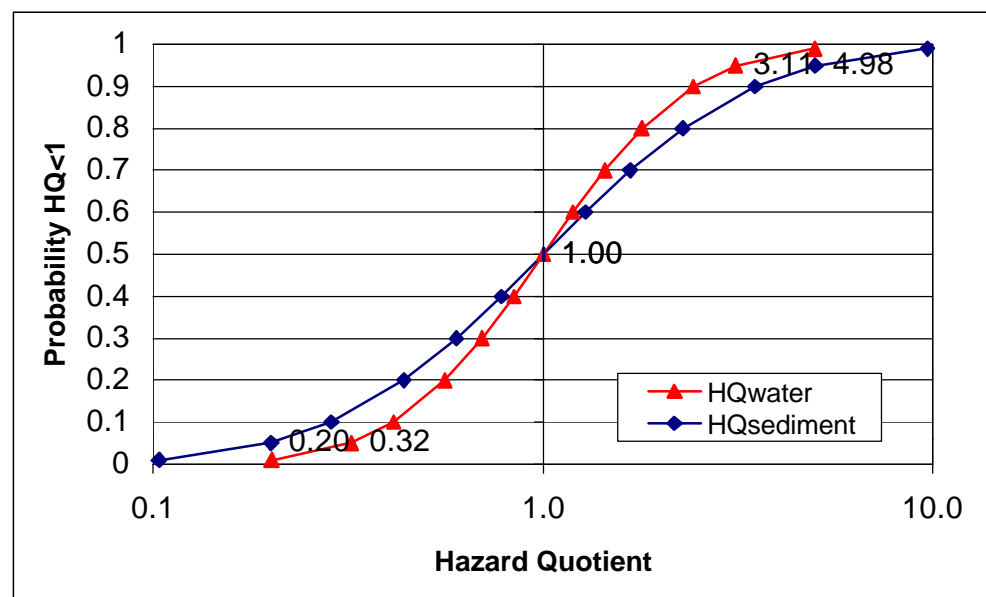


Figure 1. A graphical comparison of the confidence intervals for HQsediment based on different estimators for PNECbenthic (ecotoxicological data, Pow-based estimation or Koc-based estimation) is made in Figure 2.

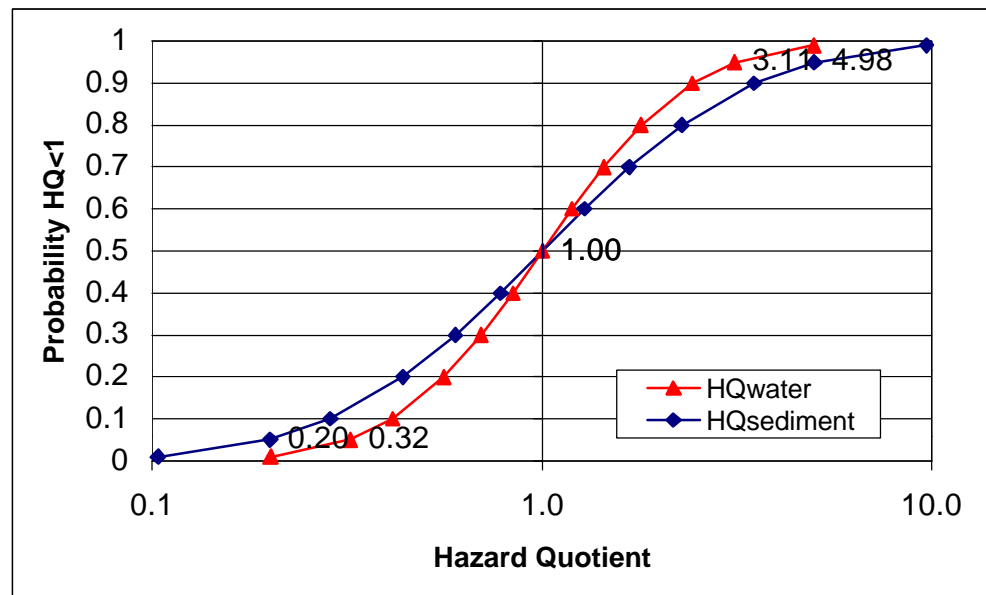


Figure 1: Uncertainty analysis results for drilling chemicals, HQ_{water} and $HQ_{sediment}$. The uncertainty in dosage has been disregarded. The numbers in the graph represent the 5% and 95% boundaries for a 90% confidence interval.

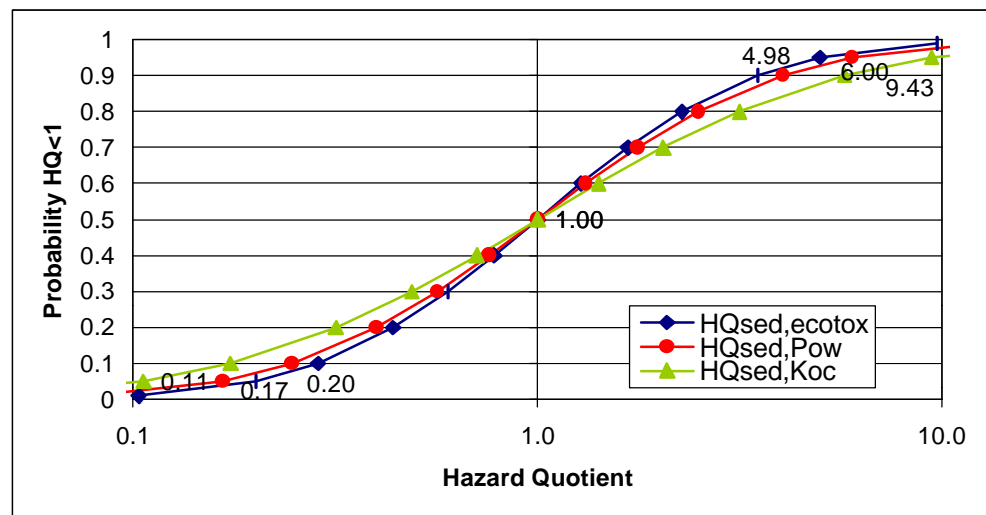


Figure 2: Uncertainty analysis results for drilling chemicals, $HQ_{sediment}$ based on ecotoxicity data, Pow-based estimate and Koc-based estimate. The uncertainty in dosage has been disregarded. The numbers in the graph represent the 5% and 95% boundaries for a 90% confidence interval.

The confidence limits given here indicate that there is a 90% likelihood that the true value for a calculated HQ of 1.0 lies within the given boundaries. When comparing the HQ for two substances the difference would be significant if the high HQ times the lower boundary is larger than the low HQ.

4.4 Uncertainty analysis for completion and other chemicals

The uncertainty of the CHARM calculations for completion and other chemicals (such as mixwater, spacing fluids, and cleaning chemicals) was investigated using a Monte-Carlo scheme. Results (HQs) were generated by randomly sampling each input parameter from distribution. What type of distribution is used and with what characteristics it is defined depends upon the parameter.

As much of the work with CHARM is for hazard assessment purposes and the fact that the sensitivity analysis has shown that most parameters only have a linear influence on the end result, not all parameters have been used in the Monte-Carlo scheme.

The following parameters have been randomised for the Monte-Carlo scheme:

- $C_{i,x}$ (PEC_{water}, batch where x stands for one of the following: mixwater; spacer, cleaning, completion)
- Ecotoxicity data – algae, crustacean, fish, sediment reworker (PNEC)

Table 22 *Randomisation characteristics of the completion and other chemicals calculation for the Monte-Carlo scheme*

| Variable | Distribution | min | max | mean/median | spread |
|--------------|--------------|-----|-----|-------------|--------|
| $C_{i,x}$ | lognormal | # | # | 3.75 | 1.72 |
| PNEC pelagic | lognormal | # | # | 6.30E-02 | 0.7 |

4.5 Uncertainty results for completion and other chemicals

The resulting calculated PEC, PNEC and HQ values have been analysed. It turns out that, not unsurprisingly when the inputs have been randomised based on either a normal or lognormal distribution that the results also follow a lognormal distribution. A Students' t-test (two-sided, equal variances) consistently gave results with p-values of 0.98 or higher.

For the purpose of judging the uncertainty in the CHARM results a 5-95% confidence interval is presented in Table 23 where the mean of the distribution has been shifted to one. In this way all uncertainty intervals are centred on one and can be compared directly. Table 23 lists both the calculated value and an idealized value that could be used as a rule of thumb.

Table 23: *Confidence interval for PEC, PNEC and HQ with a mean of one, as calculated for completion and other chemicals*

| Confidence intervals | 5% | 95% |
|-------------------------|------|-------|
| PEC _{mixwater} | 0.07 | 14.91 |
| PEC _{spacer} | 0.07 | 14.90 |
| PEC _{cleaning} | 0.07 | 14.90 |

| | | |
|---------------|------|-------|
| PECcompletion | 0.07 | 14.93 |
| PNECpelagic | 0.32 | 3.16 |
| HQmixwater | 0.05 | 19.39 |
| HQspacer | 0.05 | 19.39 |
| HQcleaning | 0.05 | 19.38 |
| HQcompletion | 0.05 | 19.42 |

The results of the uncertainty analysis show that the calculation of the PEC has a 90% confidence interval of 0.07 to 15. The uncertainty associated with the PNEC is smaller with a 90% confidence interval of 0.33 to 3. The uncertainty is highest in the HQs, which have a 90% confidence interval with 0.05 and 20 as boundaries.

4.6 Uncertainty results for completion and other chemicals, disregarding uncertainty in dosage.

Following the line of reasoning as in 4.3 results will be presented here that disregard the uncertainty around the dosage of completion and related chemicals. Please note that the correct term for this group of chemicals is “initial concentration” (Ci) not dosage. The reason for presenting the results for this group of offshore chemicals while disregarding this uncertainty is the absence of a reliable underlying data set.

As can be seen from Table 24 the PECs no longer have any uncertainty, since all other data, besides the initial concentration, used in their calculation are default values. The uncertainty in the PNECpelagic remains the same as before and as can be expected this same uncertainty is reflected in the Hazard Quotients.

Table 24: Confidence interval for PEC, PNEC and HQ with a mean of one, as calculated for completion and other chemicals, disregarding uncertainty in initial concentration

| Confidence intervals | 5% | 95% |
|----------------------|------|------|
| PECmixwater | - | - |
| PECspacer | - | - |
| PECcleaning | - | - |
| PECcompletion | - | - |
| PNECpelagic | 0.32 | 3.16 |
| Hqmixwater | 0.32 | 3.16 |
| Hqspacer | 0.32 | 3.16 |
| Hqcleaning | 0.33 | 3.16 |
| HQcompletion | 0.33 | 3.16 |

In Figure 3 the results from Table 24 are presented in graphical form for HQcompletion.

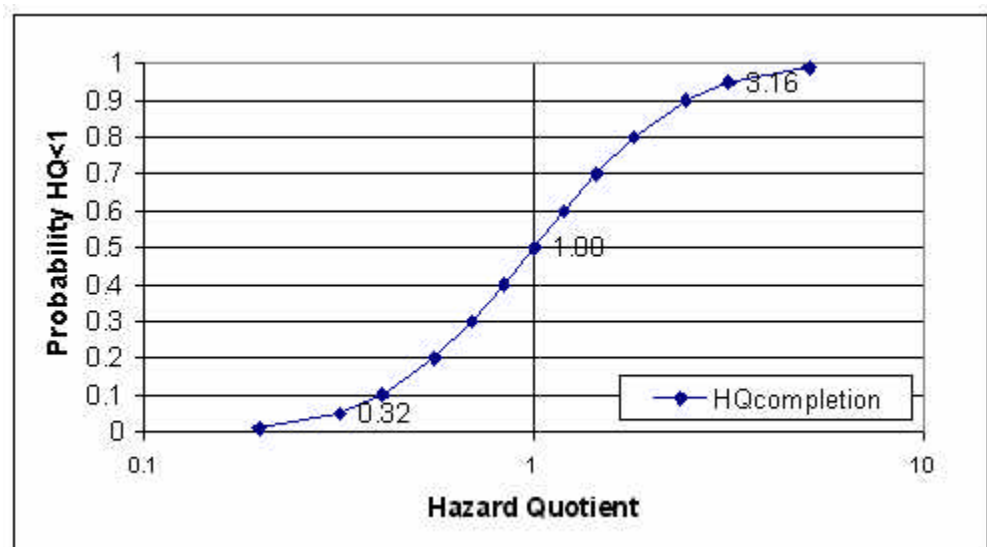


Figure 3: Uncertainty analysis results for completion chemicals, HQcompletion. The uncertainty of dosage has been disregarded. The numbers in the graph represent the 5% and 95% boundaries for a 90% confidence interval.

The confidence limits given here indicate that there is a 90% likelihood that the true value for a calculated HQ of 1.0 lies within the given boundaries. When comparing the HQ for two substances the difference would be significant if the high HQ times the lower boundary is larger than the low HQ.

5. Discussion

The discussion of the results of this study will be split into four sections.

First a short discussion of the results of the sensitivity analysis for both drilling chemicals and for the group of completion and workover chemicals is given. Second the results of the uncertainty analysis for drilling chemicals are presented. Third the results of the uncertainty analysis for completion, workover etc. chemicals are discussed. Finally a short section integrating the results is made.

5.1 Discussion of the Sensitivity analysis

The sensitivity analysis has shown that the CHARM calculations for drilling chemicals are not very sensitive for deviations in the inputs. A percentage change in input parameter results in a similar percentage change in the final result, with the exception of two inputs: Pow and dw28. The larger influence of these two can at least in part be explained by the math that is applied to them. In both cases these inputs are used to raise the base value ten to the power of the input (10^{input}). The influence of Pow (actually log Pow) seems larger than that of Koc. If however these are treated in the same way (varied with or without log-transformation) there influence is identical. Pow was varied in the sensitivity analysis after log-transformation, because this is the most used method of reporting. For Koc it is more customary to report the results without log-transformation. It can however also be available as a log-transformed value.

The fact that Pow exerts this influence when calculating the PECsediment somewhat alleviates the situation. For this calculation it is only used when the preferred input (measured Koc values) is not available. Taking a different approach, the large influence of Pow on the outcome only stresses the point that measured Koc-values be used in the PECsediment calculation.

Also for the group of chemicals referred to as completion chemicals the CHARM calculations are not very sensitive for deviations in the inputs. A percentage change in an input parameter will result in as large a change in the final result.

5.2 Discussion of the Uncertainty analysis for Drilling chemicals

For this uncertainty analysis several combinations of calculation methods were identified (Table 12). Of a total of twelve combinations four combinations were not used because this would result in an unrealistic combination of inputs and intermediary results. An example of such a combination would be calculating the

PECsediment using Pow as input while calculating the PNECbenthic using the Koc as input.

Since all the results of the eight combinations that were calculated can be grouped together, a summary of the results will presented here first. This also helps in simplifying the discussion of the results.

Table 25: Summary table for CHARM uncertainty analysis for Drilling chemicals

| Confidence interval | 5% | 95% | estimator |
|---------------------|------|------|-----------|
| PECwater | 0.07 | 15.0 | |
| PECsediment | 0.05 | 20.0 | Pow |
| PECsediment | 0.04 | 25.0 | Koc |
| PNECpelagic | 0.33 | 3.0 | |
| PNECbenthic | 0.45 | 2.2 | ecotox. |
| PNECbenthic | 0.25 | 4.0 | Pow |
| PNECbenthic | 0.17 | 6.0 | Koc |
| HQwater | 0.05 | 20.0 | |
| HQsediment | 0.04 | 25.0 | ecotox. |
| HQsediment | 0.04 | 25.0 | Pow |
| HQsediment | 0.03 | 36.0 | Koc |
| HQecosystem | * | * | |

The uncertainty analysis for drilling chemicals has shown that the PECwater has a smaller uncertainty associated with it than the PECsediment has. The PNECpelagic is slightly more uncertain than the PNECbenthic when the latter is directly based on results from ecotoxicological testing with sediment organisms. When however extrapolating PNECbenthic from PNECpelagic both estimation methods increase the associated uncertainty. The Koc performs less well than the Pow in this estimation process.

The HQwater values have the narrowest confidence interval of the Hazard Quotients. The HQsediment has a similar confidence interval when arriving at a final value using Pow for PECsediment and Pow or ecotoxicity data for PNECbenthic. When using the Koc as an estimator HQsediment has the largest confidence interval.

For HQecosystem Table 25 shows an asterix. The reason for this is that the calculated confidence interval for HQecosystem in some cases appears to be governed by HQwater and in other cases by HQsediment. Depending on the inputs, it is possible that either one is consistently the critical factor and therefore almost on its own determines the HQecosystem. Rather than defining a confidence interval based on the calculations it would seem prudent to assume the largest possible confidence interval for either underlying Hazard Quotients to be able to determine the HQecosystem. This however depends on the available data and makes it impossible to give a generic confidence interval for HQecosystem. A worst case 95% confidence interval for HQecosystem would be [0.03 ... 36].

Table 26: Summary table for CHARM uncertainty analysis for Drilling chemicals, disregarding uncertainty in dosage (M). * Please refer to the text.

| Confidence interval | 5% | 95% | estimator |
|---------------------|------|------|-----------|
| PECwater | - | - | |
| PECsediment | 0.40 | 2.5 | Pow |
| PECsediment | 0.22 | 4.5 | Koc |
| PNECpelagic | 0.33 | 3.0 | |
| PNECbenthic | 0.45 | 2.2 | ecotox. |
| PNECbenthic | 0.25 | 4.0 | Pow |
| PNECbenthic | 0.17 | 6.0 | Koc |
| HQwater | 0.33 | 3.0 | |
| HQsediment | 0.20 | 5.0 | ecotox. |
| HQsediment | 0.17 | 6.0 | Pow |
| HQsediment | 0.09 | 11.0 | Koc |
| HQecosystem | * | * | |

When the uncertainty in the dosage is disregarded as has been done in Karman and Schobben (1996), because of a weak underlying dataset, the total uncertainty included in the analysis is less. This is clear when the data from Table 25 is compared with that of Table 26 (same as Table 21). When available the PNECs should preferably be estimated from ecotoxicity test data. If this is not possible the uncertainty when using Pow is less than when using Koc. However Pow cannot be used for surface-active substances, in which case Koc is the only remaining option. Also for calculation of PECs use of the Pow in the calculations results in smaller margins of uncertainty than does the Koc.

5.3 Discussion of the Uncertainty analysis for Completion, etc. chemicals

The uncertainty analysis for completion and other chemicals has shown that all PEC calculations for this group of chemicals share the same range of uncertainty. The PNECpelagic is as uncertain as it is for drilling chemicals (Table 27). This however hardly surprising as in both cases the Monte-Carlo simulation has been based on the same lognormal distribution characteristics. The HQ-values that are calculated again share the same range of uncertainty.

Table 27: Summary table for CHARM uncertainty analysis for Completion, etc. chemicals

| Confidence interval | 5% | 95% |
|---------------------|------|------|
| PEC "completion" | 0.07 | 15.0 |
| PNECpelagic | 0.33 | 3.0 |
| HQ "completion" | 0.05 | 20.0 |

From these results it is also possible to give a estimated 90% confidence interval for the calculated HQ: [0.05 . . . 20].

When disregarding dosage (or to be more correct: initial concentration) for “completion” chemicals as a source of uncertainty. The overall uncertainty in the Hazard Quotient drops to that of the PNECpelagic (Table 28).

Table 28: Summary table for CHARM uncertainty analysis for Completion, etc. chemicals, disregarding uncertainty in initial concentration.

| Confidence interval | 5% | 95% |
|---------------------|------|-----|
| PEC "completion" | - | - |
| PNECpelagic | 0.33 | 3.0 |
| HQ "completion" | 0.33 | 3.0 |

5.4 General discussion

From this study it has become clear that not all results from the CHARM model for Drilling chemicals have similar confidence intervals. It is therefore not possible to use generic confidence intervals for the Hazard Quotients calculated for Drilling chemicals. On the other hand the calculations for Completion and Workover chemicals (including cementing chemicals like spacer fluid and mixwater as well as cleaning chemicals and other chemicals) has shown that all these have similar confidence intervals. However when the uncertainty regarding the dosage of substances is disregarded, as it was in Karman and Schobben (1996), the results are comparable with this study. The confidence interval for HQwater of [0.33 .. 3] as was found for both drilling and “completion” chemicals is similar to the final results as reported by Karman and Schobben (1996) for production chemicals. The confidence interval calculated for HQsediment is slightly larger [0.2 .. 5], when ecotoxicity data are available to derive a PNECsediment. If PNECsediment has to be estimated by extrapolating the PNECwater using either Pow or Koc, the confidence interval will be broader (ref. Table 24).

One other point to discuss is the role of different estimators used in the calculations. Especially for the drilling chemicals there are several options available. The PECsediment can be calculated using either the Pow or the Koc (with associated Ftest). The Koc-calculations lead to a higher uncertainty in the end result. Nevertheless the Koc has its place in the CHARM model. The reason is that

for surfactants (substances with surface-active properties) the alternative of the Pow is not usable. The Pow is an unreliable estimator for the environmental behaviour of such compounds, hence the usefulness of the Koc.

For similar reasons as outlined above there is a role to play for the Koc and the Pow when calculating the PNECbenthic. The preferred option however in this case is to have test results from ecotoxicological test with sediment organisms (such as *Corophium volutator*). This also leads to the smallest confidence intervals.

In the Monte Carlo scheme separate (independent) draws from the prescribed distributions were used for Pow and Koc when calculating PNECbenthic. The other calculation for PECsediment had its own randomly drawn inputs to use. A choice was made to do the analysis like this, because in this way it more closely resembles what is encountered in reality. In many cases Pow and Kow are not given as a single number, but as a range. In applications of the CHARM model a choice has been made to calculate a 'realistic worst case'. In line with approach the lower boundaries of the ranges are used when calculating water concentrations. This maximizes water concentration without being unrealistic. The upper boundaries are used when calculating sediment concentrations, which maximizes these concentrations without becoming unrealistic.

The presented results are all based on the model results for a typical North Sea oil platform. After completing all calculations for both oil and gas platforms it became clear that there were only very minor differences between the two types of platform. A choice was made to halve the data to be presented in the report and at the same time making the results more accessible.

Because of weak datasets on the dosage or initial concentration of chemicals as they occur under normal working circumstances, results are presented that neglect this source of uncertainty. For an even better understanding of the uncertainty involved in the use of the CHARM model to estimate (predict) environmental concentrations, a measuring campaign of dosage could improve our knowledge. The effort involved would not be large. A small sample of a fluid that has been made ready for use on a platform could be set aside for analysis of the realized concentration of substances relative to the intended concentrations.

In Table 29 the results of this study are summarized, together with the 90% confidence limits for production chemicals as reported by Karman and Schobben (1996). From this table it can be seen that for completion and 'other' chemicals the confidence limits are the same as for production chemicals. The same holds true for drilling chemicals when dealing with the HQwater. For the HQsediment the confidence limits are different for the possible calculation routes.

Table 29: Summary table of 90% confidence limits a $HQ=1.0$

| | 90% Confidence Limits for $HQ=1.0$ |
|--|---------------------------------------|
| Production chemicals ¹ | 0.33 – 3.0 |
| Drilling Chemicals | |
| <u>HQwater</u> | 0.33 – 3.0 |
| <u>HQsediment, ecotox</u> | 0.20 – 5.0 |
| <u>HQsediment, Pow</u> | 0.17 – 6.0 |
| <u>HQsediment, Koc</u> | 0.09 – 11.0 |
| Completion Chemicals | 0.33 – 3.0 |
| 'Other' Chemicals | 0.33 – 3.0 |

¹ from Karman and Schobben, 1996

When applying the results of this study to CHARM-calculations that are performed for Risk Analysis, the presented confidence limits for Hazard Quotients can also be applied to Risk Quotients (RQs). Provided the RQs being compared have been calculated using the same input parameters except for those describing the properties of the substances. When calculating RQs actual values at the location of the installation being studied are used for such inputs as water depth and current velocity. This makes the RQs a more reliable estimator for the environmental impact of a substance at that location than the HQ, however it also adds new sources of uncertainty. The current velocity will vary during the year and depending on weather conditions. As long as the same value is used for all substance under consideration in the Risk Analysis process for an installation this should not be problematic. In deciding which substance is preferable at a specific installation other considerations besides the RQs make come into play. As Karman and Schobben (1996) have pointed out a substance that is more likely to affect benthic organisms is may not be the preferred choice on a location with a sensitive benthic community. On the other hand the same compound could very well be the preferred option on a location where the pelagic community is more sensitive.

5.5 Using HQ as the Criterion for Selecting Alternative Chemicals

Confidence intervals around a Hazard Quotient of 1 have now been calculated for all types of offshore E&P chemicals and are presented in the following table:

| Type of chemical | Confidence interval | Range of HQ |
|-------------------------------------|---------------------|--------------|
| Production chemicals (water comp.) | [0.33 .. 3] | HQ/3 .. HQ*3 |
| Drilling chemicals (water comp.) | [0.33 .. 3] | HQ/3 .. HQ*3 |
| Drilling chemicals (sediment comp.) | [0.2 .. 5] | HQ/5 .. HQ*5 |
| Other chemicals (water comp.) | [0.33 .. 3] | HQ/3 .. HQ*3 |

Please note that these figures assume that the intended dosage of chemicals on the platform is what is actually dosed, although in practice the actual dosage may introduce additional uncertainty.

The uncertainty in HQ is relevant when comparing different products on the basis of their HQ. For example, an operator is currently using product A in the “Other Chemical” category with HQ=4 and is looking for an alternative with a better environmental performance. The available alternatives are product B (HQ=0.8) and product C (HQ=0.5).

Although both products B and C seem good candidates, for a good comparison the uncertainty ranges should be taken into account, as depicted in the figure below. It can now be seen that the confidence intervals for product A and B overlap (which means that there is a possibility that B does not necessarily have a better environmental performance than product A), while the confidence intervals for product A and C do not overlap. From this it can be concluded that product C is the only alternative for which we can be sure that it is a better alternative concerning its environmental performance.

If product C appears technically not applicable to the specific platform or when this product appears to have a worse effect on human exposure, product B is the only realistically available alternative. As we concluded before on the basis of overlapping confidence intervals that B is not necessarily better than A, a better look at the confidence intervals is required to quantify the chances. If studied in more detail it can be seen that the reported HQ of product A (=4) does not fall within the confidence interval of product B (upper limit = 2.4) and *vice versa* (HQ product B = 0.8 which is lower than the lower limit of the HQ of product A which is 1.33). This means that the probability is still significantly higher that product B has a better environmental performance.

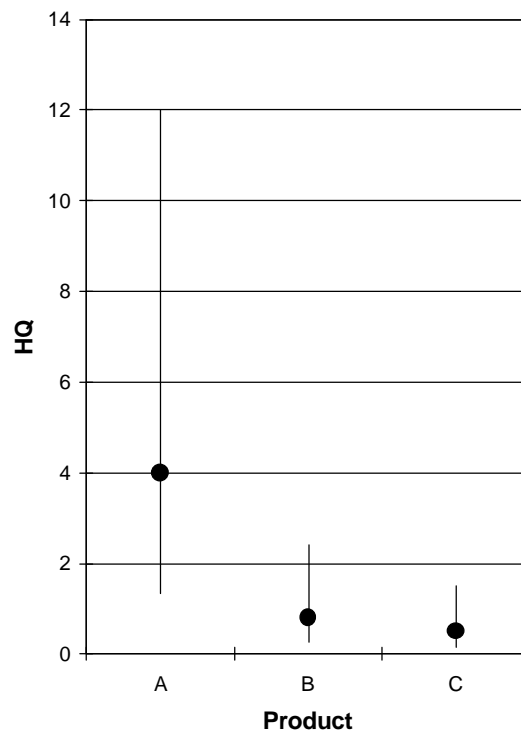


Figure 4. Example of calculated Hazard Quotients and their confidence intervals which demonstrate the use of these intervals for selecting alternative chemicals.

5.5.1 Confidence intervals for RQ's

As discussed, the range of calculated HQs presented above is the absolute minimum that could be realised and assume that there is no uncertainty in the concentration of chemical that is actually applied on the platform.

Similarly, there will be additional sources of uncertainty that have not been calculated and will impact the calculation of Risk Quotients. In practice, then, it must be assumed that the confidence limits for calculated HQs and RQs may be greater than the minimum values indicated here. Comparison and selection of chemicals must, therefore, be made with due regard to this fact.

6. Literature

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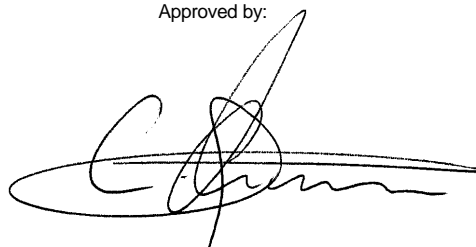
September 2, 2002 – January 1, 2003

Signature:



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February 11, 2003

Approved by:



C.C. Karman
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February 11, 2003

Appendix 1 Artificial set of ecotoxicity data

| Compound | Species | Time | Effecttype | Concentration | Unit |
|----------|-------------------|------|------------|---------------|--------|
| A | Algae | - | NOEC | 0.01 | mg.l-1 |
| A | Crustacean | - | NOEC | 0.01 | mg.l-1 |
| A | Fish | - | NOEC | 0.01 | mg.l-1 |
| A | Sediment reworker | - | NOEC | 0.01 | mg.l-1 |
| B | Algae | - | NOEC | 0.1 | mg.l-1 |
| B | Crustacean | - | NOEC | 0.1 | mg.l-1 |
| B | Fish | - | NOEC | 0.1 | mg.l-1 |
| B | Sediment reworker | - | NOEC | 0.1 | mg.l-1 |
| C | Algae | - | NOEC | 1 | mg.l-1 |
| C | Crustacean | - | NOEC | 1 | mg.l-1 |
| C | Fish | - | NOEC | 1 | mg.l-1 |
| C | Sediment reworker | - | NOEC | 1 | mg.l-1 |
| A | Algae | - | LC50 | 0.1 | mg.l-1 |
| A | Crustacean | - | LC50 | 0.1 | mg.l-1 |
| A | Fish | - | LC50 | 0.1 | mg.l-1 |
| A | Sediment reworker | - | LC50 | 0.1 | mg.l-1 |
| B | Algae | - | LC50 | 1 | mg.l-1 |
| B | Crustacean | - | LC50 | 1 | mg.l-1 |
| B | Fish | - | LC50 | 1 | mg.l-1 |
| B | Sediment reworker | - | LC50 | 1 | mg.l-1 |
| C | Algae | - | LC50 | 10 | mg.l-1 |
| C | Crustacean | - | LC50 | 10 | mg.l-1 |
| C | Fish | - | LC50 | 10 | mg.l-1 |
| C | Sediment reworker | - | LC50 | 10 | mg.l-1 |