

CHARM

CHEMICAL HAZARD ASSESSMENT AND RISK MANAGEMENT

For the use and discharge of chemicals used offshore

User Guide Version 1.5 ^⑤

CHARM IMPLEMENTATION NETWORK – CIN

2017

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A CIN REVISED CHARM REPORT

**A USER GUIDE FOR THE EVALUATION OF
CHEMICALS USED AND DISCHARGED OFFSHORE**

VERSION 1.5 ⑤

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Date: 2017

Sponsors: Netherlands Oil & Gas Exploration and Production Association NOGEP
Netherlands Ministry of Economic Affairs (EZ)
Netherlands Ministry of Housing, Spatial Planning and Environment (VROM)
Netherlands Ministry of Transport, Public Works and Water Management (V&W)
International Association of Oil & Gas Producers (IOGP)
European Oilfield Speciality Chemicals Association (EOSCA)

Revisions List ③

Version	Date	Description	Originator	Reviewed	Approved
1.5	2017	<p>Minor typos and nomenclature, update all references to Recommendations updated and some formulae corrected / clarified. The term “platform” replaced with “installation” and “release” with “discharge”.</p> <p>P8, use of half-life values derived from simulation tests.</p> <p>P12, Clarification added under Production Chemicals.</p> <p>P13, redundant explanation of injection chemicals removed, and Drilling Muds categories reworded.</p> <p>P14, sentence spacer and mixwater adjusted for clarity.</p> <p>P15, reference to HOCNF guidelines for all chemical functions added.</p> <p>P19, paragraph on injection water reworded for transparency.</p> <p>P27, section on completion, workover, squeeze treatments reworded for clarity.</p> <p>P34, note added to Box 6 to recognise PEC_{sediment} over estimation.</p> <p>P35, Section 3.3 moved to Appendix, no longer relevant.</p> <p>P35-36, half-life thresholds added to acceptability criteria.</p> <p>P36, limitations of Batch Dilution Factors (BDFs) noted.</p> <p>P37, limitation of PEC_{sediment} over estimation with $\text{Log Pow} > 6$ included.</p> <p>P39, references to HOCNF form updated</p> <p>P48, Statement after table on PLONOR chemicals removed.</p> <p>P53, noted that discharge factor of 0.33 is a minimum value.</p> <p>P58, amendments to wording for drilling chemicals and end note for clarity.</p> <p>P65, specific gravity of mud moved to site specific data table.</p> <p>P70-71, note added that values in tables relate to bulk discharge not individual chemicals.</p> <p>P73, note added that default values are for hazard assessment.</p> <p>P73-74, “used in Hazzard Assessment” added to table titles.</p> <p>P77, Appendix VIII added, relocating previous Section 3.3.</p> <p>Brackets added to Eqns: 2a, 2b, 3, 4, 5, 6.</p>	NR	CIN group	
1.4	03/02/2005	<p>P18 Brackets added to equns 2b, 4 & 5 for clarity P25 Clarification of NOEC.</p> <p>P29/71 Corrigendum to equation 26c</p> <p>P38/46/69 Residual current speed added to Tables 5 & 6</p> <p>P52/53 Chapter 5.1 moved to new chapter 6 on uncertainty analysis. Subsequent chapters renumbered</p> <p>P72 K_{oc} added to Appendix VII</p>	GP	CIN group	CIN group
1.3	31/01/2004	<p>NB Changes annotated ④ in blue text</p> <p>Cover page added</p> <p>P1 Version Number, Author list and footnote updated P2 Revision list included.</p>	GP	CIN group	CIN group

Version	Date	Description	Originator	Reviewed	Approved
		<p>P5/7/34 Use of CHARM inapplicable for inorganics added.</p> <p>P5/8 Harmonised added to OSPAR pre-screening, changed wording re log BCF and threshold values.</p> <p>P6/12/13/24/25/51/52/55/61 Squeeze & Hydrotest treatment details added.</p> <p>P8 Introduction updated</p> <p>P8/9 Reference Platforms explained</p> <p>P10 Scavengers added to list</p> <p>P11/62 OBM changed to oil phase fluids OPF</p> <p>P13 Dissolvers added to list</p> <p>P17 Text re surfactants changed</p> <p>P18 Consistency of F_{pw} & Clarification of Ct.</p> <p>P21 Removed references to PARCOM List A and OLF. P27 Table 2 PNECbenthic assessment clarified.</p> <p>P28 Clarified equation 23 (to the power of...)</p> <p>P29/43/61 Equation 26c added for assessment of surfactants</p> <p>P33 Changed sentence re MW > 600 & wording around log BCF</p> <p>P34 Comparability of HQ or RQ.</p> <p>P36 Surfactant and Injection Chemical rearranged in Scheme 1 to remove confusion.</p> <p>P37 Scheme 1 steps reordered & default values for injection water and Fatty Amides added.</p> <p>P37/38/47/50/52 Symbols added to Tables 3, 4, 5, 6, 8 and 9.</p> <p>P38 Table 5 moved from 5.1.1 to 5.1.2</p> <p>P47 Ref non-standard drill sections added.</p> <p>P53/54 Definition of Platform Density clarified.</p> <p>P68 List of default values added as Appendix V</p> <p>P70 List of equations added as Appendix VI</p> <p>P71 List of constants etc added as Appendix VII</p>			
1.2	12/07/2001			CIN group	CIN group
1.0	06/08/1999			CIN group	CIN group

Further revisions of this document will be posted on the IOGP or EOSCA websites on www.iogp.org or www.eosca.eu ⑤

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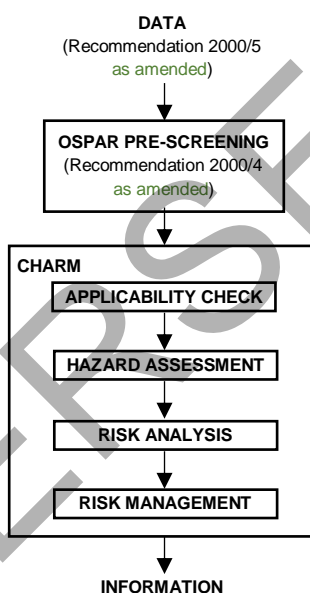
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Executive Summary

Since offshore drilling and production of oil and gas may result in environmental effects, it was decided to control the use and discharge of chemicals in the North Sea OSPAR area. Some of the participating countries within the framework of the Oslo and Paris Conventions agreed upon the development of a Harmonised Mandatory Control System (PARCOM Decision 96/3, now OSPAR Decision 2000/2 *as amended*). In this Control System, CHARM is referred to as a model for calculating the PEC:PNEC ratios with the objective to rank chemicals on the basis of these ratios.

The CHARM model was developed in close co-operation between the Exploration and Production (E&P) industry, chemical suppliers and authorities of some of the countries party to the Oslo and Paris conventions. It is used to carry out environmental evaluations on the basis of the internationally accepted PEC:PNEC (Predicted Environmental Concentration : Predicted No Effect Concentration) approach, which has also been adopted by the OSPAR convention.

The model enables a stepwise environmental evaluation of E&P chemicals, according to the following scheme:



OSPAR Harmonised ^③**Pre-screening:** Although not part of the CHARM model, the model must not be seen as separate from the OSPAR Pre-screening. Pre-screening is based upon OSPAR Recommendation 2000/4 *as amended*, according to which individual national authorities have introduced their own systems for the evaluation of E&P chemicals.

Applicability check: The PEC:PNEC approach, which is the basis for the CHARM model, does not account for long term effects of persistent and bioaccumulative substances so no foodchain effects can be assessed. The CHARM model is therefore not applicable for substances with these characteristics. **The CHARM model is also not applicable for inorganic substances.** ^③ The Applicability Check was introduced as a filter for those chemicals which should not be assessed with the CHARM model.

This effectively means that the CHARM model should not be applied to chemicals with:

i) a 28-day biodegradation value of <20% **and** a log bioconcentration factor >100,000. In those cases where no experimental bioconcentration factor value is available, this criterion can be replaced by: $\log P_{ow} > 5$ and molecular weight < 700. ③ ⑤

or

ii) half-life values derived from simulation tests submitted under REACH (EC 1907/2006) greater than 60 and 180 days in marine water and sediment respectively (e.g. OECD 308, 309 conducted with marine water and sediment as appropriate). ⑤

Additionally, two other limitations of the model have been identified. The first is that chemicals with surface active properties can only be handled by defining a number of default values, but with additional uncertainties. Furthermore, it should be noted that although the CHARM model can be used for both single substances and preparations, there is no consensus yet on how to deal with preparations. However, if the data (for example toxicity data) are only available for the preparation, then the calculation rules applied to these data in the model are based on the agreements so far reached within the CIN framework (page 33, equations 30 and 31).

Hazard Assessment: The purpose of Hazard Assessment within CHARM is to determine the Hazard Quotient, in order to select the chemicals with the lowest environmental impact. The hazard of each substance is quantified as the PEC:PNEC ratio, calculated on the basis of the intrinsic chemical properties and toxicity of the chemical, and information on the conditions on and around a standard **installation**. Standard **installations** (for both oil and gas production) have been defined for the North Sea region to be used in realistic worst case scenarios.

The calculation rules for estimating a predicted environmental concentration (PEC) are different for chemicals with different types of application, since they might be introduced into the environment in a different way. Application groups considered in the CHARM model are:

- production chemicals (with injection chemicals and surfactants as special cases)
- drilling chemicals (Water Based Muds only)
- cementing chemicals (i.e., spacer and mixwater)
- completion and workover chemicals **including well squeeze treatments and also pipeline hydrotest and preservation treating chemicals.** ③

The PNEC calculation is comparable for the chemicals from all application groups, and **is** based upon the internationally accepted OECD scheme. This means that an assessment factor (1, 10 or 100) is applied to the lowest available toxicity value (NOEC or L(E)C₅₀). The scheme is used to determine the required assessment factor.

Finally, the Hazard Quotient (HQ) is calculated, by taking the ratio of PEC and PNEC. This is done for both the water-phase and the sediment-phase of the environment. The higher of the two HQ values represents the HQ for the ecosystem. This figure can be regarded as an indication of the likelihood of adverse effects occurring due to the use and discharge of the chemical under a realistic worst-case scenario.

Risk Analysis: The difference between Hazard Assessment and Risk Analysis in CHARM is that in Risk Analysis actual data are used on the conditions on and around the **installation** from which the chemical is used and discharged. The Risk Quotient (RQ) derived in this module is therefore a site specific indication of the likelihood of adverse effects occurring due to the use and discharge of a chemical.

Risk Management: The risk management module, although not accepted by all parties involved, has been included in the CHARM model in order to enable the comparison of risk-reducing measures. The basis of this module is the Risk Analysis module, in which a site-specific Risk Quotient can be calculated for individual substances or -preparation. The Risk Management module offers the means to combine the RQ of individual substances into a single Risk estimate for a combination of chemicals. This combination is often the package of chemicals used in a specific situation (e.g., series of mud additives or a set of production chemicals). Subsequently, several alternatives for the “standard” chemical package can be compared on the basis of their cost and eventual risk reduction.

1. Introduction

Offshore drilling and production of oil and gas has become increasingly important for all OSPAR countries. These activities often lead to discharges of chemicals into the marine environment which include production chemicals, drilling muds, well cleaning fluids and cements. These discharges may result in environmental effects. To control the use and discharge of chemicals, a Harmonised Mandatory Control System (HMCS) for the Use and Reduction of the Discharge of Offshore Chemicals has been agreed upon by participating countries within the framework of the *OSLO and PARIS Conventions for the prevention of marine pollution* (currently referred to as *The convention for the protection of the marine environment of the North-east Atlantic*). In OSPAR Decision 2000/2, on a Harmonised Mandatory Control System (HMCS), the CHARM model has been adopted as a model which enables **the** calculation of relative PEC:PNEC ratios for ranking of chemicals.

The CHARM (Chemical Hazard Assessment and Risk Management) model was developed in close co-operation between the E&P industry, chemical suppliers and authorities of some of the countries party to the Oslo and Paris conventions. It can be used as a tool by governments in the harmonisation of regulations; by regulators to assist in decision making; by Operators for guiding operational improvement; and by chemical suppliers in the development of chemicals with improved environmental characteristics.

Various parts of the model have been validated in experimental programmes. The results of these programmes are not presented in this report. For more information, please refer to the original reports (Foekema *et al.*, 1998; Stagg *et al.*, 1996).

It must be noted that the CHARM model is to be applied for operational discharges of chemicals **other than inorganics** ③ in the process of drilling, completion and production. Potential risks during the transport of chemicals, handling of unused materials, **unintentional releases** due to calamities and other **releases**, such as air emissions or sanitary waste discharges, are not assessed by this model. Furthermore, CHARM does not assess specific risks that may arise from (long term) exposure to persistent chemicals. Finally, one should note that there is no consensus yet on the application of CHARM to chemical products that consist of a mixture of a number of substances (i.e., preparations). Chapter 3.3 sets out the currently agreed calculation rules for preparations.

The CHARM model cannot be used directly with chemicals having surfactant properties because several calculations in the model are based upon the $\log P_{ow}$, a non-existent parameter for surfactants. For the surfactants, the model is using default values, which introduce some additional uncertainties.

The [User Guide](#) is prepared on the initiative of the CHARM Implementation Network (CIN). The members of the CIN evaluate the CHARM model [on an on-going basis](#) in practical day-to-day situations. Their findings have led to suggestions and recommendations for [revisions of the CHARM model](#) and reports [incorporated into this current version of the Guide](#). ③

1.1 Overview of the CHARM model

The CHARM model is used to carry out risk assessments of discharges of [Exploration and Production \(E&P\)](#) ⑤ chemicals, from [installations](#) into the marine environment. This evaluation is based on the internationally-accepted PEC:PNEC (Predicted Environmental Concentration : Predicted No Effect Concentration) approach (see Chapter 3). The model enables a stepwise environmental evaluation of E&P chemicals by means of a successive Applicability check > Hazard Assessment > Risk Analysis > Risk Management process. A schematic representation of the CHARM model and a brief description of each of the components is given below.

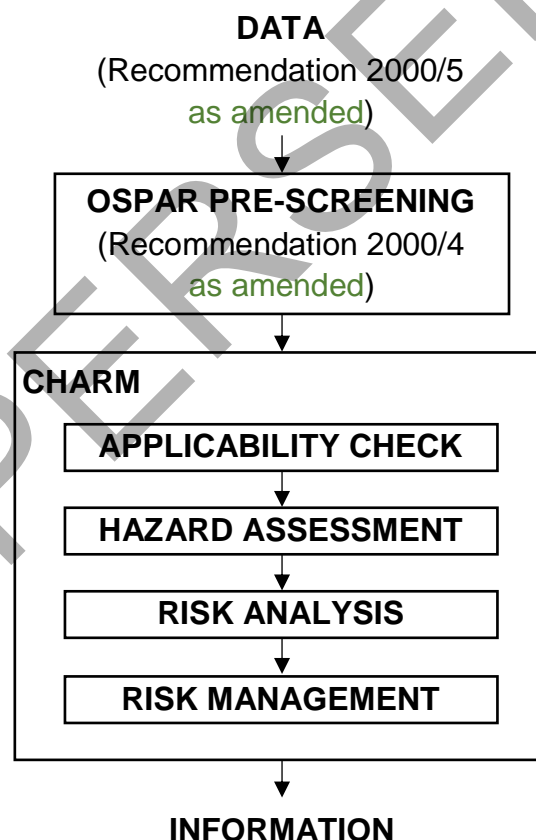


Figure 1: A schematic representation of the CHARM model ⑤

OSPAR Harmonised ③ **pre-screening** in accordance with criteria laid out in OSPAR Recommendation 2000/4 as amended ⑤ is a requirement of OSPAR Decision 2000/2. Following this decision, individual national authorities have introduced their own pre-screening system for the evaluation of E&P chemicals in addition to the evaluation with the CHARM model.

The Applicability check in CHARM identifies chemicals that might lead to specific long term 'chronic' effects since these cannot be assessed using a PEC:PNEC comparison. Those chemicals are characterised by long term persistency and a high potential for bioaccumulation. The Applicability check is therefore used to screen substances prior to the use of the CHARM model.

In CHARM, **Hazard Assessment** provides a general environmental evaluation of a chemical based on its intrinsic properties under "realistic worst case" conditions of the so called reference installations. A summary of the default values for characteristic conditions of the reference installation used in Hazard Assessment is given in Table 5. Other default values for flow, dilution and fraction released etc are given in Tables 3 and 4, and Tables 6 to 9. These are all summarised in Appendix V. ③ Hazard Assessment is primarily intended for selecting chemicals with the lowest adverse effects to the environmental compartments of concern (water and sediments). In making Hazard Assessments of chemicals it is important to use concentrations or dose rates that would expect to be relevant for the reference installation conditions. These may be different from actual concentrations or dose rates used at any specific location. ③

In CHARM, **Risk Analysis** is an evaluation of the environmental impact of the discharge of a chemical under **actual**, site specific conditions, including concentrations, dose or flow rates and installation location. ③ Risk Analysis can therefore, be used to select chemicals according to the impacts they will have on the environment at a specific site.

In CHARM, **Risk Management** is used to compare various risk reducing measures based on cost/benefit (benefit = risk reduction) analyses for a combination of chemicals.

The CHARM model can perform all standard calculations using the data reported in the **OSPAR Harmonised Offshore Chemical Notification Format (HOCNF)**.

1.2 Overview of report

Chapters 1, 2 and 3 of this report contain a description of the model, the calculation rules used and their background. Chapters 4 to 8 can be regarded as the User Guide, in which the application of the model for Hazard Assessment, Risk Analysis and Risk Management is described and explained.

Since the calculation rules of CHARM are different for chemicals from different application groups (i.e., production, drilling, cementing and completion and workover chemicals), these application groups are discussed in detail in Chapter 2. Attention is given to the specific characteristics of each of the application groups.

All of the calculation rules are described in Chapter 3, 'PEC:PNEC approach'. In this chapter the basics of the PEC:PNEC approach are elaborated upon, followed by a description of the calculation rules for estimating the environmental concentration (PEC) for each of the application groups. A detailed

description of the approach for estimating a No Effect Concentration (PNEC) is also given. This makes it possible to calculate a PEC:PNEC ratio (referred to as the Hazard or Risk Quotient).

Chapters 4, 5, 6 and 7 guide the user through the Applicability Check Hazard Assessment, Risk Analysis and Risk Management modules. Each chapter consists of a step-by-step description of the input data, processing steps and results. These chapters are supplemented by calculation flow-charts. Chapter 8 gives a list (and explanation) of all data that is necessary for performing the calculations in any of the application groups.

2. Application groups

Within CHARM, chemicals are categorised into four application groups: Production Chemicals (including injection chemicals and surfactants), Drilling Chemicals, Cementing Chemicals and Completion and Workover Chemicals. This is done in response to the fact that the application and discharge of these chemicals varies widely, resulting in the need for different modelling approaches.

2.1 Production chemicals

Production chemicals are added to either the injection water or to the produced fluids in order to: protect the installation, protect the reservoir, maintain production efficiency, or to separate the oil/gas and water. After the chemicals have been added, they partition between the produced fluids, some dissolving primarily in the oily fraction, some primarily in the water fraction, and some in both. The chemicals which move into the water phase may be discharged into the environment with the produced water. Chemicals used during well intervention or pipeline operations may remain in-situ until production commences. These chemicals will be processed with production fluids and discharged as described above ⑤. Details of a few production chemical groups are given below.

- **Corrosion inhibitors:** added to the injection water and/or the produced fluids in order to protect the installation against corrosion
- **Scale inhibitors:** water soluble chemicals added to the produced fluids in order to prevent the formation of scales
- **Demulsifiers or deoilers:** added to the produced fluids to accelerate the separation of the hydrocarbon and water phases
- **Anti-foaming agents:** added to the produced oil in order to speed up the removal of gas bubbles
- **Biocides:** added to eliminate bacteria, which produce corrosive by-products such as hydrogen sulphide
- **Gas hydrate inhibitors:** added to the production stream in order to prevent the formation of gas hydrates in pipelines
- **Scavengers:** added to remove hydrogen sulphide from produced gas or oxygen from injection water. ③

Within the CHARM model, injection chemicals are regarded as a special type of production chemicals for which separate calculation rules need to be applied. ⑤

2.2 Drilling chemicals

Drilling muds are liquids used in drilling operations to cool and lubricate the bit, to carry away drill cuttings and to balance underground hydrostatic pressure. Muds are pumped down the drill string, through the bit and then carry the drill-cuttings through the annulus back up to the surface.

Drilling muds can be divided into two broad categories based on the base fluid used, namely, Oil Based Muds (OBM) and Water-Based Muds (WBM). Historically OBM, WBM and Synthetic-Based Muds (SBM) may have been used during drilling operations. ⑤

In addition to the base fluid, drilling muds contain barite and a variety of chemicals which are added to give the mud the desired properties. These chemicals may include:

- **Viscosifiers**
- **Emulsifiers**
- **Biocides**
- **Lubricants**
- **Wetting agents**
- **Corrosion inhibitors**
- **Surfactants**
- **Detergents**
- **Caustic soda (NaOH)**
- **Salts (NaCl, CaCl₂, KCl)**
- **Organic polymers**
- **Fluid loss control agents**

The physico-chemical characteristics of WBM, and thus their applicability in drilling operations, are different from those of organic [phase fluids](#). Although WBM are the preferred environmental option, for both technical and safety reasons organic [phase fluids](#) may still be required in situations where drilling operations are more complex. These include the lower sections, specific formations, High Pressure/High Temperature wells, and non-vertical drilling operations. It is, therefore, common practice for WBM to be used for drilling the upper section of the well and organic [phase fluids](#) for the more complex sections.

[Organic phase fluids](#) are not addressed in the CHARM model. The main reason for this is that since long term effects have been demonstrated on the basis of field monitoring, the discharge of **OPF** is prohibited [except in exceptional circumstances](#). Until solutions have been found to the numerous problems related to the availability of input-parameters for organic [phase fluids](#) (e.g., dose, mudweight, aerobic vs. anaerobic data, bioconcentration data, base fluid vs. mud data, etc.), it has been decided that (components of) these muds will not be assessed through CHARM.

Water based Muds

Drilling chemicals represent more than 95% by weight of the offshore chemicals discharged to the North Sea. For the purposes of CHARM, drilling muds are assumed to be discharged in two modes:

1. “Continuous” discharges of mud adhering to the drilled cuttings. Continuous discharge is in fact a misnomer as the discharges tend to be intermittent. The rate of discharge will usually be small and the material will almost immediately be dispersed and diluted.
2. “Batchwise” discharges occur during drilling operations when the mud needs to be diluted. Some of the mud system may have to be discharged and the remainder of the system diluted. Batchwise discharges also occur at the end of a section where a new or different mud will be required in the next section. Finally, these discharges will also occur at the end of the drilling phase of the well when all operations are finished. ⑤ These discharges are larger both in volume and rate of discharge.

2.3 Cementing chemicals

After the first sections of a well have been drilled, casings are inserted in the well and cemented into place. This is done by injecting cement down into the casing. As the cement reaches the lower end of the casing, it is forced up into the annular spaces. During this process some excess cement might be forced out of the annular spaces and deposited on the sea-bed. This cement may remain liquid for several hours, during which time the discharge of chemicals into the ambient waters is considered negligible. After the cement has hardened the chemical components of the cement are locked in the inert cement matrix. As a result, chemical emissions from excess cement deposited on the sea floor are not considered within CHARM.

The last casings to be cemented in a well are called the liners. A liner is a standard casing which does not extend all the way to the surface, but is hung from the inside of the previous casing string. When cementing a liner, a spacer is pumped into the annular prior to the cement slurry to separate the drilling fluid and the cement. The volume of cement slurry to be used is normally overestimated in order to ensure that there will be adequate cementing throughout the annulus. This excess cement is brought back to the surface along with the spacer, both of which will be heavily contaminated with the drilling mud. In cases where the oil based muds are used, these wastes will not be discharged even if the contaminated drilling mud is separated. If WBM are used, these wastes may be discharged, in which case, the chemicals present in the spacer, cement slurry and excess mixwater are evaluated within CHARM.

The discharge of residual spacer, mixwater and slurry from mixing pits, fly units and equipment post cementing is considered within CHARM. ⑤

Cementing chemicals can be divided into nine categories:

- **Accelerators:** Chemicals that reduce the setting time of cement systems.
- **Retarders:** Chemicals that extend the setting time of a cement system
- **Extenders:** Materials that lower the density of a cement system, and/or reduce the quantity of cement per unit of volume of set product.
- **Weighting agents:** Materials which increase the density of a cement system
- **Dispersants:** Chemicals that reduce the viscosity of a cement slurry
- **Fluid loss control agents:** Materials which control the loss of the aqueous phase of a cement system to the formation
- **Lost circulation control agents:** Materials which control the loss of cement slurry to weak or irregular formations

- **Anti gas migration additives:** Materials which reduce the cement slurry permeability to gas
- **Speciality additives:** Miscellaneous additives e.g., antifoam agents, free water control agents

2.4 Completion, Workover, Squeeze and Hydrotest chemicals ③

Completion and workover chemicals are discussed here together due to the similarity in their use and discharge. Both groups of chemicals are used in order to optimise production of the well and act on the well or formation itself. Completion operations are carried out after drilling has been completed and before production begins. These operations prepare the well for production and can be broken down into five steps:

1. Cleaning of surface lines and surface equipment.
2. Well cleaning (i.e., cleaning of casing and pipes)
3. Displacement of the well fluids
4. The final operation. This might be perforating and subsequently closing the well to temporarily prevent production.
5. Starting production or injection. When the completion operation is finalised, the fluid in the production tubing will be displaced out of the well or pumped into the formation by a lighter fluid in order to initiate production by reducing the hydrostatic pressure. Fluids pumped into the formation will be produced back in various degrees as the production starts.

Workover operations occur during production and can be broken down into two groups:

1. Use of reactive fluids for cleaning operations, chemical squeezing and acidising
2. Use of non-reactive fluids for hydraulic fracturing.

This algorithm is also the most appropriate for assessment of chemicals used in the water for hydrotesting and preserving pipelines prior to bringing on to production. This water is generally discharged at the time of commissioning to first oil or gas. ③

The chemicals used in completion and workover fluids can be divided into the following different categories (full list of functions in Appendix of HOCNF Guidelines, OSPAR Agreement 12/05 as amended): ⑤

- **Acids:** Used to dissolve hardened materials and as a breaker in solvent fluids, kill pills and gelled fluids.
- **Alkalis:** Used together with surfactants and viscosifiers in order to control pH.
- **Well Cleaning Chemicals:** Used in cleaning fluid to reduce the surface tension between water and oil in order to disperse or dissolve the well fluids or flocculate dirt particles.
- **Dissolvers:** Used to remove scale, asphaltene or wax deposited in the well tubulars during production operations. ③
- **Viscosifiers:** Used in push pills and carrier fluids in order to increase viscosity of the fluid.
- **Breakers:** Used to reduce the viscosity of a fluid in order to regain permeability.
- **Fluid Loss and Diverting Additives:** Used in kill pills in order to stop production and also to distribute treating fluids over a zone with varying permeability.
- **Defoamers/Anti-foamers:** Used to remove, or prevent the development of foam.
- **Clear Brines/Sea water:** Used as base fluid for almost all water miscible completion fluids.
- **Corrosion Inhibitors:** Used to help prevent corrosion of the installation.

- **Surface Active Agents:** Used in fluids to lower surface tension and interfacial tension in order to break emulsions, establish favourable wettability characteristics for the reservoir rocks or casing, displace oil from oil contaminated particles and fines, etc.
- **Biocides:** Used to prevent bacterial growth in well fluids.
- **Clay Control Additives:** Used in well fluids to prevent migration of clay particles, which can plug the pore channels in the reservoir.
- **Scale Inhibitors:** Used in brines in order to inhibit scale formation.
- **Oxygen Scavengers:** Used to reduce or eliminate free oxygen in completion fluids as a corrosion prevention.

3. PEC:PNEC Approach

Within CHARM, environmental Hazard Assessment, Risk Analysis and Risk Management are all based on Hazard and Risk Quotients (HQ and RQ), which are calculated using the internationally accepted PEC:PNEC method (Basetto *et al.*, 1990). The traditional method of comparing single PEC and PNEC values by calculating the ratio of PEC and PNEC is illustrated in Figure 2.

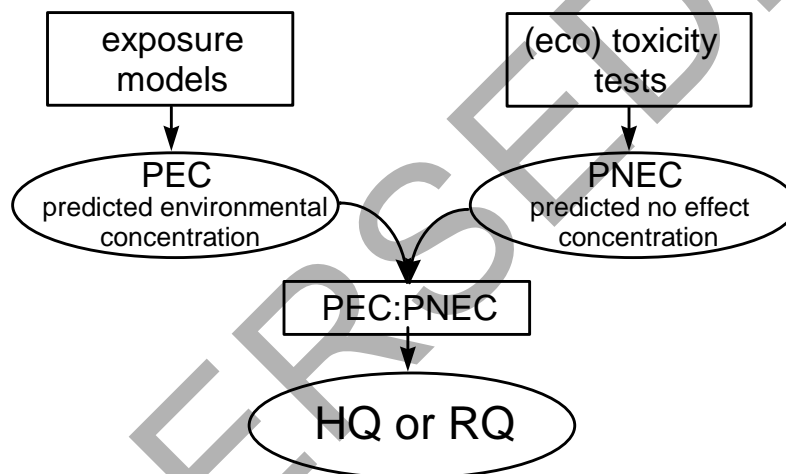


Figure 2: The traditional method of comparing PEC and PNEC in order to calculate a Hazard or Risk Quotient.

The Predicted Environmental Concentration (PEC) is an estimate of the expected concentration of a chemical to which the environment will be exposed during and after the discharge of that chemical. The actual exposure depends upon the intrinsic properties of the chemical (such as its partition coefficient and degradation), the concentration in the waste stream, and the dilution in the receiving environmental compartment.

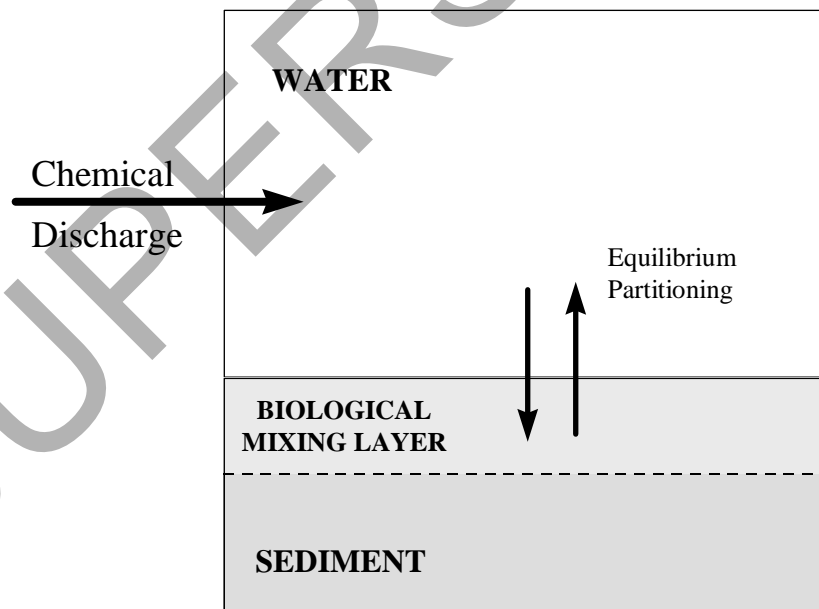
Most of the calculations within CHARM are concerned with the estimation of the concentration of a chemical in the waste stream. This is dependent upon the process in which it is used, the dosage of the chemical, its partitioning characteristics, the oil (or condensate) and water production at the **installation**, the in-process degradation mechanisms and the residence time before **discharge**.

As the name suggests, the Predicted No Effect Concentration (PNEC) is an estimate of the highest concentration of a chemical in a particular environmental compartment at which no adverse effects are expected. It is, thus, an estimate of the sensitivity of the ecosystem to a certain chemical. In general the PNEC represents a toxicity threshold, derived from standard toxicity data (NOECs, LC₅₀s, EC₅₀s)¹.

Within the CHARM model, a PNEC_{water} is extrapolated from toxicity data using the OECD method, which is accepted by most OSPAR Countries. In this method, the PNEC for a certain ecosystem is determined by applying an empirical extrapolation factor to the lowest available toxicity value. The magnitude of the extrapolation factor depends upon the suitability of the available ecotoxicological data.

By calculating a PEC:PNEC ratio for a certain chemical, the CHARM model compares the expected environmental exposure to a chemical (quantified as the PEC) with the sensitivity of the environment to that chemical (quantified as the PNEC). If the PEC:PNEC ratio (an indication of the likelihood that adverse effects will occur) is larger than 1, an environmental effect may be expected. It must be noted, however, that these results should be interpreted with care, and only used as a means to estimate potential adverse environmental effects of chemicals. Furthermore, in order to acknowledge uncertainty in the results of the model, the raw data should be considered as well when comparing chemicals.

Within CHARM the offshore environment is divided into two compartments: water and sediment. This is done in order to acknowledge the fact that a chemical present in the environment will partition between the water and organic matrix in the sediment. This is illustrated in Figure 3. The concentration of a chemical may, therefore vary greatly from one compartment to another. Consequently, two PEC values are calculated: PEC_{water} and PEC_{sediment}.



¹ NOEC, LC₅₀, and EC₅₀ are parameters derived from ecotoxicity tests.

Figure 3: Schematic representation of the environmental compartments considered within the CHARM model.

Chemicals dissolved in water may have adverse effects on the pelagic biota (i.e., plankton and most fish species). Those which accumulate in the sediment may affect the benthic biota (i.e., worms, echinoderms, crabs and bivalves). For this reason, two PNEC values are calculated: $PNEC_{\text{pelagic}}$ and $PNEC_{\text{benthic}}$.

In order to estimate a chemical's potential to cause environmental impacts, a PEC:PNEC ratio is calculated for each compartment ($PEC:PNEC_{\text{water}}$ and $PEC:PNEC_{\text{sediment}}$). The higher of the two ratios is used to characterise the maximum environmental hazard or risk associated with the discharge of a product. This approach avoids arbitrary weighing of the compartments and yet ensures protection of the other compartment by measures to minimise or reduce risks.

Table 1: An overview of the names used to indicate the compartment to which the PEC, PNEC and PEC:PNEC ratio is referring

PEC	PNEC	PEC:PNEC-ratio
Water	Pelagic	Water
Sediment	Benthic	Sediment

3.1 Calculation of PEC and PNEC for the water compartment

Below is an explanation of the method used within CHARM to calculate the PEC and PNEC values for a substance. Due to the differences in use and discharge, each application group is handled separately. The explanation of PEC calculation is comprised of a general description of the method, followed by boxes containing the equations used. For an explanation of how these rules should be applied for Hazard Assessment and Risk Analysis see Chapters 5 and 6 respectively.

3.1.1 PEC_{water}

Production Chemicals

Production chemicals are added either to the injection water (injection chemicals), or to the produced fluids. They partition between water and oil phases according to their hydrophilic properties. The fraction of the chemicals which dissolves in the produced water is discharged into the ambient waters.

In order to calculate the PEC, the amount of chemical used must be known. The standard manner of expressing the amount of production chemicals used on installations is in terms of its theoretical concentration in the total (mixture of) produced fluids. In the case of oil producing installations these fluids are oil and produced water; for gas installations these are condensate and produced water.

The amount of chemical used is sometimes, however, expressed in terms of only one fraction of the produced fluids (the oil/condensate flow or the water flow). In these cases the concentration in the total fluid should always be calculated (Equation 1).

Once this is known, the concentration of the chemical in the produced water can be calculated (Equation 2 to Equation 6). In this calculation, a mass balance equation is used assuming that chemicals do not enter the gaseous phase and must, therefore be present in the produced fluids. That

is to say, the total amount of chemical used is equal to the sum of the amount present in the produced oil (or condensate) and the amount present in the produced water.

This approach does not, however account for the amounts of chemical associated with the oil and silt particles present in the produced water. Furthermore, this approach assumes a state of equilibrium between the concentrations in the oil and water phases, which may not be the case due to the prevailing dynamic process-conditions. A safety factor is, therefore added to account for this and other uncertainties (Equation 7). It is possible that, due to this safety factor, the resulting concentration will imply that a greater amount of the chemical is present in the produced water than was originally added. In this case, the concentration of chemical in the produced water should be recalculated assuming that all of the chemical added is discharged (Equation 8 to Equation 10). If, however, the concentration of the chemical in produced water (C_{pw}) is known from experiments or produced water analysis, this value can be used in Equation 11 as C_{pws} .

For chemicals added to the injection fluid (i.e., chemicals injected continuously to aid in the production of hydrocarbons to producing wells) the actual discharge concentration cannot be estimated using the mass balance approach. Therefore the application dosage of these chemicals should be used. Due to the likely fate of these chemicals, their fraction released is automatically set at 1% (Equation 2a) when using the PIO CHARM algorithm and therefore does not require manual input. ⑤

The fate of surfactants is also difficult to predict. These substances will not partition between the oil and water phases, but remain at the interface between the phases. After separating the produced fluid, the amount remaining with the water phase and the oil phase depends upon the type of surfactant. ③ Due to this, their fraction released depends on the type of surfactant and is set between 10 and 100% (Equation 2a).

The concentration of a chemical in the ambient waters around an installation depends not only upon its concentration in the produced water, but also upon the extent to which that produced water will be diluted after discharge. The extent of dilution, in turn, depends upon the distance from the installation and the hydrodynamics of the area. Within CHARM the predicted environmental concentration of a chemical in the ambient waters around an installation (PEC_{water}) is calculated for a fixed distance “x” from the installation. The dilution factor can either be obtained using advanced hydrodynamic models or by carrying out dilution studies (e.g., using rhodamine).

Box 1: Calculation of PEC_{water} from produced water discharges

The equations in this box are only relevant -and valid- in those situations where produced water is discharged.

For production chemicals in general converting chemical dosage to concentration in total produced fluid. This equation is not necessary if the dosage is already expressed as concentration in terms of the total produced fluid.

$$C_t = \frac{F_{flow} * C_{flow}}{F_t} \quad (1)$$

in which:

- C_t = concentration of the chemical in the total produced fluid (mg.l⁻¹)
 F_{flow} = volume of flow in terms of which the dosage is expressed (m³.d⁻¹)
 C_{flow} = concentration of the chemical in that flow (mg.l⁻¹)
 F_t = total fluid production (m³.d⁻¹)

For **chemicals for water** ③ injection and surfactants, calculating the water concentration for injection chemicals and surfactants:

$$C_{pw} = \frac{f_r * C_i * F_i}{F_{pw}} \quad (2a) \quad ⑤$$

in which:

- C_{pw} = concentration of the chemical in produced water (mg.l⁻¹)
 f_r = fraction released (for injection chemicals equal to 0.01, for surfactants value depends on surfactant type (Table 4))
 C_i = concentration of the chemical in the injected fluid or, for surfactants, total fluid (mg.l⁻¹)
 F_i = fluid injected or, for surfactants, total fluid production (m³.d⁻¹) F_{pw}
 = volume of produced water discharged per day (m³.day⁻¹) ③

For all other production chemicals, the water concentration is calculated using the mass balance equation

$$C_t * F_t = (C_{o/c} * F_{o/c}) + (C_{pw} * F_{pw}) \quad (2b) \quad ④ \quad ⑤$$

in which:

- C_t = concentration of the chemical in the total fluid taking into account the % substance in the product (mg.l⁻¹) ③
 F_t = total fluid production (m³.d⁻¹)
 $C_{o/c}$ = concentration of the chemical in oil or condensate (mg.l⁻¹)
 $F_{o/c}$ = total oil or condensate production (m³.d⁻¹)
 C_{pw} = concentration of the chemical in produced water (mg.l⁻¹)
 F_{pw} = volume of produced water discharged per day (m³.day⁻¹) ③

In this equation both $C_{o/c}$ and C_{pw} are unknown. In order to solve the equation for C_{pw} , $C_{o/c}$ must be eliminated. This can be done by estimating the $C_{o/c}$ based on C_{pw} and the octanol/water partition coefficient (P_{ow}) of the chemical. The relationship between the $C_{o/c}$ and C_{pw} is given in Equation 3.

$$C_{o/c} \approx 10^{\log P_{ow}} * C_{pw} \quad (3) \text{ ⑤}$$

in which:

$C_{o/c}$ = concentration of the chemical in oil or condensate ($mg.l^{-1}$)

P_{ow} = partition coefficient between octanol and water *¹

C_{pw} = concentration of the chemical in produced water ($mg.l^{-1}$)

By substituting Equation 3 into Equation 2b we arrive at Equation 4:

$$C_t * F_t = (10^{\log P_{ow}} * C_{pw} * F_{o/c}) + (C_{pw} * F_{pw}) \quad (4) \text{ ④ ⑤}$$

Equation 4 can be rearranged to give Equation 5:

$$C_t * F_t = ((10^{\log P_{ow}} * F_{o/c}) + F_{pw}) * C_{pw} \quad (5) \text{ ④ ⑤}$$

*¹ Although the actual partitioning parameter is P_{ow} , it is usually reported as the $\log P_{ow}$. To avoid possible mistakes, in the equations in this report the parameter is expressed as $10^{\log P_{ow}}$.

Therefore:

$$C_{pw} = \frac{C_t * F_t}{(10^{\log P_{ow}} * F_{o/c}) + F_{pw}} \quad (6) \text{ ⑤}$$

in which:

C_{pw} = concentration of the chemical in produced water ($mg.l^{-1}$)

C_t = concentration of the chemical in the total fluid ($mg.l^{-1}$)

F_t = total fluid production ($m^3.d^{-1}$)

P_{ow} = partition coefficient between octanol and water

$F_{o/c}$ = total oil or condensate production ($m^3.d^{-1}$)

F_{pw} = volume of produced water discharged per day ($m^3.day^{-1}$)

Equation 7 Addition of a safety factor

$$C_{pws} = C_{pw} + (0.1 * C_t) \quad (7)$$

in which:

C_{pws} = concentration of a chemical in the produced water including a safety factor ($mg.l^{-1}$)

C_{pw} = concentration of a chemical in the produced water ($mg.l^{-1}$)

C_t = concentration of the chemical in the total fluid ($mg.l^{-1}$)

Determining if the C_{pws} is realistic

If:

$$C_{pws} * F_{pw} > C_t * F_t \quad (8)$$

in which:

C_{pws} = concentration of a chemical in the produced water including a safety factor ($mg.l^{-1}$)

F_{pw} = volume of produced water discharged per day ($m^3.day^{-1}$)

C_t = concentration of the chemical in the total fluid ($mg.l^{-1}$)

F_t = total fluid production ($m^3.d^{-1}$)

Then:

$$C_{pws} * F_{pw} = C_t * F_t \quad (9)$$

Thus the alternative is:

$$C_{pws} = \frac{C_t * F_t}{F_{pw}} \quad (10)$$

Calculation of PEC_{water}

$$PEC_{water} = C_{pws} * D_{distance\ x} \quad (11)$$

in which:

PEC_{water} = Predicted Environmental Concentration of a chemical at a certain distance from the installation ($mg.l^{-1}$)

C_{pws} = concentration of a chemical in the produced water including a safety factor ($mg.l^{-1}$)

$D_{distance\ x}$ = dilution factor at distance x from the installation (0-1)

Drilling chemicals

As explained in Section 2.2, the calculation rules in the CHARM model for drilling chemicals only address Water Based Mud (WBM). The discharge of WBMs can be continuous or batchwise. Only chemicals not appearing in the OSPAR PLONOR list, a list of chemicals and products that are natural constituents of seawater or natural products such as nutshells and clays are considered. PLONOR listed substances are those whose discharge from offshore installations does not need to be strongly regulated as, from experience of their discharge, the OSPAR commission considers that they Pose Little Or NO Risk to the environment.

In most cases, the concentration of a mud-additive in the water column is dependent upon the amount of additive present in the mud, the amount of mud discharged and its partition and degradation characteristics in sea water.

Both continuous and the batchwise discharges have to be taken into account. Although the highest concentrations are caused by batchwise discharges, both pathways will be assessed in the CHARM model. The higher of the two PEC:PNEC ratios will be regarded as worst case for the additive.

The amount of a certain additive present in the mud-system (further referred to as dosage) can be expressed as a weight percentage or as a concentration (the common unit being pounds per barrel: ppb). The first step in the calculations is, therefore, to use this dosage together with the volume of mud discharged (either continuous or batchwise) to calculate the amount of additive discharged (Equations 12 and 13). Consequently, when performing calculations on batchwise discharges, one will first multiply the dosage with V_m to obtain the mass of additive discharged (M) and subsequently divide it by the same V_m to obtain the concentration of additive in the mud. This step is necessary to yield a value for M with the correct metrics (kg), which is used for the calculation of PEC for continuous discharges. It must be noted that different mud volumes apply for batchwise and continuous discharges.

To derive the regional water concentration of an additive within continuously discharged mud, the amount of additive discharged is divided by the volume of water (during the period of discharge) in which it is diluted. To take into account that other installations in the area might also contribute to the regional concentration of a chemical, the water available for dilution is limited to the fixed area per installation defined by the standard installation density of one installation per 10 square kilometres (Equation 14). This dilution is enhanced by the residual current, which leads to refreshment of the water in the area (Equation 15).

The dilution characteristics of batchwise discharges differ significantly from those of continuous discharges, due to the increased discharge rates (i.e., $1.56 \text{ m}^3 \cdot \text{hr}^{-1}$ and $375 \text{ m}^3 \cdot \text{hr}^{-1}$ for continuous and batchwise discharges respectively - from: CIN Expert Group on Drilling Chemicals, 1998). A different calculation is, therefore required in each case.

Box 2a: Calculation of PEC_{water} for Continuous WBM discharges

For continuous discharges, the mass of a non-PLONOR additive in a WBM which is discharged can be calculated using one of the following equations, dependent upon the expression of dosage:

Dosage expressed as weight percentage:

$$M = Wt * V_m * \rho_m \quad (12)$$

in which:

M	=	amount (mass) of non-PLONOR-listed additive discharged (kg)
Wt	=	weight percentage of the non-PLONOR-listed additive in the mud (-)
V_m	=	volume of mud discharged for the specific section (m^3)
ρ_m	=	density of the discharged mud ($kg.m^{-3}$)

Dosage expressed as pounds per barrel (ppb):

$$M = X_{ppb} * V_m * 2.85 \quad (13)$$

in which:

M	=	amount (mass) of non PLONOR-listed additive discharged (kg)
X_{ppb}	=	dosage of the non PLONOR-listed additive in the mud (pounds per barrel)
V_m	=	volume of mud discharged for the specific section (m^3)
2.85	=	conversion constant from ppb to $kg.m^{-3}$

Volume of ambient water available as diluent

$$V_p = \frac{1}{\text{platf. density}} * \text{waterdepth} * 10^6 \quad (14)$$

in which:

V_p	=	volume of ambient water per <i>installation</i> (m^3)
platf. density	=	number of <i>installations</i> per square kilometre (km^{-2})
water depth	=	average water depth around the <i>installation</i> (m)
10^6	=	factor used to convert km^2 to m^2 ($m^2.km^{-2}$)

Refreshment rate of the ambient water

$$r = \frac{24 * 3600}{2 * Y / U} \quad (15)$$

in which:

- r = fraction of sea water refreshed in the receiving volume around the *installation* per day (day^{-1})
- Y = radius from *installation* corresponding to the area of ambient water available as diluent (i.e. $\pi * Y^2 = 1 / \text{installation density} * 10^6$) (m)
- U = residual current speed ($\text{m} \cdot \text{s}^{-1}$)
- 3600 = factor used to convert hours to seconds ($\text{s} \cdot \text{h}^{-1}$)
- 24 = factor used to convert days to hours ($\text{h} \cdot \text{d}^{-1}$)
- 2 = factor used to convert radius from *installation* to diameter of the area

The volume of water passing the *installation* during the period of drilling a section:

$$V_t = V_p * r \quad (16)$$

in which:

- V_t = volume of water passing the *installation* ($\text{m}^3 \cdot \text{d}^{-1}$)
- V_p = volume of ambient water per *installation* (m^3)
- r = fraction of sea water refreshed in the area around the *installation* per day (d^{-1})

PEC_{water} for **continuous** discharges of non-PLONOR additives in WBM can now be calculated using:

$$PEC_{\text{water,cont}} = \frac{M}{T * V_t} * 10^3 \quad (17)$$

in which:

- $PEC_{\text{water,cont}}$ = PEC_{water} for continuous discharges ($\text{mg} \cdot \text{l}^{-1}$)
- M = amount (mass) of non PLONOR-listed additive discharged (kg)
- T = time needed to drill a section (d)
- V_t = volume of water passing the *installation* ($\text{m}^3 \cdot \text{d}^{-1}$)
- 10^3 = conversion constant to express PEC as $\text{mg} \cdot \text{l}^{-1}$

Box 2b: Calculation of PEC_{water} for Batchwise discharges

PEC_{water} for **batchwise** discharges of non-PLONOR additives in WBM can be calculated using:

$$PEC_{\text{water}, \text{batch}} = \frac{M}{V_m} * D_{\text{batch}} * 10^3 \quad (18)$$

in which:

$PEC_{\text{water}, \text{batch}}$ = PEC_{water} for batchwise discharges (mg.l^{-1})

M = amount (mass) of non PLONOR-listed additive discharged (kg)

V_m = volume of mud discharged for the specific section (m^3)

D_{batch} = dilution factor for batchwise discharges

10^3 = conversion constant to express PEC as mg.l^{-1}

Cementing chemicals

The discharge of chemicals related to cementing operations is more straight-forward. The first aspect to consider is which discharges lead to an actual emission of cementing chemicals. An overview of the cementing operation has already been given in Section 2.3, in which discharges of spacer fluid and mixwater have been identified as the main routes for chemical discharges.

Both spacer fluid and mixwater are discharged in batches. Assuming that none of the chemicals is depleted or transformed between addition and discharge, the discharge concentration equals the initial concentration (dosage).

The volumes of the individual batches may differ for the various sections, thereby changing the dilution characteristics after discharge. In CHARM, therefore the environmental impact of cementing chemicals is evaluated by section.

The concentration of the chemicals in the water column (PEC_{water}) is thus dependent upon the dosage of the chemical and the dilution directly after discharge.

Box 3: Calculation of PEC_{water} for spacer and mixwater discharges (i.e., cementing chemicals) Mixwater:

PEC_{water} is calculated using:

$$PEC_{\text{water}} = C_{i, \text{mixwater}} * D_{\text{batch mixwater}} \quad (19)$$

in which:

$$C_{i, \text{mixwater}} = \text{initial concentration of chemical in mixwater (dosage; mg.l}^{-1}\text{)}$$

$$D_{\text{batch, mixwater}} = \text{batchwise dilution factor for mixwater (-)}$$

Spacer:

PEC_{water} is calculated using:

$$PEC_{\text{water}} = C_{i, \text{spacer}} * D_{\text{batch, spacer}} \quad (20)$$

in which:

$$C_{i, \text{spacer}} = \text{initial concentration of chemical in spacer fluid (dosage; mg.l}^{-1}\text{)}$$

$$D_{\text{batch, spacer}} = \text{batchwise dilution factor for spacer fluid (-)}$$

*Completion, Workover, Squeeze treatments and Hydrotest Chemicals*③

The characteristics of completion and workover operations have been briefly described in Section 2.4. Although the calculation rules are quite similar to those for cementing chemicals, a distinction has to be made between well cleaning (used downhole but not entering the formation), surface cleaning and other operations. During well cleaning and surface cleaning operations, discharge is considered to be 100% of the amount used; while for other operations a fraction of the chemical is retained in the formation (e.g. adsorption to the formation matrix during the operation) ⑤. This retention leads to a loss in fluid volume and a decrease in the chemical concentration in the environment. To yield a discharge concentration, the initial concentration (dosage) has to be corrected for this retention.

The environmental concentration (PEC_{water}) can now be calculated in a similar manner to the previous chemical types, by applying a dilution factor. Since completion and workover chemicals are discharged in batches, a specific dilution factor has to be applied accounting for the discharge volumes.

Box 4: Calculation of PEC_{water} for completion, workover squeeze treatment and hydrotest chemicals ③

(Surface- and well-) cleaning chemicals:

PEC_{water} is calculated using:

$$PEC_{\text{water}} = C_{i,\text{cleaning}} * D_{\text{batch,cleaning}} \quad (21)$$

in which:

$C_{i,\text{cleaning}}$ = initial concentration of chemical in the cleaning fluid (dosage; mg.l^{-1})
 $D_{\text{batch,cleaning}}$ = batchwise dilution factor for cleaning fluids (-)

Other completion, workover, squeeze treatment and hydrotest chemicals: ③

PEC_{water} is calculated using:

$$PEC_{\text{water}} = f_r * C_{i,\text{completion}} * D_{\text{batch completion}}, \quad (22)$$

in

which:

f_r = fraction released - chemical
 $C_{i,\text{completion}}$ = initial concentration of chemical in completion and workover including squeeze treatments and hydrotest fluids (dosage; mg.l^{-1}) ③
 $D_{\text{batch,completion}}$ = batchwise dilution factor for completion and workover including squeeze treatments and hydrotest fluids (-) ③

3.1.2 $PNEC_{\text{pelagic}}$

There are three steps involved in calculating $PNEC_{\text{pelagic}}$:

1. Data selection
2. Preliminary data treatment
3. Application of extrapolation factor

1. $PNEC_{\text{pelagic}}$ - Data selection

The choice of data can have dramatic effects on the $PNEC$ value. The following guidelines should be used when selecting data for use within CHARM.

- Data from, at the least, tests with algae, crustacea and/or fish should be considered.
- Only chronic NOEC and acute EC_{50} and LC_{50} values (also referred to as L/EC_{50}) may be used, of which the former is preferred. Strictly speaking, a NOEC is the highest concentration in a test at which no effect is **observed**. Often, however, NOECs are determined by calculation and defined as, for example, the EC_{10} . This is not acceptable within CHARM, and only NOECs in the strict sense of the word should be used.

- As mentioned above, either chronic NOECs or acute L/EC50s are required. In line with EU Technical Guidance, NOEC values must be derived from internationally recognised chronic test procedures. Chronic tests are generally those that cover a significant period or test organisms' lifecycle and for which the NOEC is based on the non-lethal endpoint (i.e. the algal test is included in this definition as are the fish juvenile growth test OECD215 and Daphnia reproduction test OECD 211). ④ ⑤

2. PNEC_{pelagic} - Preliminary data treatment

In theory, several data sets may be available on a single HOCNF for the same species or parameter. In these cases the following preliminary data treatment is needed:

- If, for one test species, several toxicity data based on the same toxicological criterion (effect parameter) are available, the geometric mean value (exponent of the average of logarithmically transformed effect concentrations) is used to represent this criterion for this species.
- If, for one test species, several toxicity data are available based on different toxicological criteria (e.g., survival, reproduction, growth) from similar tests, only the most sensitive effect parameter should be chosen to represent this species.

3. PNEC_{pelagic} - Application of extrapolation factor

Optimally, NOEC values should be available for algae, crustacea and fish. If this is the case, after preliminary treatment of data, the lowest of the three values is chosen and divided by an extrapolation factor of 10 to give the PNEC.

NOEC values for all three biota groups are, however, often not available and the PNEC must be calculated based on a combination of NOEC and L/EC₅₀ values or on L/EC₅₀ values alone. Table 2 indicates which toxicity values and extrapolation factors should be used given the available data. If data is available for more than one biota group, the lowest value should be used to calculate the PNEC.

A PNEC should represent a no effect level related to chronic exposure, and protect even the most sensitive species in the environment. In the calculation of a PNEC from toxicity data, extrapolation factors play an important role, and are used to account for the mismatch in the characteristics of toxicity data and the characteristics of a PNEC value. This leads to three characteristics which are covered by the extrapolation factor as explained below.

Effect level

If the effect level does not represent “no effect” (i.e., it is not a NOEC but an L/EC₅₀), an extrapolation factor of 10 is used. For most chemicals, for which a valid PEC:PNEC ratio can be calculated, this covers the ratio between the EC₅₀ and the NOEC very well.

Exposure time

For continuous discharges, the PNEC_{pelagic chronic} refers to chronic exposure, non-chronic data should, therefore, be corrected using an extrapolation factor of 10.

Batchwise discharges

For batchwise discharges, since exposure time will be short, the acute-to-short extrapolation need not be included in the extrapolation factor and the $PNEC_{\text{pelagic acute}}$ refers to acute exposure. Acute extrapolation factors of 1, 10 or 100 should be used.

Lab-field extrapolation

Since toxicity data is derived from laboratory tests, but is used to reflect field conditions when used for a PNEC, an extrapolation factor of 10 has been defined to account for this uncertainty. However, when data is available for all three trophic levels (algae, crustacea and fish) this extrapolation factor may be omitted.

Although the above does not fully reflect the OECD scheme, many of the above mentioned aspects are derived from it.

Table 2: $PNEC_{\text{pelagic}}$ calculation table for continuously discharged substances. This table is used to identify which toxicity values and extrapolation factors should be used for the calculation of a PNEC using the available data. The three biota groups considered are algae, crustacea and fish. If data is available for more than one biota group, the lowest value should be used to calculate the PNEC. $PNEC_{\text{pelagic}}$ is expressed in mg.l^{-1} .

		EC50's		
		Data available for all 3 biota groups or to calculate $PNEC_{\text{benthic}}$ data available on >1 sediment reworker tests ③	Data available for 2 biota groups or to calculate $PNEC_{\text{benthic}}$ data available on one sediment reworker test ③	No data
NOEC's	Data available for all 3 biota groups or to calculate $PNEC_{\text{benthic}}$ available on >1 sediment reworker tests ③	PNEC = Lowest NOEC/10		
	Data available for 2 biota groups or to calculate $PNEC_{\text{benthic}}$ available on one sediment reworker test ③	lowest NOEC/10 or lowest $EC_{50}/100$ Whichever is lower	lowest NOEC/10 or lowest $EC_{50}/1000$ Whichever is lower	PNEC cannot be calculated
	No data available	lowest $EC_{50}/100$	lowest $EC_{50}/1000$	PNEC cannot be calculated
NB: For batchwise discharges (drilling, cementing, completion and workover) the $PNEC_{\text{pelagic acute}}$ is calculated by dividing the extrapolation factor (as determined in Scheme 3) by 10. This yields an extrapolation factor of 1, 10 and 100 (instead of 10, 100 and 1000).				

Most sediment reworker data is available for *Corophium*. Other, less frequently tested, sediment reworker species are *Nereis*, *Echinocardium*, *Arenicola*, *Abra* or *Asterias*.

3.2 Calculation of PEC and PNEC for the sediment compartment

3.2.1 PEC_{sediment}

While the concentration of a chemical in the water (PEC_{water}) is expressed as the concentration at a fixed distance from the **installation**, the predicted environmental concentration of a chemical in the sediment (PEC_{sediment}) is expressed as the **average** concentration in the area around the **installation**. This is due to the fact that the concentration in the sediment is a result of partitioning of a chemical between water and the sediment. Sediment toxicity is, therefore, a less acute process, and can be assessed using an average concentration in the area.

Production Chemicals

Based on water-sediment partitioning, an average sediment concentration of a chemical can only be derived from an average (regional) water concentration. The produced water will therefore be diluted in the water volume surrounding the **installation**. To take into account that other **installations** in the area might also contribute to the regional concentration of a chemical, the water available for dilution is limited to the average area per **installation** in the oil or gas production field. This dilution is enhanced by the residual current, leading to refreshment of the water in the area and degradation of the chemical. Although a series of degradation processes, such as biodegradation and [photo-] oxidation, might be relevant, only biodegradation is taken into account. By excluding other degradation processes, worst case principles are followed. Together, all these processes are referred to as regional dilution (Equation 24).

Subsequently, the water-sediment partitioning behaviour of the chemical determines its initial concentration in the sediment. This parameter can be derived experimentally, or estimated from the octanol-water partition coefficient. Since this parameter indicates the potential of a chemical to dissolve in organic material, it can be used, together with the organic matter content of the sediment, to predict the sediment-water partition coefficient (Equation 26).

Once in the sediment, a chemical is subject to another kind of degradation, referred to as sediment biodegradation. If no actual sediment biodegradation data is available, it can be estimated from the 28 day degradation rate in water (Equation 25). Within CHARM, degradation in the sediment is expressed as the fraction of the chemical that is degraded in one year. The evaluation time of one year is used to allow for discrimination between the degradation rates of chemicals, and to account for all stages of annual biological and climatic cycles.

The aerobic degradation rate of a chemical in sediment is strongly dependent upon the availability of oxygen, and will therefore only occur in the top layer of sediment. The sediment layers, however, are not static, but are continually being mixed through bioturbation. It is estimated that substances in the sediment will be exposed to oxygen approximately 10% of the time. Therefore, during 1 year, the substance will be exposed to oxygen and thus susceptible to degradation for 36.5 days (10% of 365) (Equation 25).

Once each of these variables has been determined, the PEC_{sediment} can be determined (Equation 27).

Box 5: Calculation of PEC_{sediment} from produced water discharges

Calculation of 1 day degradation rate of the chemical in the water

$$d_{w1} = 1 - 10^{\frac{\log(1 - d_{wt})}{t}} \quad (23)$$

in which:

- d_{w1} = fraction of a chemical degraded in the water column in 1 day (day^{-1})
 d_{wt} = highest fraction of a chemical degraded in the water column in t (usually 28) days (days^{-1}) (Note: multiply by 0.7 if freshwater biodegradation data is used)

Regional dilution factor

$$D_{\text{regional}} = \frac{F_{pw} / V_p}{r + d_{w1}} \quad (24)$$

in which:

- D_{regional} = regional dilution factor
 F_{pw} = volume of produced water discharged per day ($\text{m}^3 \cdot \text{day}^{-1}$)
 V_p = volume of ambient water per installation (m^3)
 r = fraction of sea water refreshed in the area around the installation per day (day^{-1}) (See eq. 15)
 d_{w1} = fraction of a chemical degraded in the water column in 1 day (day^{-1})

Degradation of a chemical in the sediment in 1 year, calculated on the basis of biodegradation in the water column.

$$d_{s365} = 1 - (1 - d_{wt})^{36.5/t} \quad (25)$$

in which

- d_{s365} = fraction of a chemical in sediment that is degraded in 1 year
 d_{wt} = highest fraction of a chemical degraded in the water in t days
 t = test period used in the determination of degradation rate (days)

Sediment-water partition coefficient based on the octanol-water partition coefficient

$$P_{sw} = f_{oc} * 10^{\log P_{ow}} \quad (26a)$$

in which:

- P_{sw} = sediment-water partition coefficient ($\text{l} \cdot \text{kg}^{-1}$)
 f_{oc} = organic carbon in sediment (expressed as fraction of dry weight)
 P_{ow} = octanol-water partition coefficient

In case an experimental K_{oc} (e.g., for surfactants) is available, the P_{sw} should be calculated:

$$P_{sw} = K_{oc} \frac{F_{oc}}{F_{test}} \quad (26b)$$

in which :

f_{test} = organic carbon in sediment used for K_{oc} determination (expressed as fraction of dry-weight)

For surfactants where no experimental K_{oc} is available, the P_{sw} should be calculated:

$$P_{sw} = f_{oc} * 10^{4(1-fr)} \quad (26c) \quad ④$$

in which:

fr = fraction released for surfactants from Table 4 ③

Calculation of the $PEC_{sediment}$

$$PEC_{sediment} = C_{pws} * D_{regional} * P_{sw} * (1 - d_{s365}) \quad (27)$$

in which:

$PEC_{sediment}$ = Predicted Environmental Concentration in the sediment around the installation ($mg.kg^{-1}$)

C_{pws} = concentration of a chemical in the produced water including a safety factor ($mg.l^{-1}$) (Equation 7)

$D_{regional}$ = regional dilution factor

P_{sw} = sediment/water partition coefficient ($l.kg^{-1}$)

d_{s365} = degradation of a substance in the sediment after 1 year

Drilling Chemicals

The process of sediment-water partitioning of drilling chemicals is the same as that for production chemicals.

The only difference is found in the calculation of the regional concentration of the chemical. For drilling chemicals, this concentration is already calculated since it equals the definition of PEC_{water} for the continuous discharge of drilling chemicals. The concentration for batchwise discharges is not used for this partitioning, since it is only present for a short period of time, while the partitioning calculations assume an equilibrium situation. *The regional concentration used for the partitioning is thus represented by $PEC_{water,cont}$.*

Box 6: Calculation of PEC_{sediment} for WBM discharges

PEC_{sediment} is calculated using:

$$PEC_{\text{sediment}} = PEC_{\text{water, cont.}} * P_{\text{sw}} * (1 - d_{\text{s365}}) \quad (28)$$

in which:

PEC_{sediment} = Predicted Environmental Concentration in the sediment around the installation (mg.kg^{-1})

$PEC_{\text{water, cont}}$ = PEC_{water} for continuous discharges (mg.l^{-1}) (Equation 17)

P_{sw} = sediment-water partition coefficient (l.kg^{-1})

d_{s365} = fraction of a substance in sediment that is degraded in 1 year

It is noted that for chemicals with a Log Pow >6 Equation 28 calculates PEC_{sediment} values that are unrealistically high and the magnitude of this error increases with increasing substance Log Pow. ©

Cementing, Completion and Workover Chemicals

In the CHARM model, the PEC_{sediment} is estimated on the basis of equilibrium partitioning (water/sediment and water/biota). Since cementing, completion and workover chemicals are discharged with batches of mixwater or spacer fluid, no equilibrium situation will exist. For these short peaks of increased water concentrations, it is irrelevant to estimate a sediment concentration on the basis of equilibrium partitioning.

3.2.2 $PNEC_{\text{benthic}}$

The $PNEC_{\text{benthic}}$ can be calculated in two ways, the first of which is preferred:

- a) calculation based on toxicity data from tests performed on spiked sediments
- b) calculation based on equilibrium partitioning and the $PNEC_{\text{pelagic}}$

a) $PNEC_{\text{benthic}}$ is calculated in the same way as $PNEC_{\text{pelagic}}$ (see Section 3.1.2), where “biota groups” must be read as “sediment reworker species”. By using the rules summarised in Table 2, a $PNEC_{\text{benthic}}$ is almost always calculated from the lowest $EC_{50}/1000$, although other options might also result from the table.

As in the calculation of $PNEC_{\text{pelagic}}$, the data used must be from tests carried out according to OSPAR protocols. In this case, the HMCS (Harmonised Mandatory Control System) requires that sediment reworker tests be used if there is a likelihood that a chemical will enter the sediment. This requirement has been adopted by CHARM. $PNEC_{\text{benthic}}$ is expressed in mg.kg^{-1} dry sediment.

In sediment reworker tests, the effect concentrations are in general based on sediment weight mg.kg^{-1} . For the *Abra alba* test however, the effect-concentration is expressed as mg.l^{-1} , assuming a suspended matter concentration of 80 g.l^{-1} . The “sediment effect-concentration” can be calculated by multiplying this value by 12.5.

b) In some cases, if no data is available from sediment toxicity tests, the $PNEC_{benthic}$ can be calculated from the $PNEC_{pelagic}$ and the sediment/water partition coefficient using Equation 29. In this equation P_{sw} is obtained from equation 26.

$$PNEC_{benthic} = P_{sw} * PNEC_{pelagic} \quad (29)$$

in which:

$PNEC_{benthic}$	=	<i>Predicted No Effect Concentration for benthic systems (mg.kg⁻¹ dw)</i>
P_{sw}	=	<i>sediment / water partition coefficient (l.kg⁻¹)</i>
$PNEC_{pelagic}$	=	<i>Predicted No Effect Concentration for pelagic systems (mg.l⁻¹)</i>

This method is, strictly speaking, only applicable for relatively non-reactive, non-polar, hydrophobic, organic chemicals and some metals. It can, however, be used to estimate the $PNEC_{benthic}$ for other chemicals such as non-surface-active organic components of offshore chemicals.

Note: Section 3.3 on assessment of preparations moved to Appendix VIII, because this represents an historic approach. ⑤

4. Applicability check

A traditional PEC:PNEC analysis assesses the potential for a substance to have an acute toxic effect on the environment. However, within this approach, properties such as persistence and accumulation are not accounted for. The potential negative long term effects of substances, such as PCBs and dioxins, which possess these characteristics will therefore, be underestimated in Hazard Assessment and Risk Analysis.

In order to prevent the (invalid) assessment of these substances, an applicability check has been included in the CHARM model. The objective of this component, which is to be applied prior to Hazard Assessment and Risk Analysis, is to identify those substances with hazardous properties that are not well accounted for in the PEC:PNEC analysis.

4.1 Applicability criteria in CHARM

Determination of the applicability of data for use in CHARM is based upon two criteria: persistence and accumulation (including bioaccumulation) of the substance in question. The long-term persistency of a substance is estimated on the basis of the standard aerobic (ready) biodegradation test (OECD 306 and equivalent tests). Accumulative substances **should not be evaluated with CHARM if they exhibit either:** ⑤

- i) <20% biodegradation in 28 days, or
- ii) half-life values derived from simulation tests submitted under REACH (EC 1907/2006) greater than 60 and 180 days in marine water and sediment respectively (e.g. OECD 308, 309 conducted with marine water and sediment as appropriate).

An environmental evaluation of such chemicals using the PEC:PNEC approach will not give a true basis for comparison with other chemicals because the longterm environmental consequences of its

persistence and potential for bioaccumulation have not been taken into account. The criteria to be used for evaluation the chemical must be discussed with the relevant authorities, who may have decided to restrict the use/discharge of chemicals with these characteristics.

The accumulation potential of a substance can be calculated in two ways: based upon the experimentally derived BCF, or based upon the octanol-water partition coefficient (P_{ow}) and molecular weight of the substance. Of these two methods, the former is preferred and in the case of surfactants, for which P_{ow} cannot be determined, it is the only option, [apart from using default values of fraction released](#). ③ Persistent substances which have a log BCF equal to or greater than 5 should not be evaluated with the CHARM model.

Although the above mentioned method is preferred, accumulation potential is more often based on P_{ow} and molecular weight. [Most substances with a molecular weight higher than 700 are considered unlikely to pass through biological membranes and are therefore not likely to accumulate](#). ③⑤ Persistent substances with a molecular weight lower than 700 and a log P_{ow} greater than or equal to 5 should not be evaluated with the CHARM model.

In summary, if both of the following criteria are met, a valid environmental evaluation of this substance, or products containing this substance, is not possible using the CHARM model alone.

Persistence: <20% biodegradation in 28 days or

half-life values derived from simulation tests submitted under REACH (EC 1907/2006) greater than 60 and 180 days in marine water and sediment respectively (e.g. OECD 308, 309 conducted with marine water and sediment as appropriate). ⑤

Accumulation potential: $\log P_{ow} \geq 5$ and molecular weight <700
or $\log BCF > 5$

The evaluation of such substances must be discussed with the relevant national authorities, who may have applied restrictions to their use/discharge.

It must be noted that no log P_{ow} value is available for surfactants. The Applicability Check should, therefore, be based on a measured BCF value.

4.2 Limitations of the model

Although the Applicability Check accounts for the inherent limitations of the CHARM model (being based on the PEC:PNEC approach), it does not account for some specific limitations that have been identified during the development of the model.

[The limitations of the EOSCA BDF calculator, which has defined minima and maxima for density, rate and volume, impacts on the RQ generated within the CHARM calculator](#). ⑤

There is a limitation on the use of the model for the evaluation of chemicals with surface active properties (further referred to as surfactants). Several of the calculation rules within the CHARM model assume equilibrium partitioning between the water and the organic phase. Surfactants do not,

however, partition between phases, but are more likely to form a layer at their interface. To address this limitation, several default values are used where applicable, but it must be noted that the model is still flawed for surfactants (see also Appendix II).

Another limitation of the CHARM model is that the general methodology is applicable to single substance chemicals. However based on several assumptions, chemicals consisting of a mixture of different substances can also be evaluated with the model (see section 3.3).

By virtue of their lack of biodegradability and partitioning between water and an organic phase, inorganic substances are not assessable using the CHARM model. ③

Some chemicals may have applications in different areas of operations. When comparing the assessment (HQ or RQ) of such chemicals with other chemicals from say a different supplier, the same algorithms must be used for calculating the HQ or RQ for each chemical. The HQ or RQ calculated for say a corrosion or scale inhibitor used for Production must not be compared with the HQ or RQ of a corrosion or scale inhibitor used for Drilling, Completion or Workover. ③

The area of the model responsible for the sediment compartment concentrations within the drilling algorithm are unrealistic for substances with Log Pow >6 causing unrealistically high PEC_{sediment} values. This results in excessively large drilling HQs for the sediment compartment. The magnitude of the error increases with increasing Log Pow. ⑤

5. Hazard Assessment

Hazard Assessment is the evaluation of the potential of a substance to cause harm to the target groups exposed to it (van der Zandt & van Leeuwen, 1992). Its purpose within CHARM is to rank individual chemicals according to their predicted environmental impact in order to facilitate the selection of the least environmentally harmful alternative. However, it should be remembered that this ranking is subject to the limitations of the model as described in the introduction. Expert judgement is, therefore needed to integrate this ranking with factors which fall outside the scope of the model.

The hazard of each single substance is quantified as a PEC:PNEC ratio. This ratio is calculated using specific information on the intrinsic properties and toxicity of the chemical, and information on the conditions on and around a standard *installation*. For these purposes, standard North Sea oil and gas *installations* have been defined based on information provided by national authorities on conditions at existing *installations*. Since the standard *installations* are meant to represent the “realistic worst case” situation, the 95 percentile values on these existing North Sea *installations* were chosen.

The conditions at these standard *installations* are used as default values for calculating the PEC:PNEC values. As explained in Chapter 3, two separate PEC:PNEC ratios are calculated. Here they are referred to as Hazard Quotients: HQ_{water} and HQ_{sediment} . The higher of these two values is used to characterise the hazard and is referred to as the $HQ_{\text{ecosystem}}$. This approach avoids arbitrary weighting amongst compartments and still ensures protection of the other compartment.

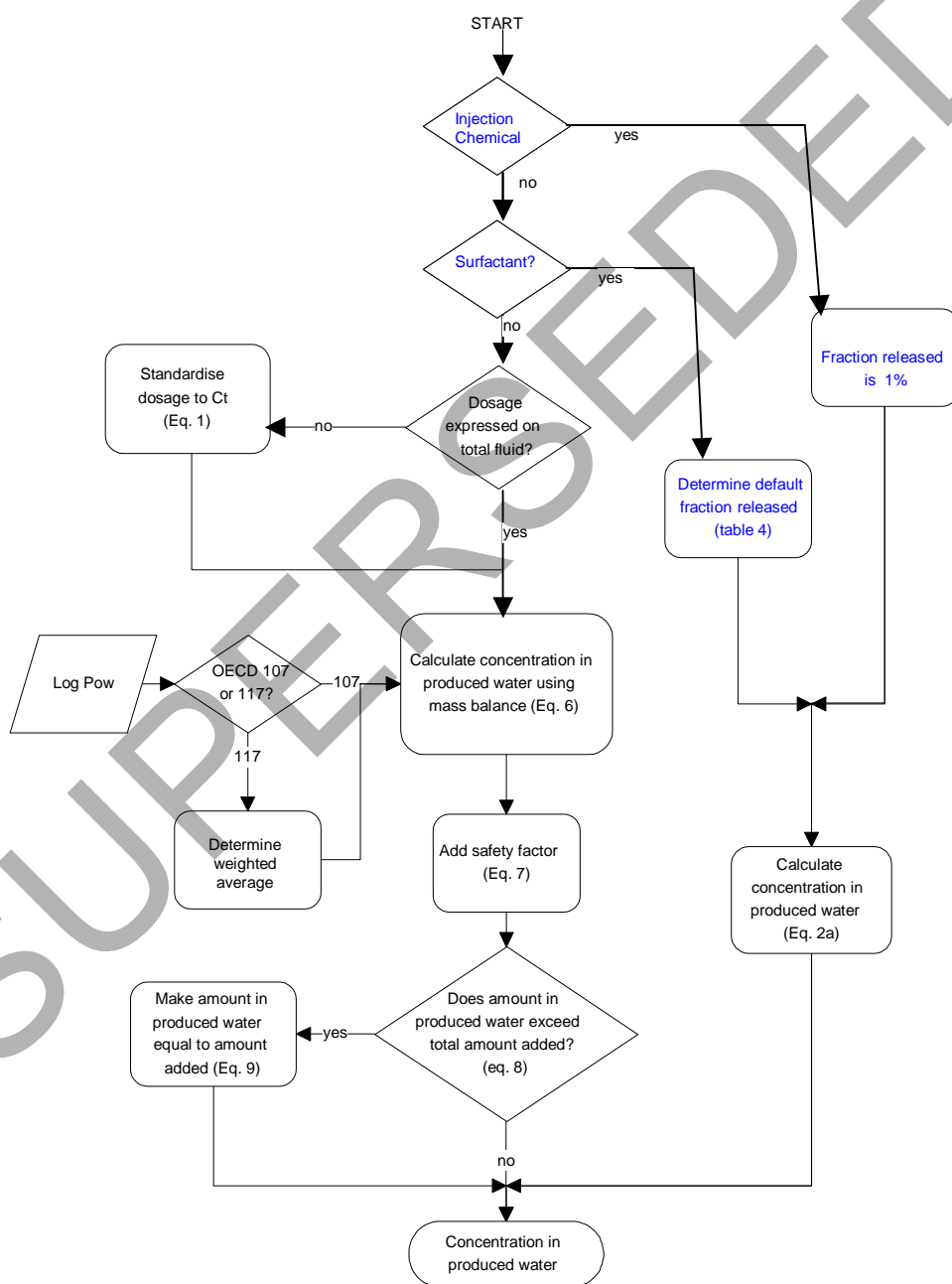
For each of the application groups, the calculation steps for Hazard Assessment are described step-by-step in the following paragraphs. In this description, the flow-charts are followed in detail. No reasoning will be given for the choice of calculation rules (since that can be found in chapter 3), but

the various parameters and their (realistic worst case) default values will be mentioned and explained. In those cases where data can be derived from the HOCNF, a reference is made to the appropriate section of the HOCNF.

5.1 Production chemicals

5.1.1 Calculation of concentration in produced water

The first step in the calculation of PEC values (PEC_{water} and PEC_{sediment}) for production chemicals is the calculation of the concentration of the chemical in the produced water. The method used for this calculation is explained in Section 3.1.1 and illustrated in Scheme 1. *Scheme 1: Concentration of a chemical in produced water* ③



The steps involved in the calculation of the concentration of a chemical in produced water are:

NB order changed to reflect rearranged Scheme 1 ③

1. If the chemical is used for water injection, the concentration in the produced water should be calculated using [the dose rate in the injection water](#) and a default fraction released of 1%, [Equation 2a](#). The default values for the flow parameters used in this step are given in [Table 3](#). ③ Data on the log P_{ow} are not needed for injection chemicals.

Table 3: Flow parameter default values used in the hazard assessment of production chemicals.

Parameter	Symbol ③	North Sea Oil installation	North Sea Gas installation	units
Water production	F_{pw}	14964	47	m ³ .d ⁻¹
Oil production		2002	-	m ³ .d ⁻¹
Gas production		-	220000	m ³ .d ⁻¹
Condensate production		-	2	m ³ .d ⁻¹
Injection water	③ F_i	16966	-	m ³ .d ⁻¹

2. If the chemical is a surfactant ([HOCNF Guidance 1.1.o](#) ⑤), since no log P_{ow} is available for these chemicals, a default fraction released, given in [Table 4](#), should be used, dependent upon the type of surfactant. [Equation 2a](#) is also used here.

NB. Justification must be provided if other fraction released values are used for Risk Assessment (See Appendix II). ③

Table 4: Default values used in the CHARM Hazard Assessment module for the calculation of the fraction of surfactants released.

Type of surfactant	Fraction released, f_r
Quaternary amines	1.0
EO-PO Block polymer demulsifier (EthoxylatePropoxylate)	0.4
Imidazolines	0.1
Fatty amines	0.1
Fatty amides ③	1.0
Primary amines (cationic type, C _≥ 12)	0.1
Phosphate esters (anionic type, C _≥ 13)	0.1
Others	1.0

3. For chemicals which are neither injection chemicals nor surfactants the dosage of the chemical should be determined using either the recommended dosage as mentioned on the [HOCNF form \(1.4\)](#) ⑤) or the actual dosage to be used on the [installation](#). Ensure the dosage is in mg.l⁻¹ and expressed in terms of the total fluid. If the latter is not the case, [Equation 1](#) can be used to convert the dosage.
4. The dosage can now be used to calculate the (initial) concentration of the chemical in the produced water, using [Equation 6](#). This equation requires the log P_{ow} value of the chemical ([HOCNF form 2.1.1](#) ⑤). If the log P_{ow} is derived using [OECD 117](#), and the P_{ow} is represented by a range of peaks in a HPLC diagram, the log P_{ow} should be calculated by taking the weighted average of all peaks which make up more than 5% of the chemical tested. *It must be noted that this approach might not be valid for all chemicals.*

5. The flow parameters are the same as used in step 1.
6. The concentration of a substance in produced water, which is not a surfactant, nor an injection chemical, is increased with a safety-factor, using Equation 7. If the final (safe) concentration in the produced water exceeds the actual amount of chemical added, the 'safe' concentration in the produced water is adjusted to 100% discharge (Equation 10).

5.1.2 Calculation of HQ_{water}

A summary of the default values for characteristic conditions of the reference installations (realistic worst case) used in Hazard Assessment is given in Table 5. ③

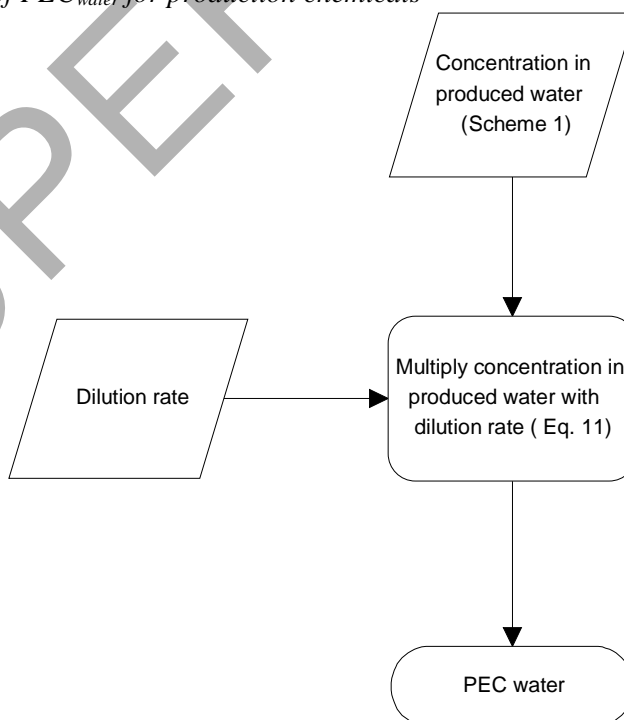
Table 5: Characteristic conditions of the reference installations (realistic worst case) used in Hazard Assessment.

Parameter	Symbol ③	North Sea oil production installation	North Sea gas production installation	units
Installation density		0.1	0.1	km ⁻²
Water depth		150	40	m
Refreshment rate	r	0.24	0.24	d ⁻¹
Corresponding Residual Current speed.	U	0.01	0.01	ms ⁻¹
Sediment organic carbon content	foc	0.04	0.04	-
Dilution at 500m.	D	0.001	0.001	-

PEC_{water}

The method used to calculate the PEC_{water} for production chemicals is explained in Section 3.1.1 and illustrated in Scheme 2.

Scheme 2: Calculation of PEC_{water} for production chemicals

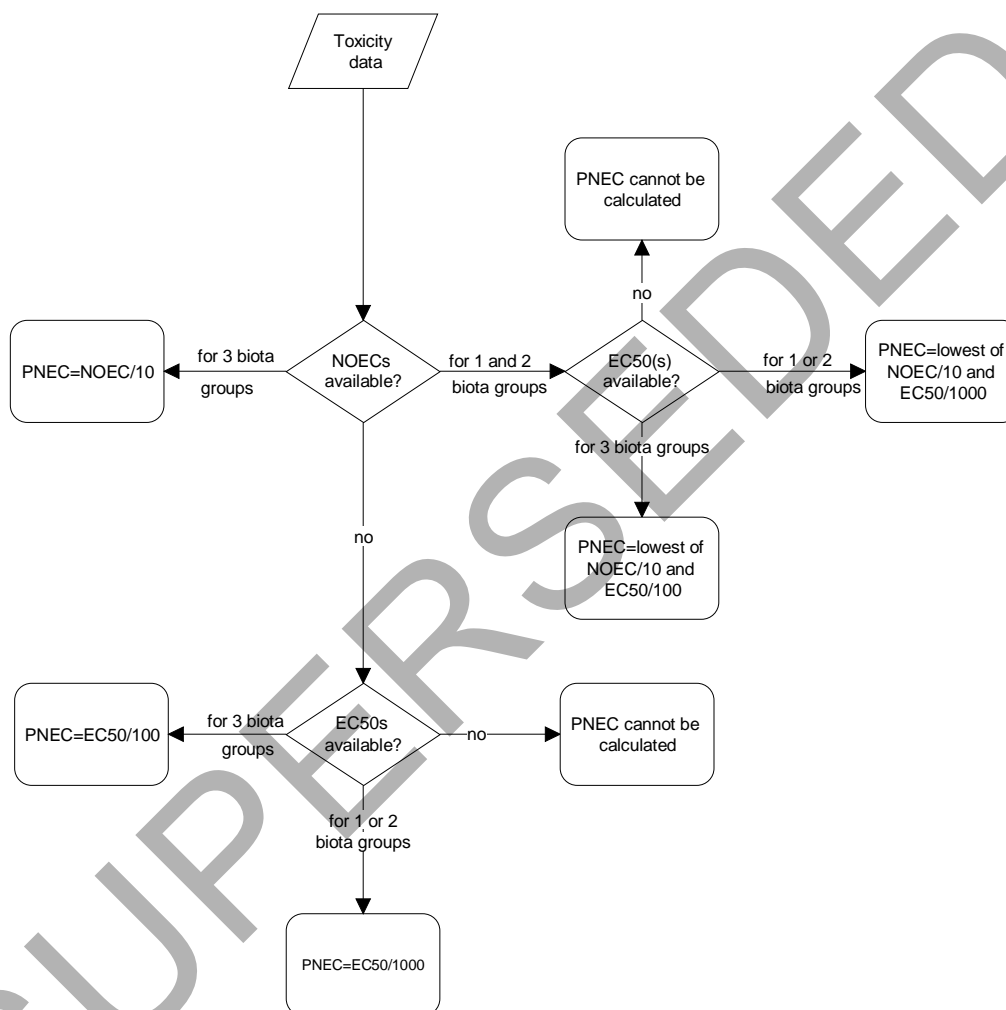


For Hazard Assessment purposes, the PEC_{water} of production chemicals is calculated by multiplying the concentration in the produced water with a dilution factor. The dilution factor (at a distance of $x = 500\text{m}$) is set to a realistic worst case default value of 0.001 (i.e., 1:1000). The resulting value is PEC_{water} .

$PNEC_{\text{pelagic}}$

The calculation of $PNEC_{\text{pelagic}}$ values is explained in section 3.1.2 and illustrated in Scheme 3.

Scheme 3: Calculation of the $PNEC_{\text{pelagic}}$ for continuous discharges of all application groups



There are three steps involved in calculating $PNEC_{\text{pelagic}}$ for Hazard Assessment purposes: data selection, preliminary data treatment and the application of an extrapolation factor. The individual steps are described in detail in Section 3.2.1. An operational description is given in the following steps:

1. Collect all available toxicity data for the chemical (EC_{50} or NOEC data, HOCNF 2.4). Although EC_{50} values may be interpolated from the test results, all NOECs must be observed data.

2. Calculate the geometric mean EC_{50} or NOEC for each effect type per species. Select the most sensitive effect type (i.e., effect type with lowest geometric mean EC_{50} or NOEC) per species to represent that species. If both NOEC and EC_{50} data are available, this process must be carried out for both NOEC and EC_{50} .
3. Apply the relevant extrapolation factor to yield the $PNEC_{\text{pelagic}}$. Follow Scheme 3 to find this extrapolation factor and the figure (NOEC or EC_{50}) to apply it to. If the outcome is “PNEC cannot be calculated” then additional toxicity data should be obtained. The process should then start again at step 1.

HQ_{water}

The Hazard Quotient for the water compartment can now be obtained by dividing PEC_{water} by $PNEC_{\text{pelagic}}$.

5.1.3 Calculation of HQ_{sediment}

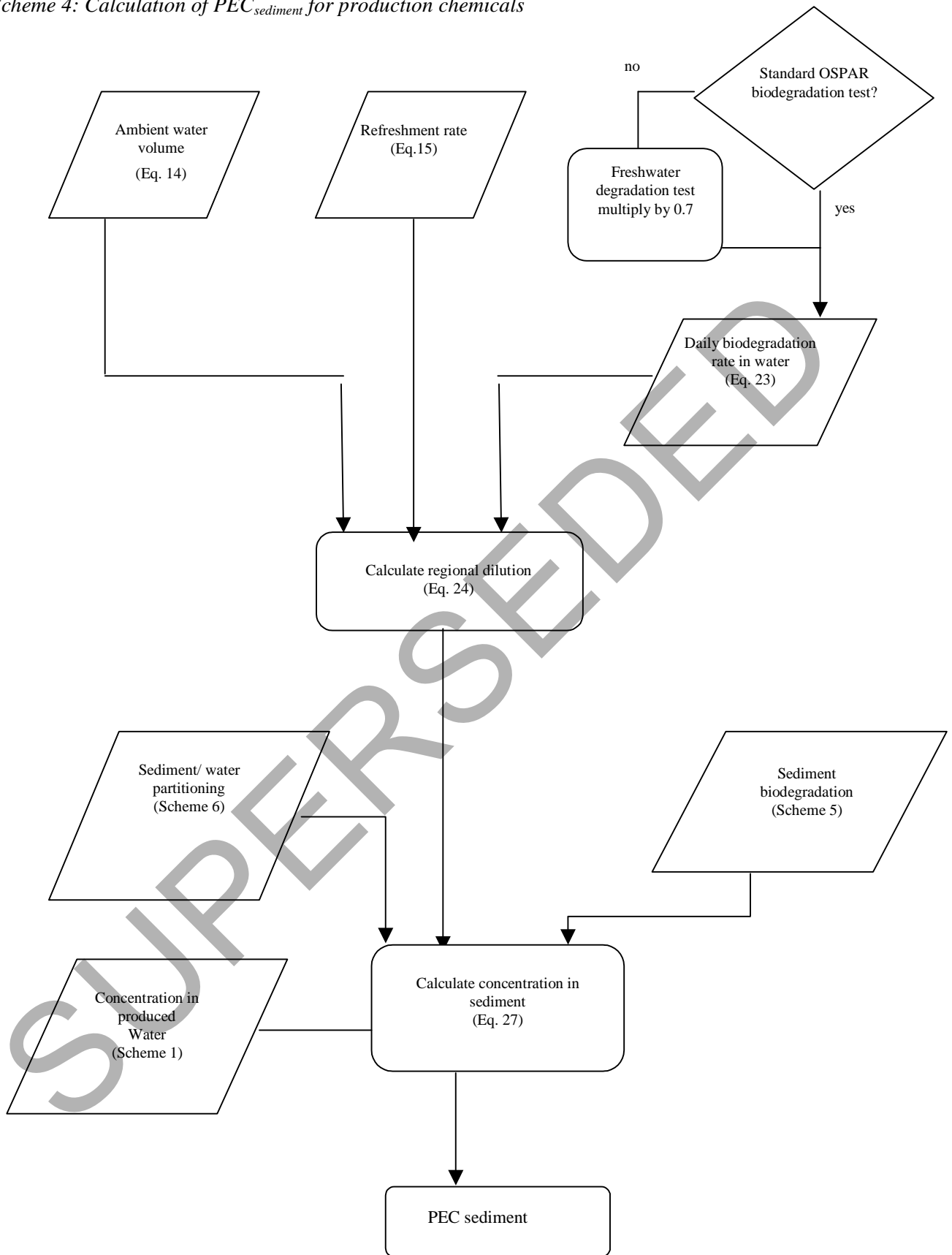
PEC_{sediment}

The procedure for calculating PEC_{sediment} is explained in Section 3.2.1 and illustrated in Scheme 4.

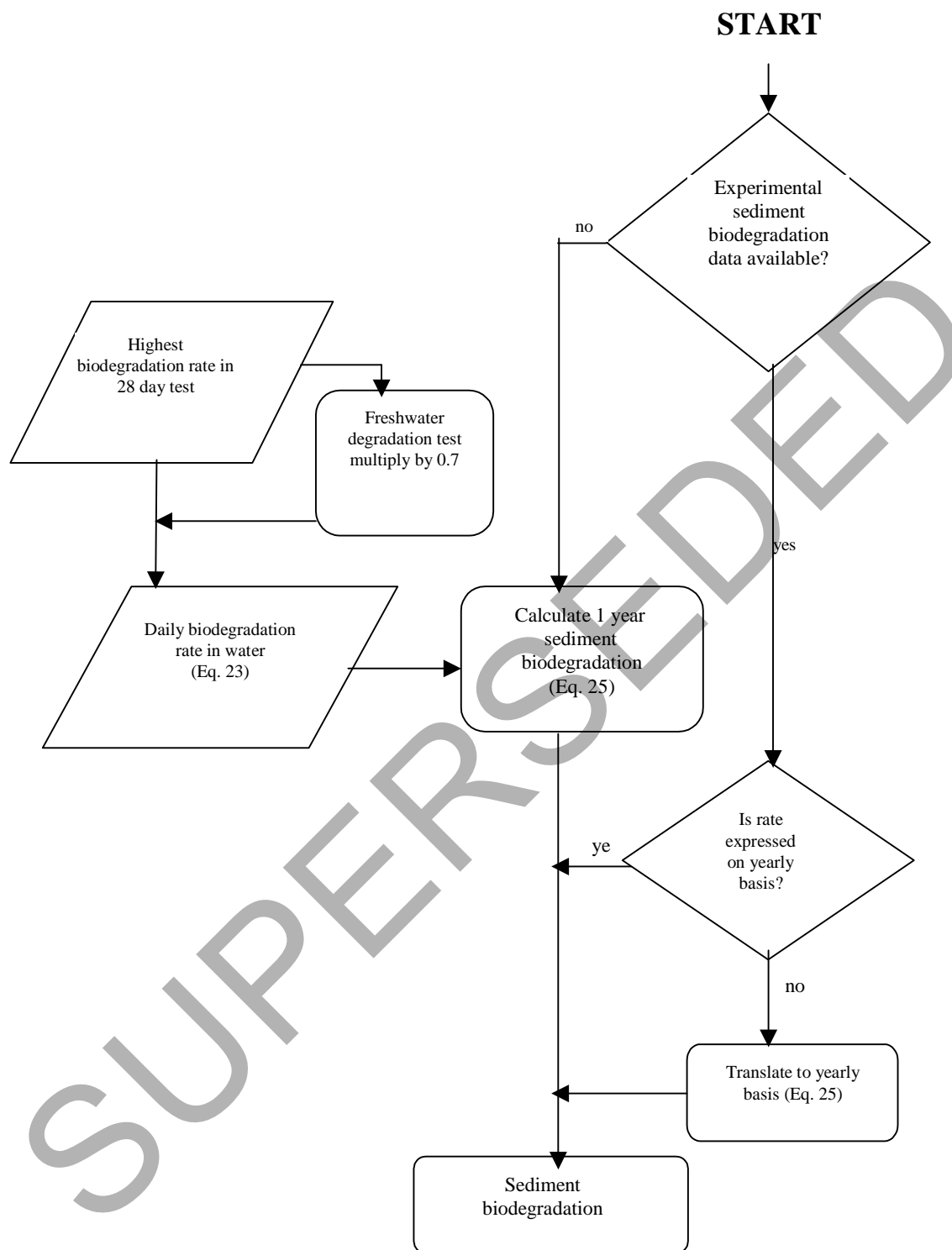
The steps involved in calculation the PEC_{sediment} for the Hazard Assessment of production chemicals are explained below.

1. First the average concentration of a chemical in the water around the **installation** should be calculated. This is done by calculating a regional dilution factor from the water volume, refreshment rate and the daily biodegradation of the chemical in the water (Equation 24).
2. Daily biodegradation in water can be calculated using the highest result from the 28-day biodegradation test (as reported in HOCNF 2.2.1, eventually corrected by multiplication with 0.7 if freshwater biodegradation data is used), and transforming it to a daily biodegradation rate using Equation 23.
3. The refreshment rate at a distance (Y) of 1784 m from the **installation** is set to a default value of 0.24 d^{-1} .
4. Water volume is calculated from **installation** density (0.1 per square kilometre) and the water depth (150m for an oil producing **installation**; 40m for a gas producing **installation**). The resulting water volumes are $15 \cdot 10^8 \text{ m}^3$ for an oil producing **installation** and $4 \cdot 10^8 \text{ m}^3$ for a gas producing **installation**.
5. The next step is to calculate the concentration in the sediment, using the concentration in produced water, the regional dilution factor, the sediment biodegradation rate and the sediment/water partitioning factor (Equation 27).
 - The manner in which the sediment biodegradation rate (in 1 year) is determined is explained in Section 3.2.1 and illustrated in Scheme 5.

Scheme 4: Calculation of $PEC_{sediment}$ for production chemicals



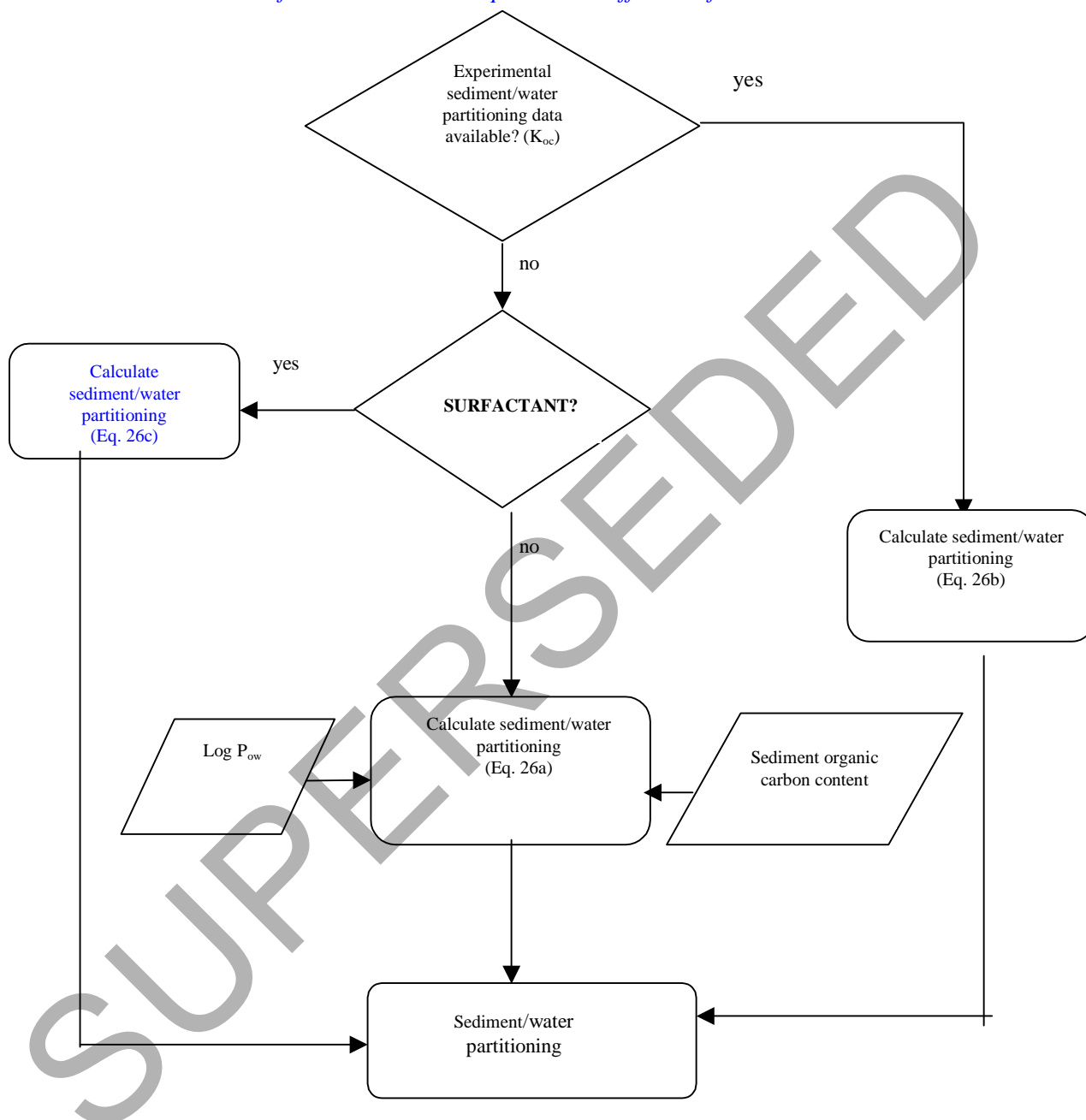
Scheme 5: Determination of the rate of biodegradation of a chemical in the sediment



The procedure for determining the sediment/water partition coefficient is shown in Scheme 6. If experimental sediment/water partitioning data is available, this data is preferred and should be used in the calculations. If experimental data is not available, and the chemical is not a surfactant, the

sediment/water partitioning can be calculated from the $\log P_{ow}$ and the sediment organic carbon content (Equation 26). The organic carbon content of the sediment is set to the default value of 0.04 (= 4%). For surfactants experimental partitioning data may be required to calculate PEC_{sediment} . Equation 26b should be used.

Scheme 6: Determination of the Sediment/water partition coefficient of a chemical. ③



For surfactants use experimental sediment/water partitioning data or default values from Table 4. ③

PNEC_{benthic}

The calculation of $PNEC_{benthic}$ is explained in Section 3.2.2.

If sediment reworker toxicity data is available, $PNEC_{benthic}$ is calculated in the same manner as $PNEC_{pelagic}$ (Scheme 3). There are three steps involved in calculating $PNEC_{benthic}$: data selection, preliminary data treatment and the application of an extrapolation factor:

1. Collect all available sediment reworker toxicity data for the chemical (EC_{50} or NOEC data, HOCNF 2.4). Although EC_{50} values may be interpolated from the test results, all NOECs must be observed data.
2. Calculate the geometric mean EC_{50} or NOEC for each effect type per species. Select the most sensitive effect type (i.e., effect type with lowest geometric mean EC_{50} or NOEC) per species to represent that species. If both NOEC and EC_{50} data are available, this process must be carried out for both NOEC and EC_{50} .
3. Apply the relevant extrapolation factor to yield the $PNEC_{pelagic}$. Sediment reworker toxicity data other than the *Corophium volutator* test is usually not available (since it is the only sediment reworker test required for the HOCNF). In practice, therefore, $PNEC_{benthic}$ can be calculated by taking the lowest from $NOEC/10$ and $EC_{50}/1000$.

If no sediment reworker toxicity data is available, $PNEC_{benthic}$ can be estimated from $PNEC_{pelagic}$, using sediment/water partitioning, as described in Equation 29. If experimental sediment/water partitioning data is available (HOCNF 2.5 referred to as K_{oc} in HOCNF), this data is preferred, and should be used in the calculations. If experimental partitioning data is not available, *and* the chemical is not a surfactant, the sediment/water partitioning can be calculated from the $\log P_{ow}$ and the sediment organic carbon content (Equation 26). The organic carbon content is set to the default value of 0.04 (= 4%).

HQ_{sediment}

The Hazard Quotient for the sediment compartment can now be obtained by dividing $PEC_{sediment}$ by $PNEC_{benthic}$.

5.1.4 Calculation of HQ_{ecosystem}

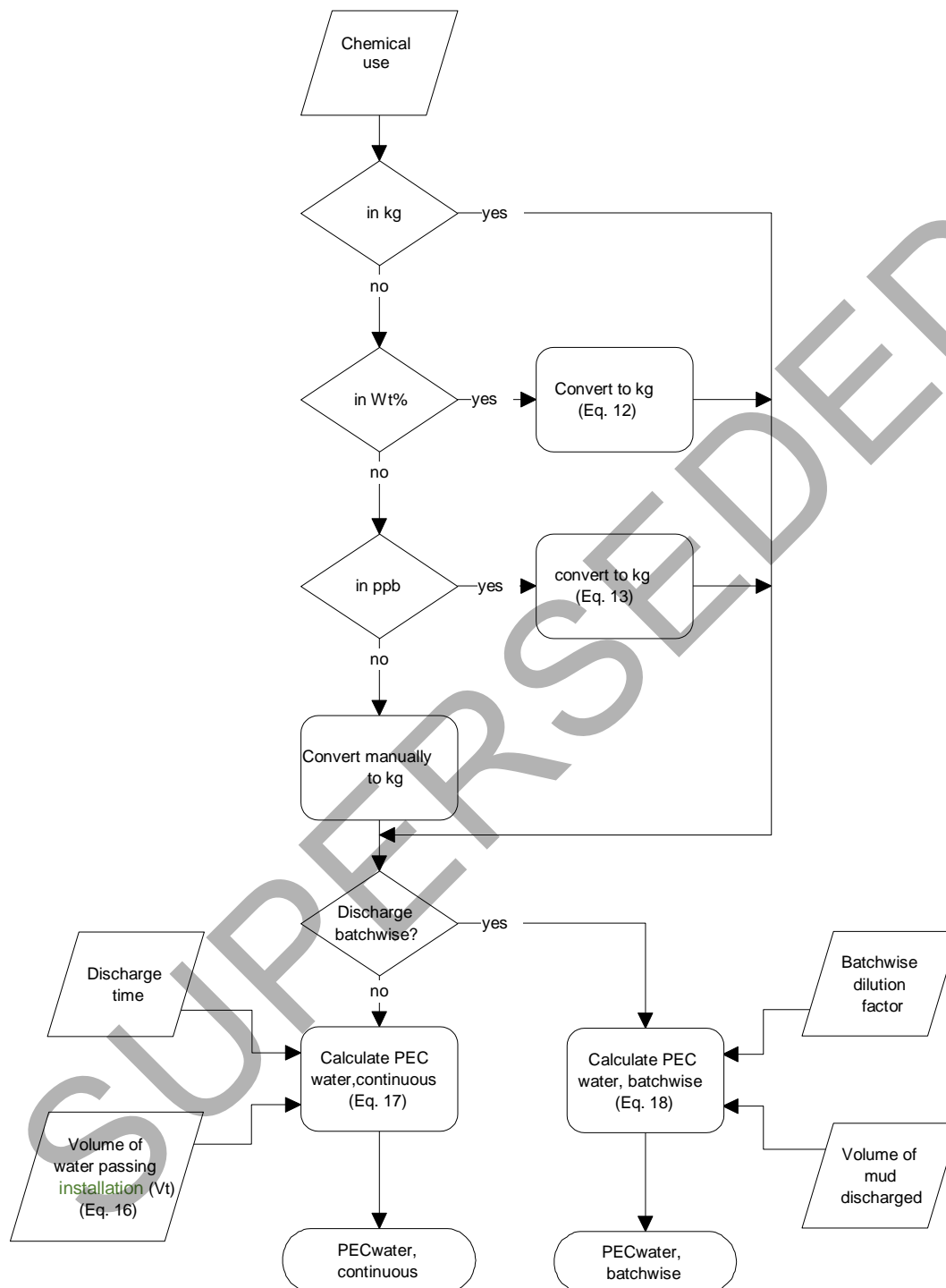
$HQ_{ecosystem}$ is obtained by choosing the higher value from HQ_{water} and $HQ_{sediment}$.

5.2 Drilling chemicals**5.2.1 Calculation of HQ_{water}***PEC_{water}*

Since drilling chemicals are the additives of drilling fluids (within CHARM these fluids are limited to water based muds), the actual dosage of the additive in the mud is the basis for the calculations. Although the dosage may be different in the various sections of the well, the CHARM calculations are

calculated for a single section only. The subsequent calculation steps are presented in Scheme 7 and described below.

Scheme 7: Calculation of the PEC_{water} for drilling chemicals.



1. Before the calculations can be performed, the chemical use (HOCNF form 1.4) of the additive has to be expressed in kg. Since this is not the standard unit used for additives, the reported dosage might have to be converted. If the dosage is expressed as a weight percentage of the total mud,

- this can be done using Equation 12. The dosage could also be expressed as pounds per barrel (ppb), in which case the dosage can be converted using Equation 13. If dosage is expressed in another unit, the user has to find their own equation to convert the dosage into kg.
- The actual calculation of the PEC is now dependent on the type of discharge. If the discharge is continuous, the calculation of the PEC is described in step 3 and if the discharge is batchwise, the calculation of the PEC is described in step 4.
 - For continuous discharges, the PEC is calculated using Equation 17 in which both discharge time (T) and the volume of water passing the installation per unit of time (V_i) are incorporated. The latter can be calculated using Equation 16 and the default data shown in Table 6 and Table 7.
 - With batchwise discharges, the PEC is calculated using Equation 18, which makes use of the volume of mud discharged and the dilution factor for batchwise discharges. The default values for both parameters are shown in Table 6 and Table 7.

Table 6: Default values for calculating the PEC for drilling chemicals (both continuous and batchwise discharge)

Parameter	Symbol ^③	Value	Unit
Installation density at 1784 m		0.1	km ⁻²
Drilling time per section	T	16	days
Water depth		150	m
Refreshment rate	r	0.24	d ⁻¹
Corresponding Residual Current speed.	U	0.01	ms ⁻¹
Batchwise dilution factor	D _{batch}	7.7 10 ⁻⁵ (1:13,000)	-

Table 7: Default data related to the drilling of the various sections

Section drilled	Length drilled (m)	Mud density (kg.m ⁻³)	Volume continuous discharge (m ³)	Volume batchwise discharge (m ³)
36"	100	-	*	-
24"	400	-	*	-
17½"	1500	1400	600	-
12¼"	1500	1600	450	375
8½"	1000	1600	250	280

For non-standard sections use defaults for 12¼" section for evaluation purposes. ^③

Only OSPAR PLONOR listed chemicals are used in the drilling of the 36" and 24" sections. ^⑤

$PNEC_{pelagic}$

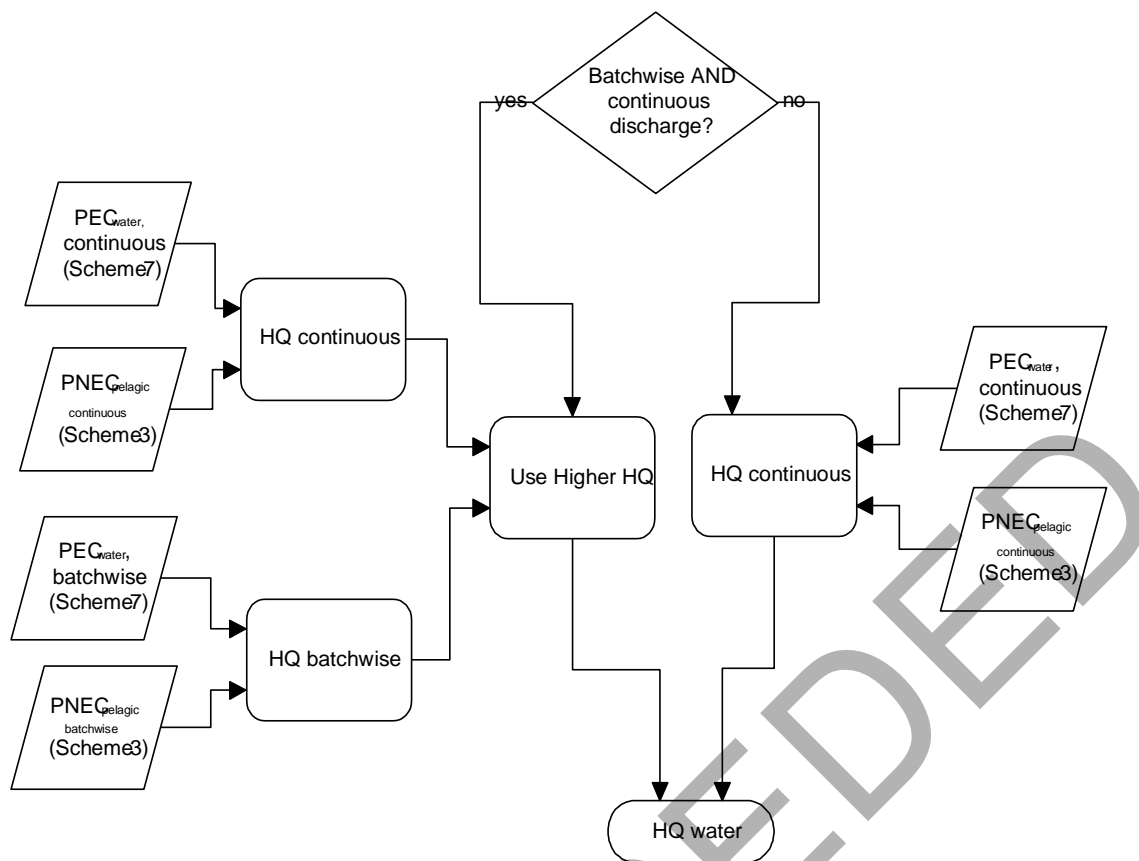
For continuous discharges, the calculation of a $PNEC_{pelagic\ chronic}$ is performed in the same way as for production chemicals. The calculation rules as presented in Scheme 3 and described in Section 5.1.2 can therefore be used for drilling chemicals as well.

For batchwise discharges, the $PNEC_{pelagic\ acute}$ is determined as explained in Section 3.1.2.

HQ_{water}

The Hazard Quotient for the water phase can be derived using the steps shown in Scheme 8.

Scheme 8: Calculation of the HQ_{water} for drilling chemicals



The steps involved in this calculation are:

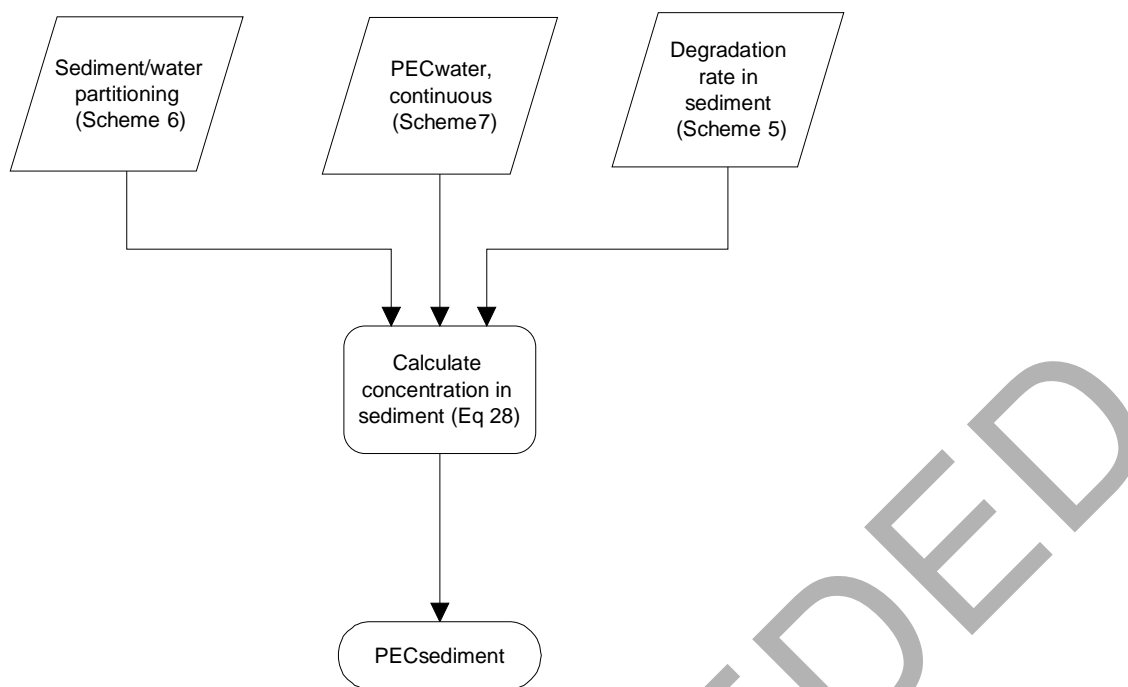
1. First determine whether only continuous discharges occur or that batchwise discharges occur as well (which is the case for the 12¼" and 8½" sections). If no batchwise discharges occur, the calculation of the Hazard Quotient is described in step (2) below; otherwise the calculation is described in step (3) below.
2. If additives in a drilling fluid, used in (one of) the top three sections, are evaluated, batchwise discharges need not be accounted for. The Hazard Quotient can then be calculated as the quotient of $PEC_{\text{continuous}}$ and an ordinary PNEC.
3. In those cases where both continuous and batchwise discharges occur, for both types of discharges a HQ needs to be calculated. The $HQ_{\text{continuous}}$ can be calculated (as in [2]) as the quotient of $PEC_{\text{continuous}}$ and an ordinary PNEC. The $HQ_{\text{batchwise}}$ should be calculated as the $PEC_{\text{batchwise}}$ divided by PNEC for batchwise discharges. The higher of the two HQ values represents the Hazard Quotient for the drilling chemical.

5.2.2 Calculation of HQ_{sediment}

PEC_{sediment}

The procedure for calculating the PEC_{sediment} is described in Section 3.2. A schematic representation of the calculation rules is presented in Scheme 9. These rules are described in the paragraphs which follow.

Scheme 9: Calculation of the PEC_{sediment} for drilling chemicals.



1. The first step in calculating a PEC for the sediment is determining the average concentration of the chemical in the water phase. This concentration is represented by the $PEC_{\text{water, cont}}$, which can be derived following the steps in the previous paragraph.
2. The second step is to calculate the concentration in the sediment, also referred to as the PEC_{sediment} . This is done using equilibrium partitioning, following Equation 28. If no experimental P_{sw} value is available, it should be calculated using Equation 26a for which a default value for the fraction organic carbon in sediment of 0.04 should be used. When experimental partitioning data are used (*i.e.* for surfactants), use Equation 26b.

$PNEC_{\text{benthic}}$

The PNEC for the benthic ecosystem is calculated in the same way as for production chemicals (see Section 5.1.3).

HQ_{sediment}

The Hazard Quotient for the sediment phase is calculated by dividing PEC_{sediment} by $PNEC_{\text{benthic}}$.

5.2.3 Calculation of $HQ_{\text{ecosystem}}$

$HQ_{\text{ecosystem}}$ is obtained by choosing the higher value from HQ_{water} and HQ_{sediment} .

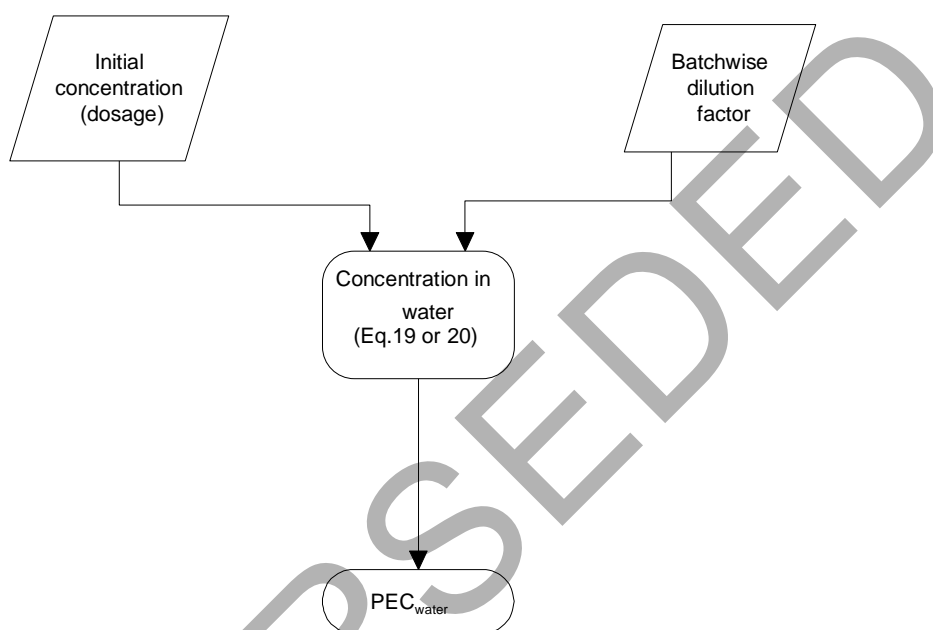
5.3 Cementing chemicals

5.3.1 Calculation of HQ_{water}

PEC_{water}

The concentration of cementing chemicals in the water, after discharge, can be calculated according to the steps presented in Scheme 10.

Scheme 10: Calculation of the PEC_{water} for cementing chemicals.



As shown above, the concentration of the cementing chemicals in the water can be calculated based on the initial concentration and the dilution value for batchwise discharges (for either spacer fluids or mixwater). This should be done using the default values shown in Table 8 in Equation 19 and Equation 20. This concentration is regarded as the PEC_{water} .

Table 8: Default values to be used for Hazard Assessment of cementing chemicals, being discharged with spacer fluid or mixwater.

Parameter	Symbol ^③	Spacer fluid	Mixwater
Dilution factor at 500m	D_{batch}	$1.2 \cdot 10^{-5}$ (1:81,000)	$2.2 \cdot 10^{-5}$ (1:45,000)

Although spacer fluids and mixwater have to be distinguished during the calculations, the same calculation rules apply. Only the default values for dilution differ for both types of fluids.

$PNEC_{\text{pelagic acute}}$

The calculation of a PNEC for the pelagic ecosystem is performed in the same way as for production chemicals. However, for batchwise discharges, exposure time will be short and the acute-to-chronic extrapolation is not needed in the extrapolation factor. The extrapolation factor (as determined in Scheme 3) should therefore be divided by 10. This yields an extrapolation factor of 1, 10 or 100

(instead of 10, 100 or 1000). The PNEC that is derived in this way is referred to as the $PNEC_{\text{pelagic acute}}$.

HQ_{water}

The Hazard Quotient for the water compartment can now be obtained by dividing PEC_{water} by $PNEC_{\text{pelagic acute}}$.

5.3.2 Calculation of $HQ_{\text{ecosystem}}$

Since only HQ_{water} is relevant for cementing chemicals, this Hazard Quotient is used to represent $HQ_{\text{ecosystem}}$.

5.4 Completion, Workover, Squeeze and Hydrotest chemicals ③

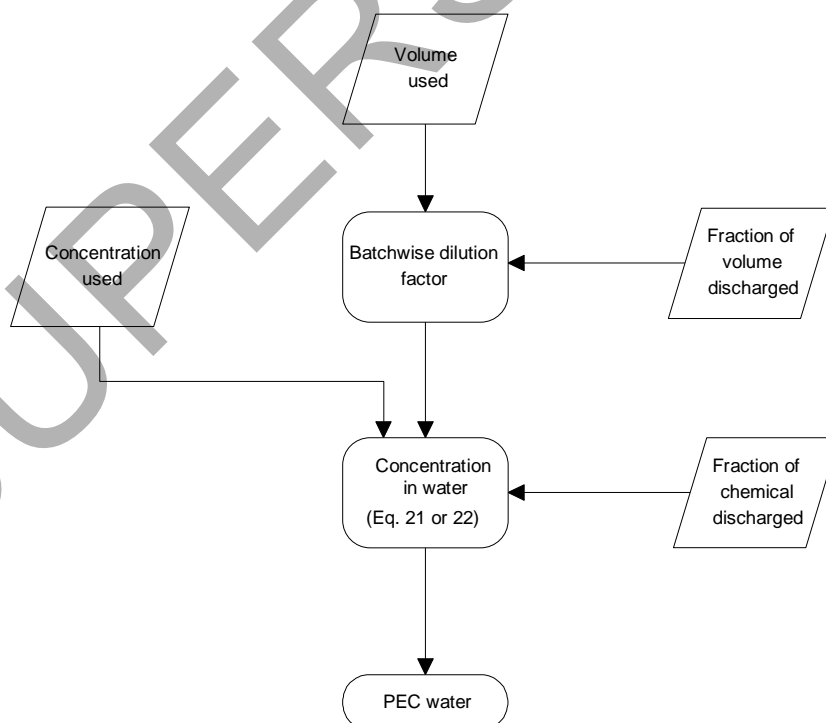
5.4.1 Calculation of HQ_{water}

PEC_{water}

The concentration of completion and workover chemicals in the water, after discharge, can be calculated according to the steps presented in:

Scheme 11. These steps are described in the paragraphs which follow. Although during the calculations cleaning chemicals have to be approached slightly different from the other chemicals, the same calculation rules apply. For cleaning chemicals, however, the fraction released should be set at 1 (all chemical is discharged).

Scheme 11: Calculation of the PEC_{water} for completion and workover chemicals



1. The first step in the calculation is to determine the correct batchwise dilution factor, which is a function of the actual discharge volume (see appendix III for a look-up table of dilution factors). If the volume to be discharged is not known, it should be estimated from the volume of fluid used by multiplying it with the fraction released (default: 0.7). The volume discharged calculated in this way can then be used to determine the expected batchwise dilution factor.
2. On the basis of the initial concentration, the (default) fraction released (see Table 9) and the dilution value (as calculated in step 1) the concentration of the completion and workover chemicals in the water can be calculated (Equation 21 and Equation 22). This concentration is regarded as PEC_{water}
3. For a squeeze treatment, the ‘initial concentration’ should be that of the chemical solution as pumped into the well. It is generally accepted that in a scale inhibitor squeeze treatment $\frac{1}{3}$ of the chemical returns as the well is brought back on line; $\frac{1}{3}$ over a variable period of time (90 days, 120 or even 180 days) and $\frac{1}{3}$ stays down-hole. The fraction released for a scale inhibitor squeeze treatment is therefore set at 0.33 as a minimum. ③ ⑤
4. For a hydrotest chemical discharged at the installation, it is considered that **all** the chemical is discharged hence a fraction release of 1. The dilution factor is set at 0.001 to be in line with production chemicals. ③

Table 9: Default values to be used for Hazard Assessment of completion and workover chemicals (specified as ‘cleaning chemicals’, ‘other chemicals’, ‘squeeze treatments’ and ‘hydrotest chemicals’). For value sources see Karman et al., 1996 and CIN meeting minutes 11 June 2002. ③

Parameter	Symbol ③	Cleaning chemicals	Other chemicals
Fraction released - chemical	fr	n.r.	0.1
Dilution factor at 500m	D_{batch}	$7.7 \cdot 10^{-5}$ (1:13,000)	$7.1 \cdot 10^{-5}$ (1:14,000)
Parameter	Symbol ③	Squeeze treatments ③	Hydrotest chemicals ③
Fraction released - chemical	fr	0.33	1
Dilution factor at 500m	D_{batch}	$7.1 \cdot 10^{-5}$ (1:14,000)	0.001 (1:1000)

$PNEC_{\text{pelagic acute}}$

The calculation of a PNEC for the pelagic ecosystem is performed in the same way as for production chemicals. However, for batchwise discharges, exposure time will be short and the acute-to-chronic extrapolation is not needed in the extrapolation factor. The extrapolation factor (as determined in Scheme 3) should therefore be divided by 10. This yields an extrapolation factor of 1, 10 and 100 (instead of 10, 100 and 1000). The PNEC that is thus derived is referred to as the $PNEC_{\text{pelagic acute}}$.

HQ_{water}

The Hazard Quotient for the water compartment can now be obtained by dividing PEC_{water} by $PNEC_{\text{pelagic acute}}$.

5.4.2 Calculation of $HQ_{\text{ecosystem}}$

Since only HQ_{water} is relevant for completion and workover chemicals, this Hazard Quotient is used to represent $HQ_{\text{ecosystem}}$.

6. Uncertainty Analysis ④

6.1 Production chemicals (Previously 5.1.5)

During the third phase of the CHARM project, an extensive uncertainty analysis was carried out. The objective of this analysis was to provide the means for comparison of calculated “Hazard Quotients” for different chemicals, acknowledging the uncertainty in the CHARM model.

In this analysis, the uncertainty in the model’s results was quantified on the basis of the general variation of those parameters for which the results are the most sensitive. The influence of chemical specific variation or the use of default values was not included in this analysis. The results of this study were used to obtain a general indication of uncertainty for HQ values calculated with the CHARM model.

For production chemicals the approximate 90% confidence intervals for each Hazard Quotient shown in Figure 4, can be set at $HQ/3$ for the lower confidence limit and at $HQ*3$ for the upper confidence limit.

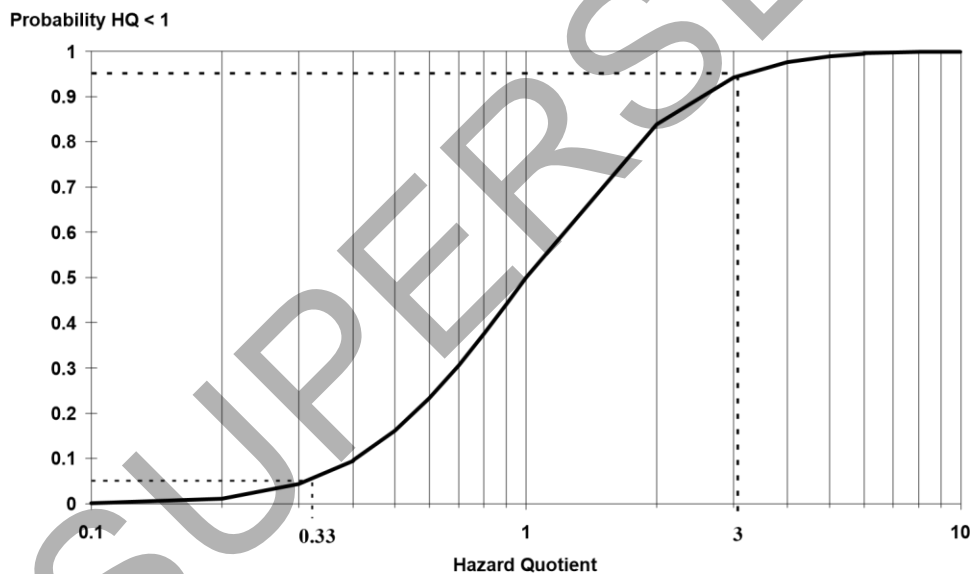


Figure 4: Result of the uncertainty analysis carried out for the CHARM project. The 90% confidence interval is indicated by the dotted lines.

6.2 Drilling chemicals ④

For drilling chemicals the 90% confidence interval for the Hazard Quotient shown in Figure 5, for the water-compartment (HQ_{water}) is also $HQ/3 - HQ*3$. For the sediment-compartment ($HQ_{sediment}$) this 90% confidence interval is $HQ/5 - HQ*5$, 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 the confidence interval should be considered wider.

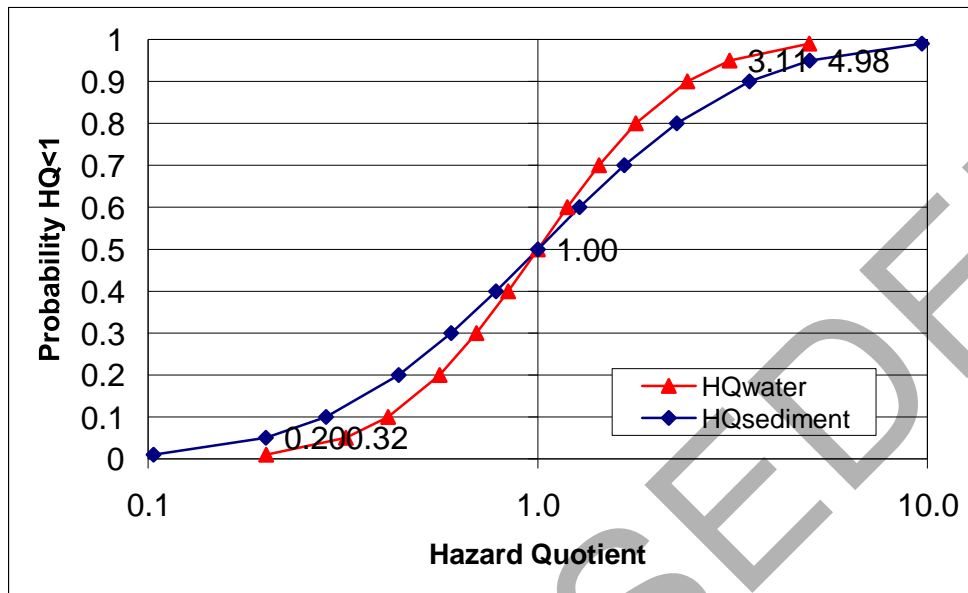


Figure 5: Uncertainty analysis results for drilling chemicals, HQ_{water} and $HQ_{sediment}$. The uncertainty in dosage has been disregarded. The numbers in the graph represent the 5% and 95% boundaries for a 90% confidence interval.

6.3 Completion, workover, hydrotest and squeeze chemicals ④

For mixwater, spacer fluids, completion, workover and cleaning chemicals the 90% confidence interval for HQ_{water} shown in Figure 6 is also $HQ/3 - HQ*3$.

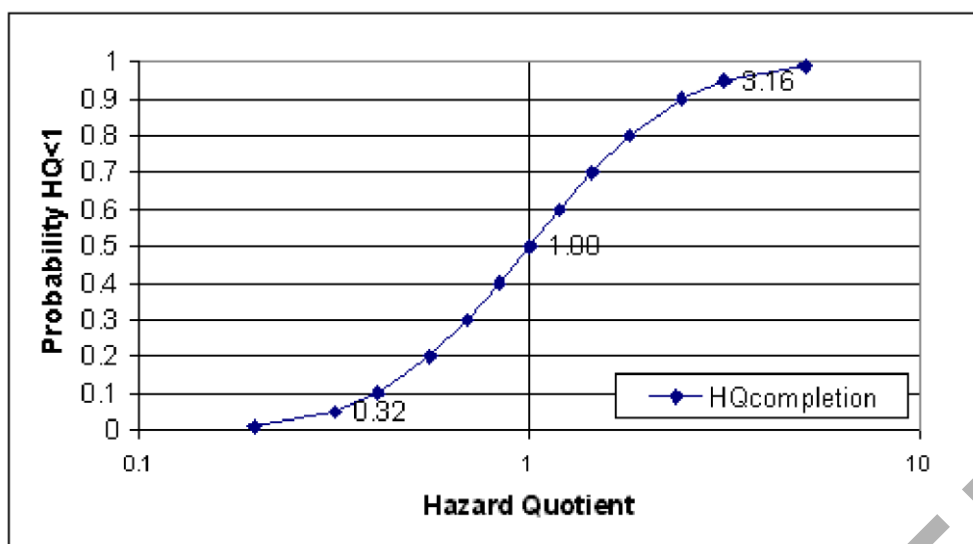


Figure 6: Uncertainty analysis results for completion and other chemicals. The uncertainty of dosage has been disregarded. The numbers in the graph represent the 5% and 95% boundaries for a 90% confidence interval.

7. Risk Analysis

Just as in Hazard Assessment, the purpose of the Risk Analysis module is to rank individual chemicals according to their predicted environmental impact in order to facilitate the selection of the least environmentally harmful alternative. Together with this, Risk Analyses can be used to calculate risk for the package of chemicals and other constituents discharged with the produced water. Risk Analysis differs from Hazard Assessment in that the specific **installation** conditions can be used instead of those of the standard **installation**. Once again, it should be remembered that this ranking is subject to the limitations of the model as described in the introduction. Expert judgement is, therefore, needed to integrate this ranking with factors which fall outside the scope of the model.

The risk associated with the discharge of each chemical is quantified as a PEC:PNEC ratio. This ratio is calculated using information about the chemical(s) to be used and, where possible, specific information on the site at which they are to be used. As explained in Chapter 3, two separate PEC:PNEC ratios are calculated, here referred to as Risk Quotients: RQ_{water} and RQ_{sediment} . The higher of these two values is used to characterise the risk and is referred to as the $RQ_{\text{ecosystem}}$. This approach avoids arbitrary weighting amongst compartments and yet ensures the protection of the other compartment.

In the current chapter, for each of the application groups defined in the CHARM model, an overview is given of those parameters for which the default data can be replaced by site specific data.

7.1 Production chemicals

For production chemicals a rather extensive list of default values are applied in the calculations to represent a worst case reference situation. The respective parameters are listed in Table 10. For each parameter, a suggestion is given as to how site specific data can be derived.

Table 10: Overview of parameters which can be replaced by actual data in Risk Analysis of production chemicals.

Parameter	Unit	Site specific data
water production	m ³ .d ⁻¹	Actual on-installation measurements
oil production	m ³ .d ⁻¹	Actual on-installation measurements
gas production	m ³ .d ⁻¹	Actual on-installation measurements
condensate production	m ³ .d ⁻¹	Actual on-installation measurements
dilution at reference distance	-	Dilution field study of the installation itself or an installation in the same region with comparable water production. It is also possible to use the results of a detailed chemical dispersion model.
surfactant fraction released	-	Mass balance study performed on the actual installation or another installation with comparable water and oil/condensate flows
injection chemical fraction released	-	Mass balance study performed on the actual installation or another installation with comparable water and oil/condensate flows
sediment organic carbon content	fraction	Data from on-site sediment samples. These data might be available from a baseline study carried out before installing the installation, but should preferably reflect the current situation.
installation density	km ⁻²	Installation density is the inverse of the area enclosed by circle the radius of which is the distance to the nearest discharging installation. The units are reciprocal kilometres squared. ③
water depth	m	Depth maps (which were at least available during construction) provide detailed depth contours of the area around the installation.
refreshment rate	d ⁻¹	The refreshment rate can be incorporating the actual residual current (which can accurately be derived from the 'Admirals map' or other maps showing detailed current patterns) in Equation 15.

7.2 Drilling chemicals

For drilling chemicals most of the data is related to sections drilled and the volume of mud discharged from these sections. The respective parameters are listed in Table 11. For each parameter, a suggestion is given as to how site specific data can be derived.

Table 11: Overview of parameters which *should be* replaced by actual data in Risk Analysis of drilling chemicals. ⑤

Parameter	Unit	Site specific data
volume of mud discharged per section (in batch and/or continuous modes, as appropriate)	m ³	Actual data concerning this parameter <i>should be</i> derived from the drilling programme. Data <i>should enable</i> the risks from both continuous and batch discharges to be evaluated, irrespective of the diameter of the drill section.
mud density	kg.m ⁻³	Actual data concerning this parameter <i>should be</i> derived from the drilling programme
discharge time	d	Actual data concerning this parameter <i>should be</i> derived from the drilling programme
batchwise dilution factor	-	Dilution field study of the <i>installation</i> itself or an <i>installation</i> in the same region. It is also possible to use the results of a detailed chemical dispersion model. Such a model was used by Bos (1998) to derive a table with default dilution factors, as presented in Appendix III.
sediment organic carbon content	fraction	Data from on-site sediment samples. These data might be available from a baseline study carried out before installing the <i>installation</i>
biota lipid content	fraction	Field study in a comparable region might have reported lipid contents of fish and/or benthic organisms. These data are usually not available for many regions
<i>installation</i> (drilling site) density	km ⁻²	<i>Installation density is the inverse of the area enclosed by circle the radius of which is the distance to the nearest discharging installation. The units are reciprocal kilometres squared.</i> ③
water depth	m	Depth maps (which were at least available during construction) provide detailed depth contours of the area around the <i>installation</i> .
Refreshment rate	d ⁻¹	The refreshment rate can be incorporating the actual residual current (which can accurately be derived from the 'Admirals map' or other maps showing detailed current patterns) in Equation 15.

NB: risk quotients are not directly influenced by the diameter of the drill sections used. Risk quotients should therefore be calculated for each drill section, irrespective of the actual diameter used. ⑤

7.3 Cementing chemicals

For the calculation of a PEC:PNEC ratio for cementing chemicals, few parameters are required for which default values are used in Hazard Assessment. The respective parameters are listed in Table 12. For each parameter, a suggestion is given as to how site specific data can be derived.

Table 12: Overview of parameters which can be replaced by actual data in Risk Analysis of drilling chemicals.

Parameter	Unit	Site specific data
volume discharged	m ³	The actual volume discharged may be obtained from the cementing plan or workover plan.
batchwise dilution factor	-	Dilution field study of the <i>installation</i> itself or an <i>installation</i> in the same region. It is also possible to use the results of a detailed chemical dispersion model. Such a model was used by Bos (1998) to derive a table with default dilution factors, as presented in Appendix III

7.4 Completion, Workover, Squeeze and Hydrotest chemicals ③

For the calculation of a PEC:PNEC ratio for completion and workover chemicals, as for cementing chemicals, few parameters are required for which default values are used in Hazard Assessment. The parameters are listed in Table 13. For each parameter, a suggestion is given as to how site specific data can be derived.

Table 13: Overview of parameters which can be replaced by actual data in Risk Analysis of completion and workover chemicals.

Parameter	Unit	Site specific data
volume discharged	m ³	The actual volume discharged may be obtained from the completion and workover plan.
fraction of volume released	fraction	Actual data on this parameter should be obtained by performing a mass balance study on comparable operations on the <i>installation</i> itself or a comparable <i>installation</i>
fraction of chemical released	fraction	Actual data on this parameter should be obtained by performing a mass balance study on comparable operations on the <i>installation</i> itself or a comparable <i>installation</i>
batchwise dilution factor	-	Dilution field study of the <i>installation</i> itself or an <i>installation</i> in the same region. It is also possible to use the results of a detailed chemical dispersion model. Such a model was used by Bos (1998) to derive a table with default dilution factors, as presented in Appendix III

8. Risk Management

The Risk Management module, although not accepted by all parties involved in the development of the CHARM model, has been included in the CHARM model in order to enable the comparison of risk

reducing measures. The basis for this module is the Risk Analysis module, in which a *site specific* Risk Quotient can be calculated for individual substances. The Risk Management module offers the means to combine the RQ of individual substances into a Risk estimate for a combination of chemicals (see Section 8.1). This combination is often the package of chemicals used in a specific situation (e.g., series of mud additives or a set of production chemicals). Subsequently, several alternatives for the “standard” chemical package can be compared on the basis of their costs and the eventual risk reduction, as described in Section 8.2.

8.1 Combining the Risk Quotient of individual chemicals

Up until now, the calculation rules in the model have led to Hazard and Risk Quotients for individual chemicals. For Risk Management purposes it may be interesting to know the risk of a package of chemicals. This enables cost-benefit analysis of risk-reducing measures in a straightforward manner.

The following paragraphs will demonstrate in which way (a set of) Hazard Quotients can be transferred into a risk estimate. Risk is defined here as the probability that biota are adversely affected by exposure to the (mixture of) chemicals.

Unless the toxicity of the individual chemicals can be assumed to be additive, the RQs cannot simply be added. In many cases, especially in larger chemical packages (10 or more chemicals), the toxicity of the individual chemicals can be regarded as independent, and additive or synergistic effects are assumed to be cancelled out by the antagonistic effects. Adding the individual RQs will therefore lead to an overestimation of the environmental risk of the package, especially for large packages.

The assumption of an independent mode of action enables the use of a statistical calculation rule for combining independent probabilities. This calculation rule (Equation 32) is based on the principle that if an organism dies due to exposure to chemical A, it can no longer die from exposure to chemical B.

First action to calculate a combined risk level is to calculate the $PEC/PNEC = RQ$ for each component of the produced water. Transfer the single RQ values to risk estimates by using Figure 7. The calculation rule from equation 32 is then used to combine the risk estimates. When the risk for the package of chemicals (and the other produced water constituents) is transferred back to one PEC/PNEC value (Figure 7) the RQ for the “produced water package” is obtained.

$$R(A+B) = R(A) + R(B) - R(A) * R(B)$$

$$R(A+B+C) = R(A+B) + R(C) - R(A+B) * R(C)$$

(32)

etc.

in which:

R = risk

A = chemical A

B = chemical B

C = chemical C

A+B = mixture of chemicals A and B

A+B+C = mixture of chemicals A, B and C

This calculation rule, however, requires RQ values to be transformed into risk estimates. TNO has developed a method for this transformation, which is used in the CHARM model. This method is based upon an assumed relationship between RQ and Risk (see Figure 7).

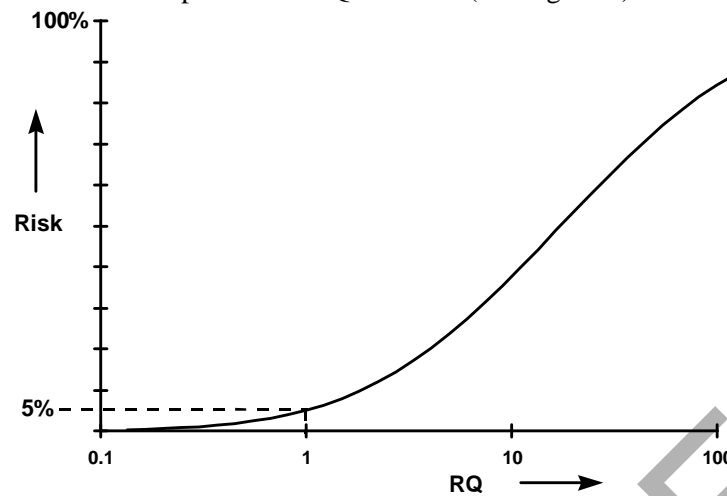


Figure 7: Relationship between risk and the risk quotient (RQ) assumed in the estimation of a probabilistic risk estimate within the CHARM model.

The relationship in shown Figure 7, which is a cumulative normal distribution, is mathematically described as:

$$Risk = \int_{y=0}^{\ln(RQ)} \left\{ \frac{1}{S_m * \sqrt{2 * \pi}} * e^{-\frac{(y - X_m)^2}{2 * S_m^2}} \right\} \quad (33)$$

in which:

- X_m = average of the logarithmically transformed data (calibrated to 2.8497)
- S_m = standard deviation of the logarithmically transformed data (calibrated to 1.7356)
- y = variable to describe the normal probability curve

The default values given here are calibrated to give an RQ of 1 at a risk level of 5% (i.e., 5% of the species are at risk, 95% are protected). The risk level used for the calibration is a political choice and could very well be replaced by another risk value that is regarded as acceptable.

Most spreadsheet applications have functions which can be used to easily describe the relationship in Figure 7, without the need to reproduce the integral function as presented in Equation 36. The function used by Microsoft Excel is the following:

=NORMDIST(X, Avg, StDev,TRUE)

in which:

X = Position on the X-axis for which the probability has to be determined. In this case it is the natural logarithm of the Risk Quotient: $LN(RQ)$

Avg = Average of the logarithmically transformed data (X_m), which should be given a value of 2.8497

StDev = Standard deviation of the logarithmically transformed data (S_m), which should be given a value of 1.7356

TRUE = Indicator for Excel that the function should be cumulative

Although this function may be different in other spreadsheet applications, they will probably use the same descriptors.

8.2 Using Risk Management graphs

The principle of Risk Management within CHARM is the comparison of risk-reducing measures in the light of their costs. A typical Risk Management graph may look like Figure 8.

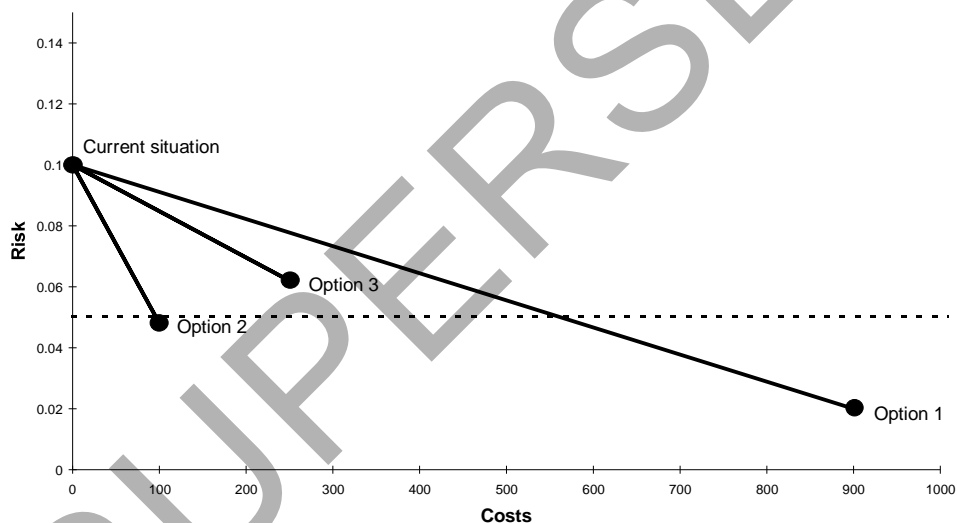


Figure 8: Example of a Risk Management graph, in which three options for risk reduction are compared with the current situation. The dotted line represents the 5% risk level, which in this example is defined as the maximum acceptable risk.

The Risk Management graph above is based upon a hypothetical example, which is elaborated upon in the following paragraphs as an example of the general use of the Risk Management module.

The hypothetical example represents a case in which the corrosion inhibitor is suspected of being responsible for the actual risk related to a current package of chemicals. The current package is therefore compared with the alternatives listed below.

1. Constructing the equipment of stainless steel, and not using the corrosion inhibitor (costs 900 units)
2. Replacing the current corrosion inhibitor with a chemical that has less impact on the environment (costs 100 units)
3. Reducing the dosage of the corrosion inhibitor, which involves more frequent maintenance (costs 300 units)

As shown in the Risk Management graph of this example (Figure 8), the highest reduction in risk is obtained from option 1. This option, however, is also the most costly, and may, therefore, not be favourable. Option 2, however, is the cheapest option and reduces the environmental risk to below the acceptable risk level. From a Risk Management point of view this is the best risk reduction option. *It must be noted that other factors than costs also affect the final choice of risk reduction options. These factors (such as technical limits), however, cannot be included in the Risk Management graph.*

SUPERSEDED

9. Synoptic list of necessary data

Presented below is a synoptic list of data required to assess a substance with the CHARM model. This list is divided into three tables containing the Chemical specific, Site specific and Environmental data needed. For each CHARM requirement the corresponding HOCNF reference number is provided.

9.1 Chemical specific data

CHARM Requirement	Description	HOCNF form Reference
Application group	The application groups are: Production chemicals, Drilling chemicals, Cementing chemicals, Completion and workover chemicals	1.4 ⑤
Type of chemical	<ul style="list-style-type: none"> Surfactants are treated differently from other chemicals within CHARM. It is therefore, necessary to know if the substance in question belongs to this category. If so, the type of surfactant and the fraction released must also be known. Injection chemicals are treated differently from other chemicals within CHARM. It is therefore, necessary to know if the substance in question belongs to this category. Standard production chemicals are all production chemicals which are not surfactants nor injection chemicals. 	1.6.b ⑤
f_r	Fraction of a chemical released into the environment. Needed for surfactants, injection chemicals and completion and workover chemicals.	-
P_{ow}	Octanol-water partition coefficient.	2.1.1 ⑤
P_{ow} determination procedure	P_{ow} can be determined using OECD Guideline 117 (HPLC) or OECD Guideline 107 (Shake flask).	2.1.1 ⑤
Toxicity data		2.3 ⑤
<ul style="list-style-type: none"> EC₅₀ NOEC 	<ul style="list-style-type: none"> Concentration at which 50% of the organisms tested are affected; or 50% effect is measured (e.g., population growth). The No Observed Effect Concentration is the highest concentration which has no effect on the tested organisms. 	
d_{w28}	Fraction of a chemical degraded in the water in 28 days	2.2.1
d_{st}	Fraction of a chemical degraded in the sediment in t days	
P_{sw}	Sediment-water partition coefficient	
Molecular weight	Molecular weight of a chemical is needed to determine if the chemical can be assessed using CHARM	1.6

9.2 Site specific data

CHARM Requirement	Description	HOCNF Reference
Type of installation	The types of installations are: Oil production, Gas production, and Drilling installations	
Dosage: • C_t, C_{flow} • $M, W\%, X_{ppb}$ • C_i	Amount of substance used (Dosage): • Concentration of production chemicals in the total produced fluid and in a particular flow • Mass, weight percentage and pounds per barrel of drilling chemicals • Initial concentration of cementing, completion and workover chemicals	1.4 ⑤
Flow in terms of which the dosage is expressed	Dosages of production chemicals can be expressed in terms of the total produced fluids, the produced water or the produced oil or gas. Dosages expressed in terms of a flow other than the total produced fluid should be converted	
ρ_m	Specific gravity of the discharged mud	⑤
F_{pw}	Total water production	
$D_{distance\ x}$	Dilution factor of a produced chemical at a certain distance from the installation.	
$F_{o/c}$	Total oil or condensate production	
F_t	Total fluid production.	
F_i	Fluid injection	
V_m	Volume of mud discharged for a specific section	
Plat. Density	Number of installations per square kilometre	
D_{batch}	Dilution factor for batchwise discharges of drilling muds, mixwater, spacer and completion fluids	

9.3 Environmental data

CHARM Requirement	Description	HOCNF Reference
U	Residual current speed. Used to calculate the refreshment rate of the ambient water.	
f_{oc}	Fraction of the sediment made up of organic carbon	
Water depth	Average depth of water around installation	
r	Refreshment rate of water around installation	

10. References

Basietto et al. (1990): Ecotoxicity and ecological risk assessment. *Environmental Science & Technology*, 24: 11-15.

Bos A (1998): Evaluation of the CHARM III model. Version 2.

Bos A (1998): Dilution factors for batchwise discharges. Version 1.

[CHARM Implementation Network \(CIN\) minutes of meeting 11 June 2002 fraction released and batch dilution factors for squeeze and hydrotest chemicals agreed.](#) ③

[CHARM Implementation Network \(CIN\) minutes of meeting 25 November 2003 equation 26c agreed for the assessment of drilling chemicals which are surfactants.](#) ③

CHARM Implementation Network (CIN) Technical Report 1.

Foekema E.M., A. Bos, P. Verstappen, C.C. Karman (1998): *Field validation of the CHARM model*. TNO-report R98/317

Karman C.C. & E.A. Vik (1996): *CHARM III. Technical background report*. TNO-report R96/354

Karman C.C., E.A. Vik, H.P.M. Schobben, G.D. Øfjord & H.P. van Dokkum (1996): *CHARM III. Main report*. TNO-report R96/355

Stagg R., D.J. Gore, G.F. Whale, M.F. Kirby, M. Blackburn, S. Bifield, A.D. McIntosh, I. Vance, S.A. Flynn & A. Foster (1996): Field evaluation of toxic effects and dispersion of produced water discharges from North Sea oil platforms. In: M. Reed & S. Johnsen (eds.), *Produced Water 2. Environmental issues and mitigation technologies*. Environmental Science Research Vol. 52, Plenum Press, New York. Pp. 81-100.

Vik E.A., S. Bakke, C.S. Fürst, A. Bos, M. Robson (1999): Substances versus preparations. Proposed handling of HOCNF data in CHARM. CHARM Implementation Network (CIN) Technical Report 4.

Appendix I: List of Abbreviations Used

Abbreviation

BCF	Bioconcentration Factor
CHARM	Chemical Hazard Assessment and Risk Management
CIN	CHARM Implementation Network
CMC	Critical micelle concentration
E&P	Exploration and production
EC ₅₀	Median effect concentration
HMCS	Harmonised Mandatory Control System
HOCNF	Harmonised Offshore Chemical Notification Format <i>HOCNF form and Guidance: OSPAR Recommendation 2010/3 as amended</i> ⑤
HPLC	High Pressure Liquid Chromatography
HQ	Hazard Quotient
LC ₅₀	Median Lethal Concentration
NOEC	No Observed Effect concentration
OBM	Oil based muds
OECD	Organisation for Economic Co-operation and Development
OPF	Organic Phase Fluid ③
OSPAR	Oslo & Paris Commissions
PARCOM	Paris Commission
PCB	Poly-chlorinated Biphenyls
PEC	Predicted Environmental Concentration
PLONOR-list	List of chemicals and products that are natural constituents of the sea or natural products such as nutshells and clays. The OSPAR commissions considers them to Pose Little Or NO Risk to the environment
PNEC	Predicted No Effect Concentration
P _{ow}	Octanol-Water Partition Coefficient
P _{sw}	Sediment-Water Partition Coefficient
ppb	Pounds per barrel
RQ	Risk Quotient
SBM	Synthetic based muds
TNO	Netherlands Organisation for Applied Scientific Research
WBM	Water based muds

Appendix II: Considerations regarding the evaluation of surfactants

Many chemicals used in offshore E&P operations have surface active properties. It would therefore be preferred to be able to evaluate the (relative) environmental impact of surfactants with the CHARM model. The calculation of the PEC is, however, very much dependent on chemical equilibrium partitioning of (organic) molecules between a water phase and an organic phase (PEC_{water}: water/oil/condensate; PEC_{sediment}: water-organic matter). Surfactants, however, are not subjected to such chemical equilibrium partitioning processes. The environmental fate of surfactants is mainly dependent on physical processes of polymolecule structures, such as the formation of suspended micelles or film at interfaces between water and other materials or fluids. As a consequence, the environmental fate of chemicals cannot adequately be calculated using mathematical calculation rules based on chemical partitioning.

A main parameter in the estimation of the PEC in CHARM is the octanol-water partition co-efficient (P_{ow}), which is generally used to estimate partitioning for organic chemicals. In addition to what is discussed in the previous paragraph, it should also be noted that for surface active chemicals no valid P_{ow} value can be obtained, as this measure is determined by mixing the chemical with an equal amount of water and octanol and subsequently dividing the concentration of the chemical in the octanol-phase by the concentration in the water-phase. Surfactants, however, do not enter either of the phases, but form a layer at the interface between them.

The problems arising in the CHARM model because of chemicals lacking a P_{ow} value, have led to several recommendations and suggestions for alternative approaches. Two suggestions, which have been subject to discussion, will be summarised in this paragraph:

- Although it is not possible to determine a P_{ow} value for surfactants, it is possible to come up with experimental data for accumulation in sediment or biota. It has been suggested to use these data with inverted calculation rules for estimating accumulation for organics, to derive a P_{ow} value for surfactants. These values derived with the inverted calculation rules should then be used as a normal P_{ow} value.
- *It must be noted that the suggested approach uses calculation rules for organics, which do not apply for surfactants. Furthermore, it is illogical to calculate a parameter which does not exist for surfactants. Finally it should be noted that the use of a default Pow does not address the more fundamental point that the PEC of surfactants cannot actually be calculated on the basis of chemical partitioning.*
- Some discussions have taken place concerning alternatives for P_{ow}. It has been suggested that a characteristic value may be found (for example by using HPLC), which might correlate with accumulation in biota and sediments. Furthermore, QSARs have been developed that can provide a pseudo P_{ow} value.
- *It is recognised that research should continue on these subjects, but must successfully be completed before these approaches can be implemented within the model.*

It was decided that experimentally-derived partitioning data would be used for the fraction released (a suggested method for sediment-water partitioning is described in Karickhoff *et al.*, 1979), when making calculations with the CHARM model.

Extensive research concerning the relationship between the hydrophobicity and the bioconcentration of surfactants has been carried out (e.g. Tolls and Sijm, 1995). Although several suggestions have been made for indicators of the hydrophobicity of surfactants (on the basis of the critical micelle concentration (CMC) or on the basis of HPLC retention time), the results are not conclusive and can therefore not (yet) be used in the CHARM model.

For surface active production chemicals (not for drilling, cementing, completion and workover chemicals) experimentally derived fraction released (e.g. from a mass balance study) can be used. In many cases, however, this information is not available. For these cases, a series of default values for the fraction released, dependent on the type of surfactant, have been agreed upon (see Table 4).

SUPERSEDED

Appendix III: Dilution factors (at 1784 m) for batchwise discharges

WBM Drilling fluid discharges

Please note that

i) the reciprocal of the dilution figures given below should be used in the model:

$\text{dilution factor} = 1 / \text{table value}$

ii) The Density, Discharge Rate and Volume refer to the bulk discharge and not to the individual chemical products within it. ⑤

Density (g/cm ³)	Rate (m ³ /hr)	Volume (m ³)	Dilution Factor
1.2	200	200	5759
		400	5641
		600	5611
	300	200	4996
		400	4996
		600	4951
	400	200	4503
		400	4540
		600	4503
200		200	11134
		400	11039
		600	11326
300	200	10029	
	400	10184	
	600	10184	
400	200	9658	
	400	9589	
	600	9519	

Density (g/cm ³)	Rate (m ³ /hr)	Volume (m ³)	Dilution Factor
1.8	200	200	17940
		400	18058
		600	18219
	300	200	17152
		400	17242
		600	16784
	400	200	16093
		400	15341
		600	15341

Cementing, completion and workover chemicals

Please note that:

i) the reciprocal of the dilution figures given below should be used in the model:

dilution factor = 1 / table value

ii) The Density, Discharge Rate and Volume refer to the bulk discharge and not to the individual chemical products within it. ⑤

Density (g/cm ³)	Rate (m ³ /hr)	Volume (m ³)	Dilution Factor
1.03	60	3	2347
		5	2079
		20	1767
		60	1678
		120	1658
	120	3	3413
		5	1949
		20	1332
		60	1185
		120	1182
	180	3	3788
		5	2717
		20	1129
		60	1041
		120	1005
1.1	60	3	40161
		5	25641
		20	18832
		60	18553
		120	18797
	120	3	42373
		5	24938
		20	10060
		60	9174
		120	9259
	180	3	55556
		5	34014
		20	10246
		60	7752
		120	7634

Density (g/cm ³)	Rate (m ³ /hr)	Volume (m ³)	Dilution Factor
1.3	60	3	52083
		5	34602
		20	29240
		60	25063
		120	25445
	120	3	59172
		5	37200
		20	13263
		60	12107
		120	12005
	180	3	82654
		5	49020
		20	14599
		60	9901
		120	9881
1.7	60	3	84746
		5	56180
		20	33898
		60	32468
		120	36232
	120	3	134048
		5	84746
		20	29940
		60	26596
		120	26385
	180	3	75188
		5	40486
		20	15015
		60	17212
		120	17241

Appendix IV: Acknowledgements

Financial support for the CHARM project was provided by the following participants (listed in alphabetical order):

- DEPA (Danish Environmental Protection Agency)
- EOSCA (European Oilfield Speciality Chemicals Association)
- E&P Forum
- Netherlands Ministry of Economic Affairs (EZ)
- Netherlands Ministry of Housing, Physical Planning and Environment (VROM)
- Netherlands Ministry of Transport, Public Works and Water Management, Rijkswaterstaat (V&W)
- NOGEP (Netherlands Oil & Gas Exploration and Production Association)
- NTN (The Norwegian Research Council)
- NSOC-D (North Sea Operators Committee - Denmark)
- OLF (Norwegian Oil Operators Association)
- SFT (Norwegian State Pollution Control Authority)
- UK DTI (Department of Trade and Industry)
- UKOOA (United Kingdom Offshore Operators Association)

SUPERSEDED

Appendix V: Summary Sheet of Default Values ③

Table 3: Flow parameter default values used in the hazard assessment of production chemicals.

Parameter	Symbol ③	North Sea Oil installation	North Sea Gas installation	units
water production	F_{pw}	14964	47	m ³ .d ⁻¹
oil production		2002	-	m ³ .d ⁻¹
gas production		-	220000	m ³ .d ⁻¹
condensate production		-	2	m ³ .d ⁻¹
Injection water	③ F_i	16966	-	m ³ .d ⁻¹

NB: Default values are used for the purposes of hazard assessment. For risk assessments, they should be replaced by site-specific data ⑤

Table 4: Default values used in the CHARM Hazard Assessment module for the calculation of the fraction of surfactants released.

Type of surfactant	Fraction released, f_r
Quaternary amines	1.0
EO-PO Block polymer demulsifier (Ethoxylate-Propoxylate)	0.4
Imidazolines	0.1
Fatty amines	0.1
Fatty amides ③	1.0
Primary amines (cationic type, C _≥ 12)	0.1
Phosphate esters (anionic type, C _≥ 13)	0.1
Others	1.0

Table 5: Characteristic conditions of the reference installations (realistic worst case) used in Hazard Assessment.

Parameter	Symbol ③	North Sea oil production installation	North Sea gas production installation	units
Installation density		0.1	0.1	km ⁻²
Water depth		150	40	m
Refreshment rate	r	0.24	0.24	d ⁻¹
Corresponding Residual Current speed.	U	0.01	0.01	ms ⁻¹
Sediment organic carbon content	f_{oc}	0.04	0.04	-
Dilution at 500m.	D	0.001	0.001	-

Table 6: Default values for calculating the PEC for drilling chemicals (both continuous and batchwise discharge) used in Hazard Assessment ⑤

Parameter	Symbol ③	Value	Unit
Installation density at 1784 m		0.1	km ⁻²
Drilling time per section	T	16	days
Water depth		150	m
Refreshment rate	r	0.24	d ⁻¹
Corresponding Residual Current speed.	U	0.01	ms ⁻¹
Batchwise dilution factor	D_{batch}	7.7	10 ⁻⁵ (1:13,000)

Table 7: Default data related to the drilling of the various sections used in Hazard Assessment ⑤

Section drilled	Length drilled (m)	Mud density (kg.m ⁻³)	Volume continuous discharge (m ³)	Volume batchwise discharge (m ³)
36"	100	-	*	-
24"	400	-	*	-
17½"	1500	1400	600	-
12¼"	1500	1600	450	375
8½"	1000	1600	250	280

Table 8: Default values to be used for Hazard Assessment of cementing chemicals, being discharged with spacer fluid or mixwater.

Parameter	Symbol ^③	Spacer fluid	Mixwater
Dilution factor at 500m	D _{batch}	1.2 10 ⁻⁵ (1:81,000)	2.2 10 ⁻⁵ (1:45,000)

Table 9: Default values to be used for Hazard Assessment of completion and workover chemicals (specified as 'cleaning chemicals', 'other chemicals', 'squeeze treatments' and 'hydrotest chemicals'). ③

Parameter	Symbol ^③	Cleaning chemicals	Other chemicals
Fraction released - chemical	fr	n.r.	0.1
Dilution factor at 500m	D _{batch}	7.7 10 ⁻⁵ (1:13,000)	7.1 10 ⁻⁵ (1:14,000)

Parameter	Symbol ^③	Squeeze treatments ③	Hydrotest chemicals ③
Fraction released - chemical	fr	0.33	1
Dilution factor at 500m	D _{batch}	7.1 10 ⁻⁵ (1:14,000)	0.001 (1:1000)

Appendix VI: A Summary of the Equations of the CHARM Model ③

1	$C_t = \frac{F_{flow} * C_{flow}}{F_t}$	18	$PEC_{water, batch} = \frac{M}{V_m} * D_{batch} * 10^3$
2a	$C_{pw} = \frac{f_r * C_i * F_i}{F_{pw}} \text{ ⑤}$	19	$PEC_{water} = C_{i, mixwater} * D_{batch, mixwater}$
2b	$C_i * F_t = (C_{o/c} * F_{o/c}) + (C_{pw} * F_{pw}) \text{ ⑤}$	20	$PEC_{water} = C_{i, spacer} * D_{batch, spacer}$
3	$C_{o/c} \approx 10^{\log P_{ow}} * C_{pw}$	21	$PEC_{water} = C_{i, cleaning} * D_{batch, cleaning}$
4 ⑤	$C_t * F_t = (10^{\log P_{ow}} * C_{pw} * F_{o/c}) + (C_{pw} * F_{pw})$	22	$PEC_{water} = f_r * C_{i, completion} * D_{batch, completion}$
5	$C_t * F_t = ((10^{\log P_{ow}} * F_{o/c}) + F_{pw}) * C_{pw} \text{ ⑤}$	23	$d_{w1} = 1 - 10^{\frac{\log(1 - d_{wt})}{t}}$
6	$C_{pw} = \frac{C_t * F_t}{(10^{\log P_{ow}} * F_{o/c}) + F_{pw}} \text{ ⑤}$	24	$D_{regional} = \frac{F_{pw} / V_p}{r + d_{w1}}$
7	$C_{pws} = C_{pw} + (0.1 * C_i)$	25	$d_{s365} = 1 - (1 - d_{wt})^{36.5t}$
8	$C_{pws} * F_{pw} > C_t * F_t$	26a	$P_{sw} = f_{oc} * 10^{\log P_{ow}}$
9	$C_{pws} * F_{pw} = C_t * F_t$	26b	$P_{sw} = K_{oc} \frac{F_{oc}}{F_{test}}$
10	$C_{pws} = \frac{C_t * F_t}{F_{pw}}$	26c	$P_{sw} = f_{oc} * 10^{4(1 - f_r)} \text{ ④}$
11	$PEC_{water} = C_{pws} * D_{distance} * x$	27	$PEC_{sediment} = C_{pws} * D_{regional} * P_{sw} * (1 - d_{s365})$
12	$M = Wt * V_m * \rho_m$	28	$PEC_{sediment} = PEC_{water, cont} * P_{sw} * (1 - d_{s365})$
13	$M = X_{ppb} * V_m * 2.85$	29	$PNEC_{benthic} = P_{sw} * PNEC_{pelagic}$
14	$V_p = \frac{1}{platf. density} * waterdepth * 10^6$	30	$HQ_{preparation} = \text{Max.valueof} \left[\frac{PEC_{substanc e_i}}{PNEC_{substanc e_i}} \right]$
15	$r = \frac{24 * 3600}{2 * Y / U}$	31	$HQ_{preparation} = \text{Max.valueof} \left[\frac{PEC_{substanc e_i}}{PNEC_{preparation}} \right]$
16	$V_t = V_p * r$	32	R(A+B) = R(A) + R(B) - R(A) * R(B) R(A+B+C) = R(A+B) + R(C) - R(A+B) * R(C) etc.
17	$PEC_{water, cont} = \frac{M}{T * V_t} * 10^3$	33	$Risk = \int_{y=0}^{\ln(RQ)} \left\{ \frac{1}{S_m * \sqrt{2 * \pi}} * e^{\frac{-(y - X_m)^2}{2 * S_m^2}} \right\}$

Appendix VII: Index of Constants, Symbols and Variables ③

ρ_m	density of the discharged mud ($\text{kg}\cdot\text{m}^{-3}$)	$F_{o/c}$	total oil or condensate production ($\text{m}^3\cdot\text{d}^{-1}$)
10^3	conversion constant to express PEC as $\text{mg}\cdot\text{l}^{-1}$	f_{oc}	organic carbon in sediment (expressed as fraction of dry weight)
10^6	factor used to convert km^2 to m^2 ($\text{m}^2\cdot\text{km}^{-2}$)	F_{pw}	volume of produced water discharged per day ($\text{m}^3\cdot\text{day}^{-1}$)
2	factor used to convert radius around installation to diameter of the area	f_r	fraction released (for injection chemicals equal to 0.01, for surfactants value depends on surfactant type (Table 4))
2.85	conversion constant from ppb to $\text{kg}\cdot\text{m}^{-3}$	F_t	total fluid production ($\text{m}^3\cdot\text{d}^{-1}$)
24	factor used to convert days to hours ($\text{h}\cdot\text{d}^{-1}$)	f_{test}	organic carbon in sediment used for K_{oc} determination (expressed as fraction of dry-weight)
3600	factor used to convert hours to seconds ($\text{s}\cdot\text{h}^{-1}$)	ι	Substance number 1 to η
A	chemical A	Koc	Experimentally derived equilibrium constant for organic carbon ④
A+B	mixture of chemicals A and B	M	amount (mass) of non-PLONOR-listed substance discharged (kg)
A+B+C	mixture of chemicals A, B and C	PEC_{sediment}	Predicted Environmental Concentration in the sediment around the installation ($\text{mg}\cdot\text{kg}^{-1}$)
B	chemical B	PEC_{water}	Predicted Environmental Concentration of a chemical at a certain distance from the installation ($\text{mg}\cdot\text{l}^{-1}$)
C	chemical C	$PEC_{\text{water, batch}}$	PEC_{water} for batchwise discharges ($\text{mg}\cdot\text{l}^{-1}$)
C_{flow}	concentration of the chemical in that flow ($\text{mg}\cdot\text{l}^{-1}$)	$PEC_{\text{water, cont}}$	PEC_{water} for continuous discharges ($\text{mg}\cdot\text{l}^{-1}$)
C_i	concentration of the chemical in the injected fluid or, for surfactants, total fluid ($\text{mg}\cdot\text{l}^{-1}$)	platf.density	number of installations per square kilometre (km^{-2})
$C_{i, \text{cleaning}}$	initial concentration of chemical in the cleaning fluid (dosage; $\text{mg}\cdot\text{l}^{-1}$)	$PNEC_{\text{benthic}}$	Predicted No Effect Concentration for benthic systems ($\text{mg}\cdot\text{kg}^{-1}$ dw)
$C_{i, \text{completion}}$	initial concentration of chemical in completion and workover fluids (dosage; $\text{mg}\cdot\text{l}^{-1}$)	$PNEC_{\text{pelagic}}$	Predicted No Effect Concentration for pelagic systems ($\text{mg}\cdot\text{l}^{-1}$)
$C_{i, \text{mixwater}}$	initial concentration of chemical in mixwater (dosage; $\text{mg}\cdot\text{l}^{-1}$)	P_{ow}	partition coefficient between octanol and water
$C_{i, \text{spacer}}$	initial concentration of chemical in spacer fluid (dosage; $\text{mg}\cdot\text{l}^{-1}$)	P_{sw}	sediment-water partition coefficient ($\text{l}\cdot\text{kg}^{-1}$)
$C_{o/c}$	concentration of the chemical in oil or condensate ($\text{mg}\cdot\text{l}^{-1}$)	r	fraction of sea water refreshed in the receiving volume around the installation per day (d^{-1})
C_{pw}	concentration of the chemical in produced water ($\text{mg}\cdot\text{l}^{-1}$)	R	risk
C_{pws}	concentration of a chemical in the produced water including a safety factor ($\text{mg}\cdot\text{l}^{-1}$)	S_m	standard deviation of the logarithmically transformed data (calibrated to 1.7356)
C_t	concentration of the chemical in the total produced fluid ($\text{mg}\cdot\text{l}^{-1}$)	t	test period used in the determination of degradation rate (days)
D_{batch}	dilution factor for batchwise discharges	T	time needed to drill a section (d)
$D_{\text{batch, cleaning}}$	batchwise dilution factor for cleaning fluids (-)	U	residual current speed ($\text{m}\cdot\text{s}^{-1}$)
$D_{\text{batch, completion}}$	batchwise dilution factor for completion and workover fluids (-)	V_m	volume of mud discharged for the specific section (m^3)
$D_{\text{batch, mixwater}}$	batchwise dilution factor for mixwater (-)	V_p	volume of ambient water per installation (m^3)
$D_{\text{batch, spacer}}$	batchwise dilution factor for spacer fluid (-)	V_t	volume of water passing the installation ($\text{m}^3\cdot\text{d}^{-1}$)
$D_{\text{distance, x}}$	dilution factor at distance x from the installation (0-1)	water depth	average water depth around the installation (m)
D_{regional}	regional dilution factor	Wt	weight percentage of the non-PLONOR-listed substance in the mud (-)
d_{s365}	fraction of a chemical in sediment that is degraded in 1 year	X_m	average of the logarithmically transformed data (calibrated to 2.8497)
d_{w1}	fraction of a chemical degraded in the water column in 1 day (day^{-1})	X_{ppb}	dosage of the non-PLONOR-listed substance in the mud (pounds per barrel)
d_{w28}	highest fraction of a chemical degraded in the water column in t (usually 28) days (days^{-1})	Y	radius from installation corresponding to the area of ambient water available as diluent (i.e. $\pi \cdot Y^2 = 1 / \text{installation density} \cdot 10^6$) (m)
d_{wt}	fraction of a chemical degraded in the water in t days	y	variable to describe the normal probability curve
F_{flow}	volume of flow in terms of which the dosage is expressed ($\text{m}^3\cdot\text{d}^{-1}$)		
F_i	fluid injected or, for surfactants, total fluid production ($\text{m}^3\cdot\text{d}^{-1}$)		

Appendix VIII: Historic Section on Assessment of Preparations ⑤

3.3 Dealing with preparations

This section has been moved from the main part of the manual to this Appendix for reference only. Initially under the HMCS preparation data could be submitted and assessed as described here. Since 2000 however (slightly later in the UK), the HMCS has required substance specific data to be submitted and assessments to be carried out on a component basis. ⑤

The PEC:PNEC approach, which is the basis of the CHARM model, is a methodology in which single PEC and PNEC values need to be available for comparison. This is not a problem in those cases in which the chemical is a single substance. The physico-chemical parameters of the substance can be used to calculate the PEC, while the PNEC can be derived from toxicity tests performed with the substance.

However, the majority of the chemicals used as offshore E&P chemicals are preparations composed of a number of substances. Although a PNEC for preparations can be derived in the same way as for substances, difficulties arise when trying to interpret the practical meaning of this information. The toxicity test is performed on the preparation before it is discharged, while when using it in the relevant process the preparation may change. Individual substances may partition according to their physicochemical properties, react with other chemicals, etc. Furthermore, after discharge other (biochemical) processes (such as biodegradation) may also influence the fate and effect of the individual substances of the preparation.

In order to make a valid PEC:PNEC analysis, preparations should also be assessed on a substance basis. While data for calculating a PEC is required be made available on a substance level, this is not the case for the toxicity data. Although several options have been studied to work around this problem (Vik *et al.*, 1999) there is, as yet, not enough scientific support for determining a PNEC for the individual substances on the basis of the toxicity data for the preparation. It was decided to use a simple approach to determine the HQ of the preparation (see below), until a better and scientifically sound method is available. Further research in this area is therefore encouraged.

One of the following approaches (depending on the type of data available) should be used to calculate a Hazard Quotient for a preparation:

- 1) If both data for PEC and PNEC are available on substance level:

$$HQ_{preparation} = \text{Max.value of} \left[\frac{PEC_{substance\ i}}{PNEC_{substance\ i}} \right] \quad (30)$$

where i = the substance number 1 to n

- 2) If data for PEC is available on substance level and data for PNEC is available on preparation level:

$$HQ_{preparation} = \text{Max.value of} \left[\frac{PEC_{substance\ i}}{PNEC_{preparation}} \right] \quad (31)$$