Approaches for Derivation of Environmental Quality Criteria for Substances Applied in Risk Assessment of Discharges from Offshore Drilling Operations

Dag Altin,† Tone Karin Frost,*‡ and Ingunn Nilssen‡

†BioTrix, NO-7022 Trondheim, Norway
‡StatoilHydro ASA, NO-7005 Trondheim, Norway

EDITOR'S NOTE:

This is 1 of 5 papers reporting on the results of a 4-year project to develop an environmental risk-based decision support tool, to assist the oil industry in establishing cost-effective measures for reducing risk to the marine environment from drilling discharges.

ABSTRACT

In order to achieve the offshore petroleum industries "zero harm" goal to the environment, the environmental impact factor for drilling discharges was developed as a tool to identify and quantify the environmental risks associated with disposal of drilling discharges to the marine environment. As an initial step in this work the main categories of substances associated with drilling discharges and assumed to contribute to toxic or nontoxic stress were identified and evaluated for inclusion in the risk assessment. The selection were based on the known toxicological properties of the substances, or the total amount discharged together with their potential for accumulation in the water column or sediments to levels that could be expected to cause toxic or nontoxic stress to the biota. Based on these criteria 3 categories of chemicals were identified for risk assessment the water column and sediments: Natural organic substances, metals, and drilling fluid chemicals. Several approaches for deriving the environmentally safe threshold concentrations as predicted no effect concentrations were evaluated in the process. For the water column consensus were reached for using the species sensitivity distribution approach for metals and the assessment factor approach for natural organic substances and added drilling chemicals. For the sediments the equilibrium partitioning approach was selected for all three categories of chemicals. The theoretically derived sediment quality criteria were compared to field-derived threshold effect values based on statistical approaches applied on sediment monitoring data from the Norwegian Continental Shelf. The basis for derivation of predicted no effect concentration values for drilling discharges should be consistent with the principles of environmental risk assessment as described in the Technical Guidance Document on Risk Assessment issued by the European Union.

Keywords: Environment impact   Drilling discharges   Environmentally safe concentrations   ERMS

INTRODUCTION

The goal of the Environmental Risk Management System (ERMS) project was to develop an integrated risk assessment model to enable the petroleum industry to identify and quantify the environmental risks from disposal of offshore drilling discharges to the marine environment (Singsaas et al. 2008; Smit, Holthaus, et al. 2008). The concept is similar to the environmental impact factor (EIF) developed for produced water, which is fully implemented and accepted as a produced water management tool for the Norwegian offshore sector (Johnsen et al. 2000). In the EIF for produced water the potential environmental impact of a given toxic stressor in the water column is predicted by the dose-related risk and effect assessment model (Reed et al. 2001) based on information of local oceanographic conditions in addition to volumes and composition of the produced water discharge.

The effects of discharges from drilling operations is of a more complex nature than produced water, as it includes particles in addition to dissolved substances, and effects on the biota in the sediments has to be evaluated in addition to the water column. The particles may cause physical stress to biota in addition to the toxic stress caused by dissolved chemicals,

and are therefore included in the EIF for the drilling discharges as a nontoxic stressor. These stressors act by physical disturbances as increased sedimentation rates, oxygen depletion in the sediments, changes in sediment grain size, and disturbances due to increased numbers of suspended particles in the water column. Derivation of threshold effect values for nontoxic stressors have been covered by other studies within the ERMS project (Smit, Holthaus, Kaag, et al. 2006; Smit, Holthaus, Tamis, et al. 2006; Smit, Holthaus, et al. 2008).

The major objective was to consider the available approaches for developing environmental quality criteria for both water column and sediments, and to reach consensus on the approaches most appropriate for the toxic stressors. The aim of the present paper is to summarize the environmental quality criteria derived for the toxic stressors, as they are important elements of effect assessment within the EIF for drilling discharges conceptual framework (Smit, Jak, et al. 2008). A literature review was performed to search for toxicological information that fulfilled the recommendations in the Technical Guidance Document on Risk Assessment (TGD; EC 2003) for calculation of predicted no effect concentration (PNEC) for relevant substances.

According to the TGD environmental risks for chemicals may be estimated by calculating the ratio between the predicted environmental concentration (PEC) and the PNEC in the same compartment (PEC/PNEC ratios; EC 2003). The

* To whom correspondence may be addressed: tkf@statoil.com

PEC is an estimate of the concentration of a chemical to which the biota will be exposed during and after discharge of the chemical. The PEC values can be either based on analytical data or derived from model calculations (exposure assessment), but care should be taken to identify and use the biological available fraction of the chemical over the bulk analytical concentration whenever possible. The PNEC is the concentration of the chemical in the environment below which it is unlikely that adverse effects on the biota will be observed. The PNEC values are usually determined on the basis of results from controlled laboratory experiments taking adequate assessment factors into account. The PNEC can also be derived using a statistical extrapolation approach when sufficient data are available. The ratio of the PEC to the PNEC indicates the likelihood of the occurrence of adverse effects on the biota, and implementation of the approach helps to identify acceptable or unacceptable risks. This identification provides the basis for environmental management or regulatory decisions. The calculations are explained in detail for both the water column and sediments by Rye et al. (2008), and will not be further addressed here.

The discharge during an offshore exploration drilling operation is generally of limited duration, and the discharges are usually not continuous but intermittent. The discharge will have possible influence on biota in both the water column and sediment, but over different time frames for the 2 compartments. During and shortly after discharge, the influence will be most prominent in the water column, but as the particles deposit the influence will be shifted towards the sediment. Drilling discharges can in most cases be referred to as acute with only a temporary impact in the water column, while the sediment effects are more of a chronic nature with exposure to biota in order of months and years.

A separate study within the ERMS project was initiated for the purpose of validation of PNEC$_{sediment}$ values derived in this study. Two different approaches, the species sensitivity distribution approach (SSD; Bjørgesæter 2006) and the Moving Window Modelling approach (Grung et al. 2005), have been performed to establish field-derived threshold effect levels based on data from the Norwegian Continental Shelf. The data used for verification is collected from a database containing the complete datasets from the environmental monitoring of the benthos in vicinity of petroleum installations on the Norwegian Continental Shelf since 1990. The data selected were relevant heavy metals, hydrocarbons, grain size, and corresponding abundance of more than 2000 different benthic species.

The largest volumes of solids generated during an offshore drilling operation are drilling muds and cuttings. Drilling muds are specially formulated mixtures of natural clays, organic polymers, weighting agents, and several other compounds suspended in a base fluid. There are traditionally 3 main types of drilling muds according to their base fluids: water-based, synthetic-based, and oil-based muds. Drill cuttings are particles of crushed formation rock from drilling of the well.

Drilling muds contains a wide range of added chemicals with different functions in the drilling process and maintenance of the well. Weighting agents and inorganic salts are the ingredients used and discharged in largest amounts, and in 2004 the discharges from drilling operations constituted 82% of the total discharges of chemicals from the offshore petroleum activity on the Norwegian Continental Shelf (OLF 2005). Most of the drilling chemicals discharged are listed as PLONOR chemicals (i.e., substances/preparations used and discharged offshore which are considered to Pose Little or No Risk to the Environment; OSPAR 2004), and are considered unlikely to pose any harm on the biota. Ideally all added chemicals shall be included from a risk assessment prospective if used in considerable amounts. Due to low priority for those substances there is limited ecotoxicological information available on the PLONOR chemicals and only a limited number of these chemicals can be included.

The main criteria for inclusion of substances in EIF drilling discharges are the total amount of chemicals used/discharged to the sea and the potential for accumulation in the water column or sediments to levels that may cause toxic or nontoxic stress to biota.

The substances selected for inclusion in the risk assessment falls within 3 categories: Metals as trace contaminants in added chemicals or in drill cuttings, natural organic substances, and chemicals added in the drilling process.

Metals

The metals of concern, based on their abundance in drilling discharges and their potential toxicity to marine organisms, include arsenic, barium, chromium, cadmium, copper, iron, lead, mercury, nickel, and zinc (Neff et al. 1987, 2000; Neff 2005). Most metals associated with drilling discharges originate from trace impurities in mud ingredients as barite, ilmenite, and clay as well as formation rock in drill cuttings. The metals present in drilling muds at substantially higher concentrations (>10-fold) than naturally present in sediments are barium, cadmium, copper, and zinc (Table 1).

Based on the mentioned criteria the following metals are recommended included in the calculations for EIF for drilling discharges in the sediment: Cadmium, chromium, copper, lead, mercury, and zinc. Concentrations of nickel in drilling discharges usually are about 10 times below concentrations in natural sediments and are therefore regarded of no concern for toxicity in sediments, but will be included for risk calculations in the water column. Metals for risk assessment in the water column include all the metals selected for the sediment, except chromium. Chromium is excluded from the water column risk evaluation because current drilling discharges contain either very low concentrations, or the chromium is in a reduced and insoluble form. Most drilling discharges contain large amounts of barium as barite; however, barium is not considered to be toxic and shall not be included for risk assessment in water column or sediments.

Natural organic substances

Natural organic compounds in drilling discharges include added organic ingredients of drilling muds or when the drilling mud is contaminated with production oil or formation hydrocarbons when drilling of hydrocarbon-bearing structures. The natural organic substances of concern, and hence evaluated for inclusion in the risk assessment, include polycyclic aromatic hydrocarbons (PAHs); the monoaromatic hydrocarbons benzene, toluene, ethylbenzene, and xylene (BTEX); alkylated phenols; and aliphatic hydrocarbons.

Polycyclic aromatic hydrocarbons—PAHs have low solubilities in water and high affinities for the organic phase of particles, as indicated by a log octanol–water partitioning coefficient (K_{ow}) ranging from 3.37 (naphthalene) to 7.0 (indeno[1,2,3-*cd*]pyrene). They are toxic and persistent in the marine environment (Neff 2002), and if present at concentrations significantly elevated over the background concentrations in sediments, they may contribute to toxic stress to sediment living organisms.

Table 1. Concentrations of selected metals in drilling muds, barite, world sediments, and natural background in sediments at Norwegian Continental Shelf (NCS). Ratio of metals concentrations in NCS barite to background sediments is included. Metals in boldface were included in the risk assessment of the sediment. Numbers in mg/kg dry weight

Metal	Drilling muds	US barite	NCS barite[a]	World sediments[b]	NCS sediments[c]	NCS barite/NCS background ratio
As	1.8–2.3	2.2	—	6.9–26	—	≈0.33[d]
Ba	720–449000	523000	—	1–2000	131 (4.6–554)	114000[e]
Cd	0.16–54.4	0.03	0.7–1.7	0.1–0.6	0.037 (0.003–0.13)	18.9
Cr	0.10–6000	11	9.8–14.3	36–110	14.6 (2.58–39.2)	0.90
Cu	0.005–307	9.7	76.6–104.7	7–33	4.10 (0.3–17.2)	18.7
Pb	0.40–4225	7.8	48.7–116	10–33	10.7 (1.92–46.5)	4.8
Hg	0.02–10.4	0.12	0.31–0.69	0.03–0.14	0.021 (0.003–0.10)	14.8
Ni	3.8–19.9	—	1.2–2.1	13–45	—	≈0.09[d]
Va	14–28	—	—	63–238	—	0.44[f]
Zn	0.06–12300	8.6	42.9–138.9	27–88	20.7 (0.42–83.7)	2.1

[a] Range for 2001–2003. Data from Neff (2005).
[b] Data from Neff (2005).
[c] Mean values and range of background concentrations based on samples from 150 reference stations in North Sea analyzed after extraction with dilute nitric acid. Data from Brakstad et al. (2006).
[d] North Sea background concentration not available, lowest value for world sediments used.
[e] Concentration in NCS barite unknown, mean value for US barite used.
[f] Average ratio of concentration in drilling muds to concentration in world sediments used.

BTEX and alkylated phenols—Both BTEX and alkylated phenols might be discharged with the drilling waste if mud systems get contaminated with hydrocarbons from the formation rock. Both groups are highly soluble and easily biodegradable, except the highly alkylated forms of phenols (Neff 2002). Neither of these is likely to be present in elevated concentrations at toxic levels for a prolonged time to cause toxic stress, and is therefore not included in the risk assessment of drilling discharges.

Aliphatic hydrocarbons—Low molecular weight aliphatic hydrocarbons up to octane, have solubilities higher than their acute toxic concentrations, and may exert toxic stress if present in water or sediments at elevated concentrations. However, as they are both volatile and easy biodegradable they are not likely to be sufficiently persistent to cause toxic stress. Aliphatic hydrocarbons with higher molecular weights than octane, have water solubilities below their acute toxic concentrations. They are readily biodegraded. However, they may cause nontoxic stress to benthic ecosystems by physically altering the sediments or cause oxygen depletion by organic enrichment, and are therefore included in the risk calculations for the sediments.

Added chemicals

Most of the chemicals added to water-based drilling muds are water soluble and have a low affinity to particles or organic carbon, as expressed by their partitioning coefficients (log K_{ow} or log $K_{oc} < 3$), and are expected to dissolve in the water column. For chemicals added to oil-based and synthetic-based drilling muds, as well as water-based muds contaminated with formation hydrocarbons, the dissolution in the water column may be limited. These chemicals have a strong affinity to particles or forms agglomerates with particles from the drill cuttings (log K_{ow} or log $K_{oc} \geq 3$). These processes will cause chemicals to deposit on the sea floor.

PLONOR chemicals—Most of the chemicals used (>90%) in normal drilling operations are termed PLONOR chemicals or "green chemicals" according to OSPAR (OSPAR 2004). Until 2003, there were no specific requirements for ecotoxicological testing of substances on the PLONOR list. A literature review for toxicological information on PLONOR substances showed that there was little information available in the literature. Provided that ecotoxicological information is available, it is recommended that PLONOR substances discharged in larger quantities shall be evaluated for inclusion in the risk assessment.

Inert PLONOR chemicals such as barite, ilmenite, bentonite clay, and quartz are expected to contribute little to the toxic stress from drilling discharges in general. However, they may cause nontoxic stress on biota in the water column from suspended particles as well as impacts in the benthic environment. Determination of threshold effect values for nontoxic physical disturbances for use in EIF for drilling discharges, are described by Smit, Holthaus, Kaag, et al. (2006), Smit, Holthaus, Tamis, et al. (2006), and Smit, Holthaus, et al. (2008).

Non-PLONOR chemicals—In the North Sea countries testing of all chemicals used and discharged in offshore petroleum activities not listed as PLONOR chemicals, is required by OSPAR (OSPAR 2000a). The information required results from biodegradation, bioaccumulation, and acute toxicity tests. Tests for 3 trophic levels covered by marine algae, crustaceans, and fish are mandatory for all substances in a product. It is recommended to include all added chemicals that are not PLONOR chemicals, preferably on a component basis, in the risk calculation of drilling discharges.

ENVIRONMENTAL EFFECTS ASSESSMENT

The main objective of the present work was to derive environmental quality criteria to be applied in risk assessment

of toxic stressors from drilling discharges. The strategy for selecting the approaches for calculating PNEC was to follow the principles set by the TGD (EC 2003). However, occasionally deviation from the risk principles was required, and alternative approaches were evaluated to reach consensus. In the following section, the different approaches evaluated for deriving PNEC values for the water column and the sediment compartment are described for the selected substances.

The PNEC values are traditionally determined based on available toxicity data from single species laboratory tests or, in a few cases, established from model ecosystem tests. Both data from freshwater and marine organisms can be used as input according to the TGD (EC 2003). If sufficient data from long-term tests covering different taxa are available, statistical extrapolation methods (species sensitivity distribution approach) may be used to derive a PNEC value. If sufficient data are not available, the PNEC should be derived from the most sensitive endpoint by using assessment factor approach and/or equilibrium partitioning approach for the sediment compartment.

LITERATURE REVIEW

In the development of the environmental impact factor for produced water toxicity data on water column species were provided for derivation of PNEC values (Johnsen et al. 2000; Frost 2002). In order to develop similar and comparable criteria for the sediments (PNEC$_{sediment}$), a comprehensive literature review was performed. The objective of the review was to search for toxicological data in the open literature that fulfilled the recommendations in the TGD (EC 2003) for calculation of PNEC values. Based on the number and diversity of quality-assured datapoints retrieved from the literature, either the species sensitivity distribution, assessment factor, or the equilibrium partitioning approach was to be chosen for calculation.

Criteria for Selection of Representative Organisms

Only studies involving test organisms matching the following criteria were considered:

- The test organisms should be living in close contact with the sediment at least for a significant part of their life cycle. For species with life stages not in intimate contact with the sediment, studies performed on those stages were rejected.
- Studies involving highly mobile species were rejected since those species are capable of moving out of the influenced area during exposure, and are likely to experience an intermittent or highly fluctuating exposure. This excludes primarily the demersal fish species and the larger crustaceans. No geographical limitations were placed on the choice of species to be included.
- For the metals only data from marine or estuarine species were used. For the PAHs, studies with freshwater species were included in addition, but restricted to the species fulfilling the criterion regarding being a true sediment organism.

Criteria for acceptance of effect data

Studies identified as containing relevant sediment toxicity data were evaluated further based on the following criteria:

- The study should be published in a scientific journal or open well documented scientific report.

- The test organisms should be well characterized regarding scientific name, life stage, and origin.
- The chemical stressor should be identified and documented properly.
- The experimental and physical test conditions should be fully documented in either the published paper or referred papers or guidelines.
- The study should be performed as spiked sediment exposures with controlled and well-documented environmental conditions.
- The scale of the study should be documented (small-scale laboratory experiment, mesocosm, or field study).
- The endpoint should be of critical concern for the organism. Either as mortality or reduction in fitness by reduction in realized offspring or alteration of behavior affecting the energy status. No discrimination of the identified toxicity data were made between the different routes of uptake in the organism, and only direct effects on the organism were evaluated excluding secondary poisoning by food chain or maternal transfer.

Summary of available effects data

The quality assured data for toxic effects of metals are summarized in Table 2 and for natural organic substances in Table 3. The data are listed as effect endpoints expressed as L(E)C50, NOECs, LOECs, or subchronic values together with data on distribution of the datapoints among trophic levels and taxonomic groups. The only exception is endpoints from studies with metals (Table 2), recording biological effects with corresponding analytical data on the metals simultaneously extracted with acid volatile sulphide. Those are listed as discrete datapoints in the table rather than calculated L(E)C50-values. The results from the literature review can be summarized as follows:

- The data are dominated by effect data with focus on acute lethality, which constitute 82% of the total number of endpoints recorded for metals and 75% for the natural organic substances.
- The effects are represented by organisms from a few major taxonomic groups. For metals 78% of the effect data are on crustaceans. Annelids are the second most abundant group with 10%. For natural organic compounds the same numbers are 95% on crustaceans. The remaining data are on annelids (5%).
- The omnivore organisms are the dominating group among the different trophic levels. For the metals and natural organic substances 87% and 85% of the data were represented by omnivore species, respectively. Data on producers and secondary consumers are scarce.
- A few components are contributing to the majority of data. For metals 65% of the toxicity data are from effect studies with copper and cadmium, while fluoranthene and phenanthrene accounts for 90% of the data for the natural organic substances.
- The data are dominated by primary responses at the level of individual organisms. Controlled experiments addressing the effects of single chemical stressors at the population level are lacking.

DERIVATION OF ENVIRONMENTAL QUALITY CRITERIA

In the following section the different evaluated approaches for deriving PNEC values for the water column and the

Table 2. Distribution of identified and quality assured endpoints for the different metals included in the literature review with corresponding indicator of effect and distribution on different trophic levels[a]

Endpoint	Ac/Ch[b]	Effect	Element						Trophic Level				Taxonomic group				Total
			Cd	Cr	Cu	Hg	Pb	Zn	P	PC	PC/SC	SC	Alg.	Annel.	Crust.	Moll.	
Behavior																	
Emergence from sediment	Ac/Ch	EC50	1	—	—	—	—	—	—	—	1	—	—	—	1	—	1
	Ac/Ch	NOEC	1	—	1	—	—	1	—	—	3	—	—	3	—	—	3
Nr. of casts	Ac/Ch	NOEC	1	—	1	—	—	1	—	—	3	—	—	3	—	—	3
Size of casts	Ac/Ch	NOEC	1	—	1	—	—	1	—	—	3	—	—	3	—	—	3
Reproductive effects																	
Fertility as reduction in brood size	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
[SEM] AVS data	Ch	—[c]	4	—	—	—	—	—	—	—	4	—	—	—	4	—	4
Physiological effects																	
Inhibition of growth	Ac/Ch	EC50	1	—	1	—	1	—	3	—	—	—	3	—	—	—	3
[SEM] AVS data	Ch	—[c]	4	—	—	—	—	—	—	—	4	—	—	—	4	—	4
Mortality																	
[SEM] AVS data	Ac/Ch	—[c]	21	13	12	—	12	12	—	—	64	—	—	—	64	—	64
Bulk concentration data	Ac/Ch	LC50	16	2	22	1	1	4	—	16	35	—	—	3	35	14	52
	Ac/Ch	NOEC	1	—	1	—	—	1	—	—	4	—	—	3	1	—	4
Post-exposure reburial	—	EC50	4	—	1	—	—	1	—	—	6	—	—	—	6	—	6
Total nr. of responses	—	—	55	15	40	1	14	21	3	16	127	—	3	15	114	14	146

[a] Ac = acute; Ch = chronic; EC = effect concentration; NOEC = no observed effect concentration; LC = lethal concentration; $Cr_{sed.}$ = chromium, spiked sediment data; $Cr_{aq.}$ = chromium, aquatic data; P = producers; PC = primary consumers; PC/SC = secondary consumers; SC = omnivores; Alg. = algae; Annel. = annelids; Crust. = crustaceans; Moll. = molluscans.

[b] Classification of an endpoint as acute or chronic is dependent on the species and duration of the study, and the results have to be evaluated on a case by case basis.

[c] Endpoints from studies recording corresponding data on concentration of extracted metals ([SEM]) and acid volatile sulphate (AVS) are recorded as discrete endpoints in the table rather than calculated single LC/EC values.

Table 3. Distribution of identified and quality assured endpoints for the different natural organic substances included in the literature review with corresponding indicator of effect and distribution on different trophic levels[a]

Endpoint	Ac/Ch[b]	Effect	Ace	Fuel	Flu	Phe	Pyr	P	PC	PC/SC	SC	Crust.[c]	Annelids	Total
			Substance					Trophic level				Taxonomic group		
Behavior														
Emergence from sediment	Ac/Ch	EC50	—	—	—	—	1	—	—	1	—	—	1	1
Egestion	Ac/Ch	LOEC	—	—	—	1	1	—	—	2	—	—	2	2
	Ac/Ch	NOEC	—	—	—	1	1	—	—	2	—	—	2	2
Grazing	Ac/Ch	IC50	—	1	3	1	—	—	—	5	—	5	—	5
	Ac/Ch	LOEC	—	—	2	—	—	—	—	2	—	2	—	2
	Ac/Ch	NOEC	—	—	2	—	—	—	—	2	—	2	—	2
Reproductive effects														
Fertility (brood size)	Ch	EC50	—	1	3	1	—	—	—	5	—	5	—	5
	Ch	LOEC	—	—	1	3	—	—	—	4	—	4	—	4
	Ch	NOEC	—	—	2	3	—	—	—	5	—	4	1	5
Developmental time of eggs	Ch	LOEC	—	—	—	2	—	—	—	2	—	2	—	2
	Ch	NOEC	—	—	—	2	—	—	—	2	—	2	—	2
Hatching success of eggs	Ch	LOEC	—	—	—	2	—	—	—	2	—	2	—	2
	Ch	NOEC	—	—	—	2	—	—	—	2	—	2	—	2
Mortality	Ac/Ch	LC50	7	1	55	22	3	—	16	72	—	87	1	88
	Ac/Ch	LOEC	—	—	4	12	—	—	4	12	—	16	—	16
	Ac/Ch	NOEC	—	—	3	12	—	—	4	11	—	15	—	15
Total nr. of responses			7	3	75	64	6	—	24	131	—	148	7	155

a Ac = acute; Ch = chronic; EC = effect concentration; LOEC = lowest observed effect concentration; IC = inhibiting concentration; NOEC = no observed effect concentration; Ace = acenaphthene; Fuel = diesel fuel; Flu = fluoranthene; Phe = phenanthrene; Pyr = pyrene; P = producers; PC = primary consumers; PC/SC = omnivores; SC = secondary consumers; Crust. = crustaceans.

b Acute/chronic. Classification of an endpoint as acute or chronic is dependent on the species and duration of the study, and the results have to be evaluated on a case by case basis.

c Including aquatic insects.

Table 4. PNEC values for metals used in risk assessment in water column for produced water discharges by use of the Assessment Factor approach. Values in boldface are recommended used as PNEC for risk assessment of drilling discharges in the water column of drilling discharges. Numbers in µg/L

Component	PNEC derived by different approaches			
	NCS[a]	AF[b]	SSD[c]	EAC[d]
Zinc	0.3–1.4[e]	0.46[f]	**3.07**	0.5–5 (f)
Copper	0.02–0.5[e]	0.02[f]	**0.64**	0.005–0.05 (f)
Nickel	—[g]	1.22[f]	**1.53**	0.1–1 (p)
Cadmium	0.004–0.023[e]	0.028[f]	**0.18**	0.01–0.1 (f)
Lead	0.02–0.081[e]	0.182[f]	**2.49**	0.5–5 (f)
Inorganic mercury	0.001–0.003[e]	0.008[f]	**0.04**	0.005–0.05 (f)

[a] NCS: Background concentration at the Norwegian Continental Shelf.
[b] PNECs based on use of Assessment Factor approach recommended in the 1st edition of the TDG (EC 1996).
[c] Data from Källqvist (2007).
[d] EAC = ecotoxicological assessment criteria. (f) firm and (p) provisional values. Data from OSPAR (2000b).
[e] Data from OLF (1998).
[f] Data from Frost (2002).
[g] No data available.

sediment compartment are presented for natural the organic substances, metals and added chemicals.

Predicted no effect concentration for water

Natural organic compounds with log $K_{ow} < 3$ are assumed to dissolute in the water column and will exert most of their possible impacts there. The natural organic compounds included in EIF for drilling discharges all have log $K_{ow} \geq 3$, and their contribution to the dissolved concentrations in the water column are assumed to be limited. As a consequence the focus in the water column has been on derivation of water quality criteria ($PNEC_{water}$) for metals and added chemicals. To harmonize the EIF calculations for produced water and drilling discharges, calculation of PNECs shall be based on the same approach. In the EIF for produced water, the assessment factor approach is used for determining the $PNEC_{water}$ (Johnsen et al. 2000; Frost 2002), as described for the freshwater environment in the TGD (EC 1996). Recently the TGD has been revised, and a risk assessment approach for application in the marine environment was introduced (EC 2003), demanding higher assessment factors.

The PNEC values for metals in the EIF for produced water have currently been updated in accordance to the revised TGD (EC 2003). Values based on species sensitivity distribution approach were established (Källqvist 2007), and are implemented in the EIF for drilling discharges (see Table 4; values in boldface).

Until the PNEC values for the organic compounds in EIF for produced water are updated, the similar PNEC approach (assessment factors) applied for added produced water chemicals is also recommended for drilling fluid chemicals in the water column (EC 1996). However, provided the chemical is released as an intermittent release, the assessment factor can be lowered by a factor 10 because long-term exposure is not likely (EC 2003). There might be cases during drilling operations implying release and exposure of longer duration, and lowered assessment factor cannot be justified. As a consequence the assessment factor needs to be judged for the various discharge scenarios case by case.

For most non-PLONOR substances only acute toxicity data are available, and thus the use of the maximum assessment factor of 1000 is required (as described for the freshwater environment). Provided that discharge of the substance can be considered intermittent, the PNEC for the water column can be derived by use of an assessment factor of 100 applied to the lowest $L(E)C_{50}$ value from short-term tests from algae, crustaceans, and fish (EC 2003).

Predicted no effect concentration for sediment

The literature review revealed insufficient data to fulfil the requirements for data quality and diversity to utilise statistical extrapolation methods to derive PNEC values, and the approach was not evaluated any further.

Chemicals with log $K_{ow} \geq 3$ are assumed to associate with mud particles and cuttings and mainly deposit on the sea floor. These include naturally organic substances such as PAHs and aliphatic hydrocarbons as well as some added organic drilling fluid chemicals.

Assessment factor approach—The lack of toxicity data with focus on chronic endpoints for metals and natural organic substances in the reviewed literature demands for use of high assessment factors. All the relevant data were acute toxicity data from short-term studies requiring assessment factors of 1000 or 10000 (EC 2003). Calculated values for $PNEC_{sediment}$, based on the most sensitive species, are listed in Table 5 for organic substances and in Table 6 for metals. All values were either within or below the range of the reported natural background concentrations from the Norwegian Continental Shelf (Table 5 and 6). Due to the limitations in data diversity and lack of chronic studies, the assessment factor approach was not considered for calculation of $PNEC_{sediment}$ for those substances.

Equilibrium partitioning approach—In absence of toxicity data for sediment organisms the TGD is open for an alternative calculation of $PNEC_{sediment}$ by use of the equilibrium partitioning approach (EC 2003). The theoretical basis for this approach is well established and has been tested for both non-ionic organic substances and metals (USEPA 2003a, 2003b). The equilibrium partitioning approach is based on the observation that porewater concentration of a substance is correlated more closely with toxicity to organisms than the

Table 5. Calculated PNEC values for sediments for PAHs and aliphatic hydrocarbons from reviewed literature data and field based PNEC values as well as background concentrations in different sediments where data were available. PNEC values in boldface are recommended for risk assessment of PAHs and aliphatic hydrocarbons in sediment

Component	PNEC derived by different approaches						
	NCS sediments[a]	AF[b]	EqP	f-SSD[c]	ER-L[d]	TEL[e]	EAC[f]
Acenaphthene	—	0.0433	2.3[g]	—	0.016	0.00671	—
Fluoranthene	<0.048[h]	0.0023	3.0[i]	—	0.600	0.113	0.5–5 (p)
Phenanthrene	<0.046[h]	0.01	2.4[j]	—	0.240	0.0867	0.1–1 (f)
Pyrene	<0.054[h]	0.147	—	—	0.665	0.153	0.05–0.5 (p)
C_0-C_3 naphthalenes	—	—	2.05[k]	—	—	—	—
2–3 ring PAHs	—	—	0.11[k]	—	—	—	—
4+ ring PAHs	—	—	0.40[k]	—	—	—	—
L_{MW} PAH	—	—	—	—	0.552	0.312	—
H_{MW} PAH	—	—	—	—	1.700	0.655	—
Σ PAH	0.072[l]	—	—	0.158	4.022	1.684	—
Aliphatic hydrocarbons	—	—	319.5[k]	—	—	—	—

[a] NCS sediments: Background concentration of the Norwegian Continental Shelf. Units in μg/g dry weight.
[b] PNEC values for sediment derived by the assessment factor approach on data from the literature review and 1% organic carbon in the sediment. Data from Frost et al. (2006).
[c] Field-based threshold values derived by bootstrap f-SSDs (Brakstad et al. 2006).
[d] ER-L = effects range-low. The ER-L value represents values at the low end range of levels (10th percentile) at which effects were observed in compiled studies and represents values at which toxicity may begin to be observed in sensitive species. Concentrations below the ER-L are considered to be within the defined no effects range. Data from Long et al. (1995).
[e] TEL = threshold effect level. TEL is the concentration at which adverse effects to sediment-dwelling fauna would be observed infrequently. Data from MacDonald (1994).
[f] EAC = ecotoxicological assessment criteria. (f) firm and (p) provisional values. Data from OSPAR (2000b).
[g] Data from USEPA (1993a).
[h] Data from OSPAR (1998).
[i] Data from USEPA (1993c).
[j] Data from USEPA (1993b).
[k] PNEC values calculated by the equilibrium partitioning approach (USEPA 1997, 2003a, 2003b) based on 1% organic carbon in the sediment. Data from Frost et al. (2006).
[l] Mean background sediment concentrations of selected PAHs for the Norwegian Continental Shelf based on all reference and regional stations. Data from Bjørgesæter (2006).

total bulk sediment concentration. $PNEC_{sediment}$ values can thus be estimated based on the toxicity to organisms of substances in aqueous solution. Based on evaluation of different sediment quality criteria approaches, the equilibrium partitioning approach is recommended for calculation of $PNEC_{sediment}$ in the EIF for drilling discharges.

For added chemicals, PAHs and aliphatic hydrocarbons, the method for determination of sediment quality criteria ($PNEC_{sediment}$), applied to, e.g., nonionic organic compounds by USEPA (1997, 2003a, 2003b), is used for calculation of PNEC in the EIF for drilling discharges. The current $PNEC_{sediment}$ is thus calculated from the water quality criteria ($PNEC_{water}$) for the individual organic compounds multiplied by their corresponding partitioning coefficient as shown in Equation 1.

$$PNEC_{sediment} = K_{p_{sediment}} \times PNEC_{water} \qquad (1)$$

in which:

$PNEC_{sediment}$ = predicted no effect concentration in sediment [mg/kg]
$PNEC_{water}$ = predicted no effect concentration in water [mg/L]

$K_{p_{sediment}}$ = partition coefficient between sediment and porewater [L/kg]

The $K_{p_{sediment}}$ is the partitioning coefficient between sediment and porewater. Organic carbon appears to be the dominant sorption phase for nonionic organic substances in naturally occurring sediments and thus controls the bioavailability (Di Toro et al. 1991). Derivation of K_p values for nonionic organic substances can then be determined from the weight fraction of organic carbon–water (f_{oc}) multiplied by the partition coefficient organic carbon–water (K_{oc}). K_{oc} is not usually measured directly but is closely related to the octanol–water partition coefficient (K_{ow}), which has been measured for numerous compounds, and is recommended used in cases where no value for K_{oc} is available. The K_{oc} values used for calculation of $PNEC_{sediment}$ for the PAHs and aliphatic hydrocarbons are described by Frost et al. (2006).

The $PNEC_{water}$ values currently applied for PAHs and aliphatic hydrocarbons in the produced water EIF (Johnsen et al. 2000; Frost 2002) are used in the calculation of $PNEC_{sediment}$ for organic substances described in Equation 1. An overview of alternative approaches for calculation of

Table 6. Calculated PNEC values for sediments for metals from reviewed literature data and field-based threshold values as well as background concentrations of metals in different sediments where data were available. PNEC-values in boldface are recommended used for risk assessment for metals in sediment

Metal	Background concentrations		PNEC derived by different approaches							
	World[a]	NCS[b]	AF[c]	EqP[d]	f-SSD[e]	MWM[f]	ER-L[g]	TEL[h]	EAC[i]
Ba	1−2000	131 (4.6–554)	—	—	2286	848	—	—	—
Cd	0.1−0.6	0.037 (0.003–0.130)	0.0013	**0.04**	0.062	0.030	1.2	0.68	0.1–1 (p)
Cr	36−110	14.6 (2.58–39.2)	0.147	29.37	**10.08**	10.47	81	52.3	10–100 (p)
Cu	7−33	4.10 (0.3–17.2)	0.0068	**4.13**	6.46	3.23	34	18.7	5–50 (p)
Hg	—	0.021 (0.003–0.100)[j]	0.0015	2.49	**0.104**[j]	0.020[j]	0.15	—	0.05–0.5 (p)
Pb	10−33	10.7 (1.92–46.5)	0.029	**10.9**	14.65	9.93	46.7	30.2	5–50 (p)
Zn	27−88	20.7 (0.42–83.7)	0.0319	**21.16**	30.97	19.15	150	124	50–500 (p)

[a] World background concentrations. Data from Neff (2005).
[b] NCS sediments: Background concentration of the Norwegian Continental Shelf. Units in mg/kg dry weight. Mean values and range of background concentrations from the Norwegian Continental Shelf based on analysis of samples from approx. 150 reference stations extracted with nitric acid. Data from Brakstad et al. (2006).
[c] PNEC values calculated by the assessment factor approach used on reviewed sediment toxicity literature data as described in the TGD (EC 2003).
[d] PNEC values calculated by the equilibrium partitioning (EqP) approach as described in the TGD (EC 2003).
[e] Field-based threshold values derived by bootstrap f-SSDs (Brakstad et al. 2006).
[f] Field-based threshold values derived by the MWM-approach (Brakstad et al. 2006).
[g] ER-L = effects range-low. The ER-L value represents values at the low end range of levels (10th percentile) at which effects were observed in compiled studies and represents values at which toxicity may begin to be observed in sensitive species. Concentrations below the ER-L are considered to be within the defined no effects range. Data from Long et al. (1995).
[h] TEL = threshold effect level. TEL is the concentration at which adverse effects to sediment-dwelling fauna would be observed infrequently. Data from MacDonald (1994).
[i] EAC = ecotoxicological assessment criteria. (f) firm and (p) provisional values. Data from OSPAR (2000b).
[j] Based on total concentration of Hg.

PNEC$_{sediment}$ for PAHs and aliphatic hydrocarbons is presented in Table 5. The values recommended used for PNEC$_{sediment}$ for naphthalenes, 2 to 3 ring PAHs, 4+ ring PAHs and aliphatic hydrocarbons by use of the equilibrium partitioning approach, are listed in boldface.

In a similar way the PNEC values derived for added drilling fluid chemicals applied to the water column in EIF drilling discharges are used in the calculation of PNEC$_{sediment}$ (Eqn. 1). For added chemical substances with a log $K_{ow} > 5$ an additional assessment factor of 10 is used in the calculation of PNEC$_{sediment}$ in Equation 1, to account for additional uptake in biota by ingestion of sediment (EC 2003).

The recommended values for PNEC$_{sediment}$ used for risk assessment of metals in the sediment compartment are shown in Table 6 (in boldface). The values are derived from the equilibrium partitioning approach using the principles as described in the TGD (EC 2003). PNEC$_{sediment}$ values for metals are based on partitioning between barite and seawater in the sediment ($K_{P_{barite/seawater}}$), together with PNEC$_{water}$ added to the natural background concentration of metals in the sediment, as expressed in Equation 2. This method is similar to the equilibrium partitioning approach described by Crommentuijn et al. (1997, 2000).

$$PNEC_{sediment} = K_{P_{sed.\,barite/seawater}} \times PNEC_{water} + C_{b_{sediment}} \quad (2)$$

In which:

PNEC$_{sediment}$ = predicted no effect concentration in marine sediment [mg/kg]

$K_{P_{sed.barite/seawater}}$ = partition coefficient between barite particles and seawater [m^3/m^3]

PNEC$_{water}$ = predicted no effect concentration in water [mg/L]

$C_{b_{sediment}}$ = background concentration in the marine sediment [mg/kg]

The values for PNEC$_{water}$ for metals shown in Table 4 (in boldface) are used in the calculation of PNEC$_{sediment}$ in Equation 2.

For metals the partition coefficients should be based on measured values rather than estimated partitioning values as for nonionic organics. The partition coefficient related to EIF for drilling discharges in Equation 2 is expressed as the partitioning between the deposited barite particles and the porewater in the sediment compartment, and deviates from the TGD where partition coefficients expresses the partitioning between the bulk suspended particles and water.

The $K_{P_{barite/seawater}}$ values for the metals are derived from the scientific literature and laboratory experiments simulating conditions in the sediment (Neff 2008). The present approach of applying log K_p for metals between the barite particle and porewater in the sediment ($K_{P_{barite/seawater}}$), instead of using the partitioning between sediment and porewater as recommended in the TGD, provides a more reliable approach to calculation of sediment quality criteria for metals for use in the context of risk assessment of drilling discharges.

The PNEC$_{sediment}$ values for metals are also compared to other alternative approaches for derivation of PNEC$_{sediment}$ in Table 6.

VALIDATION OF THE RECOMMENDED PNEC$_{SEDIMENT}$ VALUES

Validation of the theoretically derived values for PNEC$_{sediment}$ was performed by 2 different approaches; the bootstrap f-species sensitivity distribution (f-SSD) approach (Bjørgesæter 2006) and the Moving Window Modelling approach (Grung et al. 2005) based on field sediment monitoring data from the Norwegian Continental Shelf. The data used for validation were collected from a database containing the complete datasets from the environmental monitoring of the benthos in vicinity of petroleum installations since 1990, covering selected metals, hydrocarbons, grain size, and abundance of more than 2000 different benthic species. Due to the natural process of degradation of organic substances in the sediment, the dose–response relationship between chemical input and observed effect on the fauna in the sediment will get obscured over time, implying that reliable data for validation could only be calculated for the metals (Brakstad et al. 2006).

The comparison study showed a good correlation between the PNEC$_{sediment}$ values derived by the equilibrium partitioning approach and the values from field data, as presented in Table 6. The exceptions were chromium and mercury. For these 2 elements the data calculated by the equilibrium partitioning approach was less conservative than the field-derived data. Choosing the more conservative approach, the field-derived PNEC values for these metals will be used in EIF drilling discharges until improved information is obtained from case studies and ongoing R&D projects. The higher value for PNEC$_{sediment}$ for mercury derived by the equilibrium partitioning method, is most likely caused by the extremely low solubility of HgS in barite under both oxidizing and reducing conditions making it difficult to experimentally determine an reliable partition coefficient (Neff 2008). Chromium in drilling muds and cuttings may be present in more mobile forms than the solid chromium oxide (Cr(OH)$_3$), which were used for deriving the partition coefficient (Neff 2008) used in calculating the PNEC$_{sediment}$ by the equilibrium partitioning approach.

CONCLUSION AND RECOMMENDATIONS

Metals in the water column

The species sensitivity distribution approach described by the TGD (EC 2003) is recommended for determination of PNEC$_{water}$ for metals. Values for PNEC$_{water}$ derived from use of species sensitivity distributions have been established by Källqvist (2007) for the relevant metals to be included in EIF for drilling discharges.

Natural organic substances/added drilling chemicals in the water column

Discharges to sea of BTEX and low weight aliphatic hydrocarbons are not considered to be sufficiently persistent to cause toxic effects to organisms in the water column, and are not included for risk assessment in the EIF for drilling discharges.

The assessment factor approach applied for added chemicals in EIF for produced water is recommended for drilling fluid chemicals in the water column. Provided the chemical is released as an intermittent release rather than continuously, the assessment factor applied can be lowered by a factor of 10. This however needs to be judged for the various discharge scenarios on case by case basis.

Natural organic substances/added drilling chemicals in the sediment

All chemical substances with log $K_{ow} \geq 3$ are assumed to attach to particles and will deposit at the sea floor or stay suspended in the water column adsorbed to particles. The equilibrium partitioning approach applied to nonionic organics by US Environmental Protection Agency (USEPA; USEPA 1997, 2003a, 2003b) is recommended for calculating PNEC$_{sediment}$ for organic substances, including both natural substances as PAHs and aliphatic hydrocarbons as well as added drilling chemicals.

Metals in the sediment

The equilibrium partitioning approach based on the principles described in the TGD (EC 2003) is recommended for derivation of PNEC$_{sediment}$ for metals. The current calculation for metals applied in EIF for drilling discharges is based on the measured partition coefficient of the metals between the barite particle and pore water in the sediment (Neff 2008). This approach will simulate the actual conditions in the sediment compartment after discharge from drilling activities in a realistic way.

The PNEC$_{sediment}$ for metals based on the equilibrium partitioning approach corresponds well with PNEC values derived from the monitoring data by bootstrap f-SSDs and the Moving Window Modelling approach, except for chromium and mercury. The reason for this difference is not fully understood, and until more reliable data are available it is recommended to use the field-based PNEC values derived by the bootstrap f-SSD approach until the values can be updated with new knowledge.

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