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Toxicity of Drilling Discharges

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Abbreviations

BTEX: Benzene, toluene, ethylbenzene, and xylenes

DREAM: Dose-related Risk and Effect Assessment Model

EIF: Environmental Impact Factor

ERMS: Environmental Risk Management System

EqP: Equilibrium Partitioning

F-TEL: Field derived Threshold Effect Level

FTV: Field Threshold Value

HOCNF: Harmonized Offshore Chemical Notification Format

Kp : the distribution coefficient of a chemical between the solid and aqueous phases, expressed as the concentration of a substance sorbed to solids (mg substance per kg solid) divided by the concentration dissolved in porewater (mg/l) in different compartments (soil, sediment, suspended matter).

K_{ow} : the octanol/water partition coefficient, an indicator of the relative affinity of a nonpolar organic compound for the ambient water phase and the tissue lipids of an organism.

K_{oc} : the organic carbon/water partition coefficient, an indicator of the relative affinity of a nonpolar organic compounds for the water phase and the dissolved and particulate organic phases in sediments.

MOD: Environmental Monitoring Database (Miljøovervåkingsdatabasen). A data base covering all results from the environmental monitoring survey carried out for the offshore petroleum industry on the Norwegian Continental Shelf since 1990

NCS: Norwegian Continental Shelf

OBM: Oil Based drilling Mud

OECD: Organisation for Economic Co-operation and Development

OSPAR: Oslo-Paris Convention for the protection of the Marine Environment of the North-East Atlantic

PAH: Polycyclic Aromatic Hydrocarbons

PEC: Predicted Environmental Concentration

PNEC: Predicted No Effect Concentration

PLONOR chemicals: Substances/Preparations Used and Discharged Offshore which Are Considered to Pose Little or No Risk to the Environment (OSPAR, 2004)

SBM: Synthetic Based drilling Mud

SKIM: Co-operation forum for offshore chemical producers and suppliers, industry and environment authorities in Norway

SSD: Species Sensitivity Distribution

TEL: Threshold Effect Level

TGD: Technical Guidance Document

US EPA: US Environmental Protection Agency – the US environmental agency with primary responsibility for regulating ocean discharges from offshore platforms.

WBM: Water Based drilling Mud

EXTENDED SUMMARY

The purpose of the "Toxicity" task was to contribute to the overall objective of the ERMS project (Environmental Risk Management System); to develop an EIF tool for drilling discharges (EIF_{DD}). In the present report, the output from this task is described; the focus is on toxicity as the stressor. The concept of the EIF_{DD} addresses ecological risk assessment in both the water column and sediment compartments.

The following topics have been addressed in the present task:

- Evaluation and selection of metals and organic drilling discharge chemicals for inclusion in the risk calculation in the water column and the sediment;
- Sediment toxicity literature review on selected metals and hydrocarbons;
- Summary of necessary input data (partition coefficients) for calculation of PEC for drilling waste chemicals in the water column and the sediment compartments;
- Evaluation and selection of approaches for calculation of PNEC values for the water column and the sediment compartment. Validation of the environmental risk assessment; toxicity threshold values derived from literature data versus field data.

The strategy for the EIF drilling discharge development was to follow the principles of environmental risk calculation described by the EU Technical Guidance Document (TGD) (EC, 2003). Where deviation from the risk principles described by the TGD is found appropriate or necessary, the alternative approach selected is fully described and justified.

Selection of substances for inclusion in EIF drilling discharges

Recommendations of the substances/chemicals selected for inclusion in the risk calculation of drilling discharges for both the water column and the sediments is outlined in the present report. The substances are selected based on the following criteria:

- Relative concentration in drilling mud and cuttings;
- Potential bioavailability and;
- Toxicity or potential for other non-toxic disturbances (burial, oxygen depletion etc.) to marine organisms.

Metals

Based on the criteria for selection of chemicals, the following metals should be included in the EIF calculations for 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. Chemicals selected for risk calculation for the water column include all the metals, except chromium, chosen for sediments, plus nickel. Chromium was excluded from the water column risk calculations because modern drilling discharges contain very low concentrations or reduced (insoluble) chromium. Most drilling discharges contain large amounts of barium (as barite); however, barium is not considered toxic and, therefore the contribution to toxicity risk for barium in the water column and sediments will not be included.

Natural organic compounds

Natural organic compounds in drilling waste include organic ingredients of drilling muds (particularly oil based and synthetic based drilling mud), substances that arise when production oil gets into the drilling mud or completion/reworking fluid system during penetration of a hydrocarbon-bearing reservoir, compounds from cuttings ingredients and from the geologic formations being drilled. The natural organic chemicals of potential interest include polycyclic aromatic hydrocarbons (PAH), aliphatic hydrocarbons, monocyclic aromatic hydrocarbons (BTEX), and alkylated phenols. Therefore, these components have been evaluated for inclusion in the risk calculation.

Benzene, toluene ethylbenzene, and xylenes (BTEX: log K_{ow} 2.13 – 3.20) are unlikely to be present at elevated (above background for seawater and sediments) concentrations in drilling discharges. Because of their high volatility, any BTEX released to the ocean in drilling discharges are not sufficiently persistent in the water column or sediments to cause toxic effects in resident marine organisms. Therefore, BTEX should not be included in the risk calculations for drilling discharges.

Polycyclic aromatic hydrocarbons (PAH) have a high affinity for the organic phase of sediments, as indicated by log K_{ow} ranging from 3.37 (naphthalene) to 7.0 (indeno(1,2,3-cd)pyrene). They have a toxicity and are persistent in the marine environment that, if present at concentrations significantly higher than background concentrations in marine sediments, they could contribute to the harm of drilling discharges to sediment dwelling marine organisms. Therefore, PAH should be included in the risk calculations for drilling wastes in the sediments.

Alkylated phenols, except the highly alkylated phenols, have a low toxicity and are highly soluble and biodegradable (Neff, 2002a). Their concentrations, if present in drilling discharges, are expected to be below toxic levels and should therefore not be included in the risk calculation for drilling discharges. The more highly alkylated phenols, particularly octylphenols and nonylphenols, although toxic, are not expected to be present at toxic concentrations in drilling discharges and are not expected to accumulate to high concentrations in sediments. Alkylated phenols are therefore recommended not included in the risk calculation for drilling discharges.

Aliphatic hydrocarbons above decane are so insoluble that they have a low bioavailability and toxicity to marine organisms. They may cause damage to benthic ecosystems by physical/chemical alteration of sediments (e.g., organic enrichment leading to oxygen depletion) at a high concentration, and should therefore be included in the risk calculations for the sediments.

The natural substances of this type (typically with high sediment organic carbon/water partition coefficient, K_{oc}) have a have a strong affinity for adsorption to organic matter in the sediment or in the water column. They may also have “sticky” properties when present at concentrations greater than a few percent in the discharge that cause the discharged chemicals or solids to form “agglomerated” particles or be attached to cuttings particles. Therefore, organic compounds with log K_{ow} or log K_{oc} larger than 3 are assumed to be “attached” to particles or to form “agglomerated particles”. Since naturally occurring substances that might be present in drilling discharges have log K_{ow} greater than 3, they are assumed to be attached to cuttings/mud particles and deposited on the sea floor; their impact will be on the sea floor ecosystem. Therefore, they should be evaluated for inclusion in the risk calculations for the sediments. However, they are recommended excluded from the risk calculation in the water column.

Added chemicals

Most of the chemical ingredients in water based mud (WBM) are expected to dissolve in the water column. Chemical substances with low K_{oc} or K_{ow} values (< 1000 or log K_{ow} < 3) are assumed to dissolve (completely) in the water column. For other types of mud (OBM and SBM, as well as crude oil from the geological formation), the dissolution of the chemicals in the water column may be slow and limited. As described for the natural organic compounds, the chemical substances of this type (typically with high partition coefficient, K_{oc}) may have a strong affinity for adsorption to organic matter in the sediment or in the water column. The “agglomeration” process is a well-known for OBM and SBM types of mud cuttings (Bulk OBM or SBM are not intentionally discharged) (Rye, 2006). Therefore, chemical substances with large K_{oc} or K_{ow} values ($\geq$ 1000 or log $K_{ow} \geq 3$) are assumed to deposit on the sea floor. The agglomerated particles will in general have a relatively high density and sink to the sea floor rapidly (Neff et al., 2000). The chemicals attached to them will experience the same fate.

Most of the chemicals used (> 90%) in normal drilling operations are so-called PLONOR chemicals or green chemicals, which are *Substances/Preparations Used and Discharged Offshore which Are Considered to Pose Little or No Risk to the Environment*. Until 2003, there were no specific requirements for ecotoxicological testing of substances on the PLONOR list. However, a literature search for toxicological information on PLONOR substances was conducted. The literature review showed that there is little toxicology information available most PLONOR chemicals and that the quality of the existing data is poor (inorganic salts and sugars that were considered non-toxic in sea water and were omitted from consideration).

Although discharge of the solid PLONOR chemicals, such as barite and ilmenite, bentonite clay, and quartz are expected to contribute little to the toxicity or risk from a discharge due to their low solubility and bioavailability, they may cause physical effects in the benthic environment (physical disturbances of suspended matter). Toxicity threshold values were established as part of the Task 2 with focus on non-toxic, physical disturbances from particles in drilling wastes (Smit et al., 2006a,b).

It is recommended that the most frequently used PLONOR substances discharged in large quantities should be evaluated for inclusion in the risk calculation of drilling discharges.

The added non-PLONOR chemicals are most used in small amounts. In the North Sea countries, testing of all chemicals used and discharged in offshore petroleum activities is required by OSPAR. The information required includes results of biodegradation, bioaccumulation and toxicity tests. Toxicity tests must be performed for one or more marine algae, crustaceans, and fish for all substances in a product.

Therefore, it is recommended to include all added chemicals that are not considered as green chemicals (non-PLONOR), preferably on a component basis, in the risk calculation of drilling discharges.

Sediment toxicity literature review on selected metals and hydrocarbons

The objective of the literature review was to screen the open scientific literature for ecotoxicological studies in marine sediments on the selected metals and polycyclic aromatic hydrocarbons (PAHs). Toxicological endpoints were sought that fit the recommendations laid out in the EU Technical Guidance Document (EU-TGD; EC 2003) for calculation of the Predicted No Effect Concentration (PNEC) for the sediment compartment for these two groups of substances. If available, the results from whole-sediment tests with benthic organisms should be applied for calculation of $\text{PNEC}_{\text{sediment}}$, by use of either the assessment factor approach or, if reliable toxicity data are not available, the Equilibrium Partitioning (EqP) approach of quality assured data points retrieved from the literature should be used to estimate the $\text{PNEC}_{\text{sediment}}$.

The literature review of marine sediment ecotoxicology did reveal relevant data for use in calculation of $\text{PNEC}_{\text{marine sediment}}$ by applying assessment factors for all evaluated metals. However, there is a lack of ecotoxicological endpoints from chronic long-term studies in data from the reviewed literature. Further, there is a general lack of any information on toxicity of metals to some major benthic phyla such as cnidarians (hydroids), echinoderms and mollusks (bivalves and gastropods). All the data found for sensitive species were acute data (lethality) from short-term studies, which implies that an assessment factor of 1000 or 10000 should be applied.

However, the results from testing whole sediments should be carefully evaluated since several factors can contribute to variability in the test results. Of major importance to the availability of metals in sediment are the influence of iron (as hydrous oxides), total organic carbon, and sulphide concentration in the sediment. The physical or chemical species of a metal in the sediment has a marked effect on its availability and toxicity to marine organisms, and understanding of metal speciation is necessary for understanding the impacts from metals.

Several studies over the past two decades have shown a correlation between concentration of different metals (nickel, lead, zinc, copper and cadmium) in the sediment interstitial (pore) water and toxicity to different marine and freshwater benthic organisms (amphipods) indicating that the acute toxicity is controlled by the concentration in the interstitial water rather the total bulk concentration in the sediment. Likewise, a comparison between the bulk metals concentration in field collected sediments and the acute response of amphipods and polychaetes, no causal relation between total bulk metal concentration and acute response (mortality) was found. Therefore, application of the assessment factor approach to information on toxicity of metals to benthic organisms (whole sediment tests) is not recommended for calculation of $PNEC_{marine\ sediment}$ of metals.

By normalising concentrations of metals in weak acid extracts of sediments (SEM) to concentrations of co-extracted acid volatile sulphide (AVS) in the sediment (expressed as SEM/AVS ratio) instead of bulk concentration, yields a better agreement between the observed mortality and the “bioavailable” concentration of metal (exchangeable metal ions) in the sediments. However, under oxidising conditions and in areas with low productivity, AVS has little to none effect on controlling the bioavailable fraction of the metals. Iron oxides and organic carbon, in addition to AVS, are important binding phases for reactive metal species in the sediments and therefore limit the reactive pool that is bioavailable to benthic organisms. Grain size also influences the toxicity of metals in sediments.

The SEM/AVS-approach can be used in support to other “toxicity threshold criteria” (PNECs) used in the risk evaluation of the marine benthic environment. However, because of the variability of the AVS, both in time and with shifting sediment physical and chemical characteristics of the environment, care has to be taken during planning, sampling, analysis and interpretation of the analytical data. This method has only been tested using acute lethality as the endpoint. Therefore, its applicability to predicting chronic effects is uncertain at present. As a consequence, its immediate application is limited to acute toxicity predictions. Therefore, SEM/AVS-approach will most likely add strength and support to the chosen approach for calculation of PNEC.

It is recommended that regional AVS, SEM and interstitial water concentration data from the NCS should be provided as a test-case to evaluate if the approach should be included in the regular surveys as supportive data for interpreting the chemical data from metal analysis and corresponding calculated $PNEC_{marine\ sediment}$ in field areas where metals may be of concern. As demonstrated in both laboratory experiments with spiked sediments as well as field-collected sediments, the SEM/AVS-approach has proved its potential for explaining the acute effects observed of selected metals. According to US-EPA, normalising the SEM/AVS to organic carbon in the sediment could further strengthen the approach.

The approaches for calculation of environmental risk of drilling discharges

Input to Calculation of PEC for Metals

The approaches selected to calculate the risk contribution from toxicity to the marine environment from drilling waste discharges are described in Chapter 5, addressing both risk in the water column and the sediment compartment. This environmental risk calculation will serve as the basis for calculation of the contribution from toxicity, as one of the main stressors, to the EIF for drilling discharges.

The relative risk of chemicals in drilling discharges is estimated by comparison of the Predicted Environmental Concentration (PEC) and the Predicted No Effect Concentration (PNEC). In this report, the PEC is defined as the concentration of the bioavailable fraction of a chemical in water or sediment. The PNEC is defined as the safe concentration (no observed effect concentration) of the bioavailable fraction of a chemical in water or sediment.

Most of the metals associated with drilling discharges to the ocean are present in insoluble or sparingly soluble forms, mostly associated mud barite or ilmenite used as weighting agents in water-based (WBM), oil-based (OBM) and synthetic-based (SBM) drilling muds. The metals in barite are present primarily as metal sulphide inclusions in the barite crystalline matrix.

An important input parameter to the estimation of the PEC of metals from drilling discharges in the discharge plume, in the water column or in sediment pore water, is the solid/water partition coefficient (Kp) for metals between weighing agent particles and metals dissolved in the water phase.

There is limited information on metal partitioning for weighting agents such as barite, ilmenite, hematite etc. Therefore, one of the objectives of this task was to establish reliable barite-water distribution coefficients ($Kp_{barite-water}$) for metals both for the water column and the sediments. This task has been accomplished with data from the scientific literature.

Escape of metal ions from the metal sulphide in barite and into the dissolved phase in water is controlled by dissolution/precipitation kinetics of the solid sulfides in sea water (high ionic strength) and not by simple partitioning. Although solubility products (K_{sp}) of the metal sulfides describe an ideal equilibrium state, the rates of metal sulphide dissolution are needed to estimate the concentrations of dissolved metals from solid barite in the water column and sediments. The rapidly dissolved fraction is used to estimate the PEC for the water column and the slowly dissolved fraction is used to estimate the PEC for sediment pore water. Water column and sediment PECs for metals associated with drilling mud barite were estimated from data in a recently completed report to the U.S. Minerals Management Service on dissolution rates of barium and several metals from barite in sea water and different pH buffers. These estimates were compared to data on the exchangeable fraction of metals in WBM discharged to the Mediterranean Sea. This analysis showed that drilling mud metals have a low bioavailability and toxicity to marine organisms.

The ranges of barite particle-seawater partition coefficients (Kp and log Kp) for metals in barite and the selected Kp values recommended applied for metals in the water column are summarised in Chapter 5 (Table 5.3). The potentially bioavailable fraction of a metal in the discharge plume decreases as log K_p increases. Thus, cadmium and zinc are the most bioavailable metals from barite in the discharge plume, with log K_p ranging from 2.6 to 4.3. It is recommended to apply the lower level of the $Kp_{barite-water}$ range as input to the model calculation, representing the highest potential for metal leaching to the water phase.

The Kp data for barite-seawater mixtures in pH 6 buffer and the selected Kp values recommended applied for metals in the sediments are summarised in Table 5.4.

Calculation of PNEC

Calculation of toxicity threshold values (PNECs) for metals, polycyclic aromatic hydrocarbons (PAHs), and drilling fluid chemicals applied in risk assessment in water column and sediment should be undertaken by follow the principles of environmental risk calculation described by the EU Technical Guidance Document (TGD) (EC, 2003).

The PNEC values traditionally are determined on the basis of available toxicity data from single species laboratory tests or, in a few cases, established from model ecosystem tests, taking into account adequate assessment factors (EC, 1996, 2003). Use of both freshwater and marine data is recommended in TGD for PNEC derivation. If sufficient data from long-term tests are available, statistical extrapolation methods may be used to derive a PNEC.

Water column

For organic substances with a log K_{ow} below 3 probably exert most of their effects in the water column. They desorb relatively rapidly from drilling waste particles. Therefore, only substances with log K_{ow} or log K_{oc} less than 3 are included in the risk calculation of the water column. Naturally occurring substances, such as polycyclic aromatic hydrocarbons (PAHs) and most aliphatic hydrocarbons are excluded from risk calculation in water column.

Derivation of toxicity threshold values (PNECs) for drilling fluid chemicals applied to risk assessment in the water column should be based on a similar approach to that being applied for added chemicals in EIF produced water (Johnsen et al., 2000). The PNEC values were determined by applying the assessment factors as described for the freshwater environment (EC, 1996). At that time sufficient data from long-term tests were not available for all groups of components representing the composition of produced water, and therefore statistical extrapolation could not to be used to derive PNEC values.

In 2003 the freshwater EU-TGD was revised and a risk assessment approach for application in the marine environment was included (EC, 2003). In principle, higher assessment factors (a factor 10 compared with EC 1996) should be applied for the marine environment than for the freshwater environment. However, the PNEC values for the individual groups of produced water is currently being updated in accordance to the revised marine TGD (EC, 2003) in a project conducted by the Norwegian Oil Industry Association (OLF). Provisionally, the similar approach being applied for added chemicals in EIF produced water are recommended for the water column for drilling discharges; applying the assessment factors as described for the freshwater environment (EC, 1996). Adjustments according to the criteria in the revised TGD (EC, 2003) will be undertaken when the OLF project is finalised in 2007.

Dependent on the number of ecotoxicological data and type of data available, the PNEC should be derived by using assessment factors or the SSD approach following the principles of TGD (EC, 2003). However, the assessment factor applied can be lowered provided the substance is released to the environment batch-wise (intermittent release, Chapter 2.5), rather than continuously. For intermittent releases, the TGD recommends to lower the assessment factor by a factor of 10, because long-term exposure is not expected. The use of this approach needs to be justified and judged on case-by-case basis. There might be cases during drilling operations implying release (and exposure) of longer duration and the reduced assessment factor cannot be justified, and where a higher assessment factor is required. Consequently, the determination of assessment factor applied for calculation of PNEC for individual chemical substances discharged during drilling operations needs to be judged for the various discharge scenarios/options (cementing, completion, BOP testing etc.) and on case-by-case.

For most PLONOR and non-PLONOR substances used in drilling operations only acute toxicity data are available and thereby use of the maximum assessment factor (1000) is required. Provided that discharge of the substance is considered intermittent the PNEC for EIF calculation of the water column can be derived by use of an assessment factor of 100 applied to the lowest L(E)C50 value of at least three short-term tests from three trophic levels (algae, crustacean and fish), according to TGD applied to the freshwater environment (EC, 1996).

In principle, a similar approach to that described for deriving PNEC values for natural organic substances, should also be applied for the metals. However, the experience from the PNEC values currently being used for metals in the EIF calculation of produced water, is that the PNEC for some metals (e.g., Cu) were lower or in the same range as the natural background concentration in seawater on e.g. the Norwegian continental shelf.

If sufficient data from long-term tests are available, the statistical extrapolation approach, Species Sensitivity Distribution (SSD), described by TGD for the marine compartment, is recommended applied for determination of PNEC values. The ongoing project initiated by OLF aiming for establishment of PNEC values for metals based on the SSD approach. Until the new set of PNEC values is available for metals following the TGD guidance and its requirements, it is recommended to utilise the toxicity threshold values applied in The Netherlands, used for derivation of the "Integrated Environmental Quality Objectives" prepared by the Dutch National Institute of Public Health and the Environment (Crommentuijn et al., 1997). So-called Maximum Permissible Concentrations ($MPC_{\underline{water}}$), is the concentration above which the risk for the ecosystem is considered unacceptable (VROM, 1989), taking into account existing national background concentrations following the so-called "added risk approach".

The $MPC_{\underline{water}}$ is calculated from the Maximum Permissible Addition ($MPA_{\underline{water}}$) derived from laboratory toxicity data on organisms that are representative of the Dutch coastal environment. This $MPA_{\underline{water}}$ is used as the concentration of a metal in a specific compartment that may originate from anthropogenic sources and be considered acceptable when added to the background concentration ($Cb_{\underline{water}}$). Background concentration is regarded as the concentration that is present in rural sites due to natural causes only. The $MCP_{\underline{water}}$ is defined as the sum of the $MPA_{\underline{water}}$ and $Cb_{\underline{water}}$.

As a temporary approach, Norwegian adapted $MPC_{\underline{water}}$ values based on dissolved background concentrations of metals from Norwegian marine surface waters should be applied. However, the data on background concentrations of metals in the north-eastern part of the North Sea and the Norwegian Sea are limited and need to be reviewed with regard to quality. When they are provided, region specific background concentration should be addressed. Therefore, the $MPA_{\underline{water}}$ values of the metals (Table 5.9) derived by Crommentuijn et al., (1997, 2000) should be applied as $PNEC_{\underline{\ water}}$ values for the selected metals of the water column without taking site-specific background concentrations into account.

The present approach is not ideal and reliable since $MPA_{\underline{water}}$ values were derived from data on species that were representative for the Dutch environment only, excluding data on other species from other areas. The statistical extrapolation approach (SSD), in accordance to TGD guideline for the marine environment, is being examined in the ongoing OLF project and will be the selected approach provided that sufficient chronic aquatic toxicity data are available for metals.

Sediment

In general, the same strategy applied for calculation of PNEC based on aquatic toxicity data also should be applied to sediment data, in accordance to the TGD (EC, 2003). If results from whole-sediment tests with benthic organisms are available, the PNEC sediment should be derived using assessment factors. Only long-term tests studying sub-lethal endpoints are considered applicable to marine risk assessment because of the long-term exposure of benthic organisms to sediment-bound substances that occur under field conditions.

Chemical substances that are highly hydrophobic or insoluble with log K_{ow} or log K_{oc} greater than 3 ($\geq$ 3; hydrophobic) are assumed to accumulate in the sediment on the sea floor (associated to settled cutting/mud particles) and are therefore recommended included in the risk assessment of the sediment compartment.

The literature review of marine sediment ecotoxicity did reveal relevant data for use in calculation of $PNEC_{marine\ sediment}$ by applying assessment factors for the evaluated individual PAHs and the diesel fuel, but data were available only for a minor number of PAHs. All the data for sensitive species were acute data (lethality) from short-term studies, which implies that an assessment factor of 1000 should be used for calculation of $PNEC_{sediment}$. The $PNEC_{sediment}$ value for individual PAH compounds were found well below the reported mean natural background concentrations from the Norwegian Continental Shelf (NCS). The use of assessment factors for calculation of $PNEC_{sediment}$ based on the ecotoxicological endpoints from the scientific literature were not applicable under realistic conditions and therefore not considered valid (see Table 5.10).

In absence of sufficient amount of relevant ecotoxicological data for sediment-dwelling organisms the EU-TGD (EC, 2003) opens for a provisionally calculation of $PNEC_{sediment}$ by use of the equilibrium partitioning method (EqP). The EqP method is based upon the observation that interstitial/pore water concentration is correlated more closely than bulk sediment concentrations with toxicity in benthic organisms. The PNECs for the chemical substances can be estimated based on the acute and chronic toxicity to marine organisms of the dissolved estimated concentration of substances in aqueous solution.

For non-ionic organic substances, including added chemicals, PAHs and aliphatic hydrocarbons (with log K_{ow} or K_{oc}-values > 3), the EqP equation for determination of Sediment Quality Criteria (SQC) applied to e.g. non-ionic organic compounds (PAHs) by US-EPA (1997, 2003a,b) is also recommended for calculation of $PNEC_{sediment}$ in EIF drilling discharges. The current SQC or the $PNEC_{sediment}$ is determined from the water toxicity threshold ($PNEC_{water}$) for the individual organic substance multiplied by the Kp for the particular substance.

At present the PNEC approach (EC, 1996) applied to produced water constituents is recommended to represent the acceptable effects concentration of substances in the interstitial/porewater (Johnsen et al., 2000; Frost, 2002). For added chemical substances with a log K_{ow} >5, an additional assessment factor of 10 is added to the EqP approach used, to account for ingestion of sediment (EC, 2003).

The Kp is the partitioning coefficient between sediments and water. Organic carbon appears to be the dominant sorption phase for non-ionic organic substances in naturally occurring sediments and thus controls the bioavailability in sediments (Di Toro et al., 1991). Derivation of Kp values for non-ionic organic substances is suggested expressed as shown in Equation 3 described by TGD (Chapter 5.2.2), and is determined from the weight fraction of organic carbon-water ($f_{\mathbf{oc}}$) multiplied by the partition coefficient organic carbon-water ($K_{\underline{oc}}$).

$K_{\underline{oc}}$ is not usually measured directly. However, $K_{\underline{oc}}$ is closely related to the octanol-water partion coefficient ($K_{\underline{ow}}$) which has been measured for many compounds, and is recommended used if no $K_{\underline{oc}}$ value is available. $K_{\underline{oc}}$ should be derived from $K_{\underline{ow}}$ by following Equation (Di Toro et al., 1991) for non-ionic organic substances.

Recommended values for $PNEC_{\underline{\mathbf{sediment}}}$ for aromatic and aliphatic hydrocarbons by applying the equilibrium partitioning method is presented in Chapter 5, Table 5.12.

The similar recommendation as for non-ionic organic chemicals was made regarding the development of $PNEC_{sediment}$ or SQC for metals, except that Kp should be based upon measured (empirical) values (partitioning between sediment -water) and not estimated from $f_{\underline{oc}}$ and $K_{\underline{oc}}$, as for non-ionic organics. However, it was recommended that background concentrations must be taken into account in SQC for metals which occur naturally in the environment. The Dutch EqP approach applied by Crommentuijn et al. (1997, 2000) was recommended for determination of the $MPC_{\underline{sediment}}$ or $PNEC_{sediment}$ for metals presented by Equation 6 and 7 (Chapter 5.2.2).

The Kp related to drilling discharges is expressed as the partitioning between the deposited particles and the porewater in the sediment compartment and deviates from TGD in that $Kp_{susp\text{-}water}$ expresses the partitioning between the suspended particles and water (Equation 5), and is also different from the Dutch approach that is based upon the relationship of the substance between the concentration in the solid phase in the sediment and the pore water (Yland, 1996). For those areas or regions where reliable $Kp_{sediment\text{-}water}$ values are lacking it is recommended to use the $Kp_{sed.\ barite\text{-}water}$ values as basis for determination of $PNEC_{\mathbf{sediment}}$ shown in Table 5.13.

An overview of the input data and the calculated PNEC values recommended applied for metals for the sediment compartment is presented in Table 5.13. The $PNEC_{sediment}$ ($MPC_{\_sediment}$) was calculated using Equation 7 (Chapter 5.2.2). The $PNEC_{\_sediment}$ values are based upon experimentally derived $Kp_{\mathbf{barite\text{-}seawater}}$ values for the sediment together with water quality criteria ($PNEC_{water}$ or MPA_{water}) added to the mean background concentration ($Cb_{sediment}$) of metals in the sediment (on the NCS). Preferably, it is recommended that region specific background concentration values for metals should be used.

The Kp $_{\text{sed. barite-water}}$ value derived for chromium and mercury was not found reliable (Chapter 5.1). It is therefore recommended that region specific field-derived values (F-TEL), addressed in Chapter 7, should be used as PNEC values for Cr and Hg until more reliable Kp values are available.

Table 1 is summarising which compounds that should be included and the recommended PNEC approaches in risk assessment of drilling discharges of the water column and the sediment.

Table 1: Selected compounds and PNEC approaches for risk assessment in water column and sediments from drilling discharges.

Compounds	Sediment	Approach	Water	Approach
Cd	X	EqP $^{5)}$	X	SSD $^{3)}$
Cr	X	F-TEL		
Cu	X	EqP $^{5)}$	X	SSD $^{3)}$
Hg	X	F-TEL	X	SSD $^{3)}$
Ni			X	SSD $^{3)}$
Zn	X	EqP $^{5)}$	X	SSD $^{3)}$
Aliphatic hydrocarbons	X	EqP $^{4)}$		
PAH	X	EqP $^{4)}$		
Added chemicals Log Pow < 3$^{1)}$			X	Assessment factor $^{2)}$
Added chemicals Log Pow > 3$^{1)}$	X	EqP $^{4)}$		

$^{1)}$ PLONOR chemicals should be evaluated for inclusion depending on amount, time and place

$^{2)}$ According to TGD (EC, 1996).

$^{3)}$ SSD approach; MPA values applied in The Netherlands (Crommentuijn et al., 1997).

$^{4)}$ EqP approach; based on effects concentration in water (PNEC$_{\text{water}}$) is based on the assessment factor approach (EC, 1996).

$^{5)}$ EqP approach; based on MPA values applied in The Netherlands (Crommentuijn et al. 1997, 2000).

Comparison of calculated and field derived PNECs (F-TELs)

Generally, there was good correlation between the PNEC values derived from the equilibrium partitioning (EqP) method and the F-TELs derived from field data on the NCS (Table 7.1 and Appendix 8.4.2 – MEMO Comparing results from the approaches), with the exception for chromium and mercury where the EqP approach is less conservative. Sticking to the conservative approach, the F-PNEC's for these two metals will be used until we have gained more information from case studies and ongoing projects.

The study shows that the TELs from the US and Canadian Sediment Quality Guidelines (SQG) are generally higher for all the selected components. This might be due to the fact that the US and Canadian SQGs were derived from coastal and laboratory species, so both the fauna and the environmental conditions are different. Interactions between the investigated component, adsorption (and less bioavailability) and other components present in the field can also lead to lower TELs compared to laboratory data were only one component is present. The various TELs based upon US and Canadian SQGs are further addressed in Chapter 7.4.

1. INTRODUCTION

1.1. Background

The main goal of the ERMS project was to develop an integrated risk assessment model to enable the oil industry to characterize and quantify the environmental risks from discharging drilling wastes to the marine environment. The work is built on the Environmental Impact Factor (EIF), the environmental risk based management tool developed by the oil industry and being used for produced water discharges from offshore platforms, in response to regulatory goals established by the Norwegian government in the White Paper No. 58 “Zero Discharge Report” issued in 1997 (Norwegian Ministry of the Environment, 1997: SFT, 1999; Johnsen et al., 2000).

The EIF is predicted by the Dose related Risk and Effect Assessment Model (DREAM) based on information about local oceanographic conditions and volumes and composition of the produced water discharges. The EIF for produced water is a measure of the volume of seawater that contains high enough concentrations of produced water substances/chemicals to exceed a pre-determined risk criterion. The EIF provides a regional-scale, quantitative estimate of the potential ecological risks to marine organisms from produced water discharges (Johnsen et al., 2000). The EIF provides a powerful management tool to establish cost-effective mitigation measures for reducing harm to the marine environment from discharges to the Norwegian Sector of the North Sea from offshore oil and gas operations (Frost, 2002; Grini et al., 2002).

The EIF produced water addresses environmental risk in the water column, based on toxicity as the only stressor. The EIF for drilling discharges also takes into account risk in the sediment compartment by estimation of the area of sea floor that contains high enough concentrations of drilling chemicals to exceed pre-determined toxicity threshold values (Smit et al., 2006b),. The present report addresses the toxicity contribution from drilling discharges in both the water column and on the seabed. The EIF for drilling discharges also covers other parameters than toxicity: burial; oxygen depletion; and change in grain size in the sediment (Smit et al., 2006a), and disturbances due to the presence of suspended particulate matter in the water column (Smit et al., 2006c). These parameters will be the subject of other reports in the ERMS project.

Most of the mass of drilling discharges is composed of solids that settle rapidly from the water column and settle on bottom sediments down-current from the discharge. DREAM predicts the mass per unit area and aeral extent of deposition of solids from drilling discharges on the sea floor, and the concentrations of the drilling chemicals of concern, metals and petroleum hydrocarbons, in sediments. The model then uses these data to predict the area of sea floor where toxicity threshold concentrations of the drilling chemicals in sediments exceed predetermined toxicity thresholds. DREAM also predicts the volume of seawater near the discharge where concentrations of dissolved chemicals from drilling discharges exceed an aquatic toxicity threshold.

The toxicity component of EIF for drilling discharges has been developed in accordance with the principles of risk and hazard assessment described by the European Union (EU) in the Technical Guidance Document (TGD) (EC, 1996, 2003). Environmental risks for chemicals in different marine environmental compartments are estimated by calculation of PEC/PNEC ratios. The PEC (Predicted Environmental Concentration) is an estimate of the concentration of a chemical to which the biota will be exposed during and after the discharge of the chemical. The PNEC (Predicted No Effect Concentration) is the concentration of the chemical in the environment below which it is unlikely that adverse effects on the biota inhabiting a particular environmental compartment will occur. The ratio of the PEC to the PNEC indicates the likelihood of the occurrence of adverse effects from drilling discharge chemicals in the water column and sediments.

The present report summarizes the results from the Toxicity task within the ERMS project (Environmental Risk Management System). The contribution from this task to the ERMS project is related to toxicity issues of the development of EIF for drilling discharges.

1.2. Objectives and Scope of Report

The purpose of the "Toxicity" task was to contribute to achieve the overall objective of the ERMS project (Environmental Risk Management System); to the development of an EIF tool for drilling discharges (EIF_{DD}). In the present report the output from this task is outlined and the focus is on toxicity as the stressor. The concept of the EIF_{DD} addresses both risk assessment in water column and sediment compartment.

The following topics have been addressed in this task:

- Selection of metals and organic drilling discharge chemicals for inclusion in the risk calculation in the water column and the sediment
- Sediment toxicity literature review on selected metals and hydrocarbons
- Provide data input for calculation of PEC of the water column and the sediment compartment (partition coefficients)
- Selection of approach for calculation of PNEC of the water column and the sediment compartment
- Validation of the environmental risk assessment; toxicity threshold values derived from literature data versus field data

The strategy of the EIF drilling discharge development has been to follow the principles of environmental risk calculation as described by the EU Technical Guidance Document (TGD) (EC, 1996, 2003). The TGD also was the approach in risk calculation for the EIF produced water. The harmonization of these two methods is crucial if comparison of impacts from discharges from produced water and discharges from drilling operations is requested. In cases where deviation from the risk principles described in the TGD was found appropriate or necessary, the alternative approach selected has been fully described and justified. Chapter two contains a summary of the TGD on risk assessment for the marine environment.

The substances/chemicals selected for inclusion in the risk assessment for drilling discharges are described in Chapter 3. Criteria for selection of chemicals for inclusion in the risk assessment for drilling discharges include, adequacy of aquatic toxicity data, mass of the chemical discharged to the ocean, and evidence from field monitoring studies of environmental impacts of the chemicals.

Calculation of toxicity threshold values (PNECs) for metals, polycyclic aromatic hydrocarbons (PAHs), and drilling fluid chemicals applied to risk assessment in the water column were based on similar approach being applied for EIF produced water. However, a few adjustments were introduced to the method for drilling discharges and these are described in Chapter 5. A comprehensive effort was allocated to derivation of PNEC values as the basis for risk calculation of the sediment compartment. Although, the number of toxicity data for most existing substances and infaunal and epibenthic organisms was known to be limited, a thorough literature review of toxicity to sediment biota (Chapter four) was carried out in order to derive PNEC values based on sediment toxicity data. In accordance to the TGD, the results from whole-sediment tests with benthic organisms, if available, should preferably be applied for calculation of $PNEC_{sediment}$, by use of Species Sensitivity Distribution (SSD) plots or assessment factors. The final approach for derivation of PEC and PNEC for both water column and the sediment is described and discussed in Chapter 5.

1.3. Drilling Discharges

The largest-volume solid wastes generated during drilling of oil and gas wells offshore are drilling muds (also called drilling fluids) and drill cuttings. Drilling muds are specially-formulated mixtures of natural clays, organic polymers, weighting agents, and other ingredients suspended in water, a petroleum material, or a synthetic liquid organic mixture. There are three types of drilling fluids: water based (WBM), synthetic based (SBM) and oil based (OBM). Cuttings containing small amounts of WBM, SBM, or occasionally OBM may be permitted for discharge to sea, depending on environmental regulations for different coastal and offshore areas of the world. Bulk discharges of WBM are permitted in some areas. Drill cuttings are particles of crushed sedimentary rock produced by the action of the drill bit. Drilling muds are usually reprocessed and recycled as much as possible during drilling. Eventually, they are altered by exposure to high temperatures and pressures in the well or by dilution with water and clay-sized cuttings particles to the point where they can not be recycled. Then, they may be discharged to the environment (if permitted by local regulations), reinjected into a well, sent to shore for reprocessing or disposal in a land fill, incinerated (OBM), or applied to agricultural land as a soil amendment (WBM only).

1.3.1. Composition and discharges of drilling fluids

Most drilling of offshore oil and gas wells in the North Sea (including the Norwegian Sector), the Gulf of Mexico, and other offshore production areas is achieved with WBM (Neff et al., 2000; Melton et al., 2004; OGP, 2003; Neff, 2005). This is due to strict regulations on discharges of OBM and SBM. Discharge of diesel based drilling fluids was prohibited within the OSPAR area in 1984, while discharges of OBM as contamination on cuttings have been prohibited in Norway since 1993 (and 1996 within the OSPAR area). The use of SBM in the North Sea has been minor after 2001, due to the OSPAR Decision 2000/3 *on the Use of Organic-Phase Drilling Fluids (OPF) and the Discharge of OPF-Contaminated Cuttings,* in which the requirements for discharges of SBM as contamination on cuttings were tightened. Paragraph 3.1.6 states “the discharge into the sea of cuttings contaminated with synthetic fluids shall only be authorised in exceptional circumstance” (OSPAR Decision 2000/3).

An example of chemicals used and discharged from drilling operations is given in Table 1.1. Drilling muds contain of a vide range of chemicals with different functions in well drilling and maintenance; weighting agents and inorganic salts are the drilling mud ingredients used and discharges in largest amounts. The drilling discharges constitute 82% of the total discharges of chemicals form the offshore petroleum activity on the Norwegian Continental Shelf (NCS) in 2004. Most of the drilling chemicals are so called green or PLONOR (OSPAR List of Substances/Preparations Used and Discharged Offshore which Are Considered to Pose Little or No Risk to the Environment). These substances are typically salts, cellulose and weak acids that are expected to pose little or no risk of harm to the environment. Table 1.1 summarises the functional groups of chemicals with use greater than 1000 tonnes and discharge greater than 100 tonnes on the NCS in 2004.

Table 1.1 Functional groups with use > 1000 tonnes and discharge > 100 tonnes on the Norwegian Continental Shelf in 2004.

Function	Use (tonnes)	Discharge (tonnes)
Lost circulation chemicals	12141	1193
Scale inhibitor	2778	893
Completion chemicals/fluids	19644	3273
Clay stabiliser	6080	4089
Cementing chemicals	26175	1845
pH regulating chemicals	2617	340
Weighting agents and inorganic chemicals	178226	53976
Viscosity reducing chemicals (incl. lignosulfonates, lignite)	6554	3714

While coarse cuttings particles and flocculated clays from the drilling operation usually settle near the discharge point, the finer-grained particles in the drilling discharge, such as unflocculated clay and fine barite particles often are transported in the water column over larger distances before settlement.

Depending local environmental regulations, toxicity testing of whole drilling muds or testing on substance level for all added chemicals may be required. There also may be a requirement for toxicity testing of the used drilling fluid before discharge to sea. The various requirements for toxicity testing and environmental regulations in different regions of the world are presented in Chapter 3 and 6.

1.4. Validation

A separate task in the ERMS project was initiated to validate toxicity data and hence the PNEC values derived from the scientific literature. The goal of this task was to develop environmental threshold effect levels (TEL) from field-derived effect data. The project aimed to:

1. Derive Threshold Effect Level (TEL) values from field derived effect data to be applied for validation of the toxicity threshold values (PNECs) based on data from laboratory studies available in the literature, and
2. Suggest Threshold Effect Level values (TELs) to be applied for final risk calculation modelling if data from the scientific literature was not found appropriate.

For this validation a database called MOD containing results from all the environmental surveys carried out on the NCS since 1990 were used. Alternatively, field-derived threshold values (sediment quality criteria) derived in the US and Canada, or other parts of the world where such information is available may be applied as described in Chapter 7.

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2. THE TECHNICAL GUIDANCE DOCUMENT (TGD) APPROACH TO ENVIRONMENTAL RISK ASSESSMENT

2.1. Introduction

A summary of the marine risk assessment principles as described in the EU Technical Guidance Document (TGD) (EC, 1996, 2003) is presented in this Chapter. First, the exposure in the marine environment and calculation of the Predicted Environmental Concentration (PEC) of organic non-ionic substances and metals in both the water column and the sediment compartment is addressed. Then various approaches are described for prediction of toxicity "threshold values" or Predicted No Effect Concentration (PNEC) of these substances for the two marine compartments.

The PEC (Predicted Environmental Concentration) is an estimate of the expected concentration of a chemical to which the biota will be exposed during and after the discharge of the chemical. The PNEC (Predicted No Effect Concentration) is the concentration below which it is not likely that adverse effects will occur in the biota of a particular environmental compartment. The ratio of the PEC and the PNEC indicates the likelihood of the occurrence of adverse effects (the risk). Implementation of the PEC/PNEC approach helps identify acceptable or unacceptable risks. This identification provides the basis for environmental management or regulatory decisions.

A number of regulations/directives (93/67, 98/8, 1488/94) require that an environmental risk assessment be carried out on notified new substances, on priority existing substances, active substances, and substances of concern in a biocidal product. The risk assessment for each substance should be carried out for both inland environmental compartments (aquatic, terrestrial and air) and for the marine environment.

The guidance document (TGD) includes advice on the following issues:

- How to calculate PEC and PNEC for a substance, including an assessment of food chain accumulation and secondary poisoning;
- How to make qualitative estimates of PEC and PNEC for a substance for those cases where a quantitative assessment of the exposure and/or effects is not possible;
- How to conduct a PBT (persistence, bioaccumulation and toxicity) assessment;
- How to decide on the testing strategy (if further tests are needed to revise the PEC and/or PNEC).

The test and assessment strategies in the TGD are based on current scientific knowledge and experience. The guidance has been developed mainly from the experience gained on individual organic substances. This implies that the risk assessment procedures described cannot always be applied without modifications to certain groups of substances, such as inorganic substances and metals. This means that the methods that may be applied to assess risk of metals, metal compounds, petroleum substances, and ionisable organic substances may need to be addressed differently with respect to some parameters.

2.2. PECs and PNECs

Predicted environmental concentrations (PECs) can be derived from available measured data and/or model calculations. The PNEC values usually are determined on the basis of results from single species laboratory tests or, in a few cases, established from model ecosystem tests, taking into account adequate assessment factors. The PNEC can be derived using an assessment factor approach or, when sufficient data are available, from statistical extrapolations. A decision whether or not a substance presents a risk to organisms in the environment is made based on the PEC/PNEC ratio. In some cases, the current quantitative risk assessment approach does not provide sufficient confidence that the environmental compartment is sufficiently protected. Therefore, the PBT assessment has been developed with the aim of identifying these cases.

PEC values are derived for local as well as regional scales; each PEC is based on a number of specific emission and environmental fate characteristics with respect to time and scale. The environmental risk assessment should include emission and exposure calculations for a substance during all stages of its life cycle from production to disposal in each environmental compartment (air, soil, water, sediment) potentially exposed. In the present Chapter, there is a focus on the risk in the marine environment, including the water and sediment compartment.

2.3. Environmental Exposure Assessment

For the estimated release of substances, a distinction usually is made between substances that are emitted through point sources at specific locations and substances that enter the environment through diffuse (non-point source) releases. Point source releases have a major impact on the environmental concentration on a local scale and also contribute to the concentration on a larger scale. The concentrations of substances released from point sources are assessed for a generic local environment, so-called “standard environment” (averaged values over 24 hours, or reasonable worst-case values). This means that the local PEC is calculated on the basis of daily release rate, regardless of whether the discharge is intermittent or continuous. It represents the concentration expected at a certain distance from the source on a day when discharge occurs. In principle, degradation and distribution processes are taken into consideration for the local PEC. The regional PEC takes into account the further distribution and fate of the substance over a wider area. It also provides a background concentration to be incorporated in the calculation of the local PEC. This is specifically for natural chemicals such as metals and some organo-metallic compounds. Relevant site-specific information can be used, if it is available, to improve the assessment.

First priority is given to measured data for determination of PEC, if it is available. These data will be carefully evaluated for their adequacy and reliability according to criteria, such as an evaluation of sampling/analytical methods employed and the geographic and time scale of the measurements. Preferably, the measured data should be compared to the model-estimated PEC and a representative PEC should be based on a measured and a calculated PEC for risk characterisation. For existing substances, the generic “reasonable worst case” exposure concentration should be based on modelling and, measured data from site-specific or monitoring information, can then be used to revise the calculated concentrations.

2.3.1. Calculation of Local PEC for the Marine Aquatic Compartment – PEC_{water}

Normally, as a first approach, only dilution and adsorption to suspended matter need to be considered in the derivation of the local PEC for the water column in the marine environment. The local PEC_{water} for the marine environment can then be calculated according to Equation 1:

Equation 1: Calculation of local PEC $_{seawater}$ for the marine environment (TGD approach)

$$PEC_{water} = \frac{C_{discharge}}{DILUTION * (1 + Kp_{susp} * SUSP_{water} * 10^{-6})}$$

in which:

PEC_{water} = *local concentration in seawater during emission episode* $[mg*l^{-1}]$
$C_{discharge}$ = *concentration of the substance in the discharge* $[mg*l^{-1}]$
$Kp_{susp\text{-}water}$ = *solid-water partition coefficient for suspended matter* $[l*kg^{-1}]$
$SUSP_{water}$ = *concentration of suspended matter in seawater* $[mg*l^{-1}]$
DILUTION = dilution factor [-]

The concentration at the regional scale ($PEC_{water,regional}$) is used as background concentration in seawater for the local scale.

The fraction of a substance present in the water column that is bound to suspended matter can be calculated by use of partition coefficients. As described in the TGD, a substance is removed from the aqueous medium by adsorption to suspended matter. Adequately measured data with respect to partitioning coefficients and degradation rates should be used, when available. If empirical data are not available, partitioning may be modeled. It should be noted that reliable partitioning data are available only for organic, non-ionic substances. More specific information may be required for ionisable substances (pH-dependence of K_{ow} and water solubility, as indicated by the acidity constant, pK_a), surface active substances (see section 2.1.8), and metals. Partitioning of metals between dissolved and adsorbed phases in seawater depends on the physical form (solid or dissolved ion or neutral species) and chemical form (chemical species) of the metals introduced to the sea and physical/chemical properties (pH, Eh, dissolved oxygen, carbonate, sulphide, etc.) of the receiving environment.

In certain circumstances, it may be possible to identify specific emission points which would allow the use of more precise information regarding the available distribution and fate processes and thus improve the assessment. Such “site-specific” assessments should only be used when it is known that all the emissions emanating from the particular point in the life cycle, arise from a limited number of specific and identifiable points. In “site-specific” assessments, due account can be taken of the true dilution of the given discharge as well as the impact of degradation, volatilisation, etc. in the derivation of the PEC. This can be done by using valid dispersion and dilution models, taking site specific conditions into account.

2.3.2. Calculation of Local PEC for the Marine Sediment Compartment - PEC_{water}

The concentration in the freshly deposited sediment is taken as the $PEC_{sediment}$ for the sediment; therefore, the properties of the suspended matter are used. The concentration in bulk sediments can be derived from the corresponding concentration in the water column by predictions from Equation 2, assuming thermo-dynamic partitioning equilibrium (Di Toro et al., 1991):

Equation 2 Calculation of local $PEC_{sediment}$ for the marine environment (TGD approach)

$$PEC_{sediment} = [Kp_{susp\text{-}water} / RHO_{susp}] * PEC_{water} * 1000$$

in which:

*PEC_{water} = local concentration in seawater during emission episode [mg*l-1]*
*$Kp_{susp\text{-}water}$ = suspended matter-water partitioning coefficient [m3*m-3]*
*RHO_{susp} = bulk density of suspended matter [kg*m-3]*
*$PEC_{sediment}$ = predicted environmental concentration in sediment [mg*kg-1]*

Highly adsorptive or insoluble, solid substances may not be considered subsequently with the approach described above, as they are not in equilibrium distribution between water and suspended matter because of their strong association with suspended matter; however they may be desorbed or dissolved after ingestion by benthic organisms.

2.3.3. Partition Coefficients – Marine Exposure Assessment

The distribution of a substance in the environment can be predicted from partition coefficients (Kp), which describe the relative concentration between environmental compartments (water, suspended or sediment particles) at equilibrium. The ionic strength, composition, and pH of seawater, compared with freshwater, have potential effects on the partitioning of a chemical among environmental compartments. This is particularly true for ionizable chemicals, such as metals and phenols. To a large extent, these effects are associated with differences in water solubility and/or speciation of the chemical, compared with freshwater.

Organic Non-Ionic Substances

Adsorption to solid surfaces is the main partitioning process, in addition to volatilization, that controls the distribution of nonpolar organic chemicals in surface waters and sediments. Sorption of nonpolar organic chemicals to suspended matter or sediment particles are controlled by the organic phase of the particles. Therefore, normalization of adsorption to the concentration of organic carbon in the particles improves the accuracy of the estimated partitioning. The magnitude of adsorption of a substance to sediment and suspended matter can be obtained from:

- Direct measurements;
- Simulation testing (modeling);
- Sediment organic carbon/water partition coefficient (K_{oc}) measured by an HPLC-method or adsorption studies, or estimated from the octanol/water partition coefficient (K_{ow}) or aqueous solubility of the chemical.

If no published K_{oc} is available, it may be estimated from the octanol/water partion coefficient (K_{ow}).

Since measured data on fate processes in each environmental compartment (water, sediment, suspended matter) usually are not available, the solid-water partition coefficient (Kp) for the two solid compartments (sediment/suspended matter) can be calculated from the K_{oc} value, and the fraction of organic carbon in the compartment (standard environment) by predictions outlined in Equation 3:

Equation 3 Calculation of Kp of non-ionic organic substances (TGD approach)

$$Kp = F_{oc} * K_{oc}$$

in which:

*K_{oc} = partition coefficient organic carbon-water [l*kg-1]*

*F_{oc} = weight fraction of organic carbon in compartment [kg*kg-1]*

It is assumed that all adsorption can be related to the organic carbon content of the solid phase (sediment/suspended matter). This is only valid for organic non-ionic substances. If no K_{oc} is available for organic non-ionic substances, K_{oc} can be estimated from K_{ow} using the following Equation 4 of DiToro et al. (1991):

Equation 4 Calculation of Koc

$$\text{Log } K_{oc} = 0{,}00028 + 0{,}983 * \log K_{ow}$$

in which:

*K_{oc} = partition coefficient organic carbon-water [l*kg-1]*

K_{ow} = octanol-water partioning coefficient

Surface Active Substances

For surface active substances (surfactants) K_{ow} is experimentally difficult to determine and this parameter may not be sufficiently descriptive of the adsorption/desorption behaviour (The predictive value of log K_{ow} for such estimations may be too low). Instead, it may be appropriated to obtain measured K_p values. Partition coefficients should be corrected to the pH of the environment.

Metals

Partitioning of metals between the aqueous phase and sediment/suspended matter should be described on the basis of measured sediment/water and suspended matter/water equilibrium partition coefficients (Kp) instead of using K_{oc}, as usually is done for organic substances. Although many metals tend to adsorb from the dissolved phase to particulate organic matter, K_{oc} does not adequately describe this partitioning because there are other sorptive phases in the particles. Kps for dissolved metal species and ionized chemicals should be based on direct measurements of partitioning behavior.

One should be aware that Kp values are both site and compound specific, and depend on the speciation of the metal both in the solid and the aqueous phase. The speciation is strongly influenced by environmental factors, such as temperature, redox conditions, pH, and composition of both the aqueous and solid phases.

It is recognised that the most bioavailable metal species are present as dissolved forms in the water column or sediment pore water in sediments. Metals associated with labile or exchangeable phases of suspended and sediment particles also may be bioavailable. Other uptake routes may also be important, especially for metals with high Kp values. At the present time there is no approach available to treat these processes quantitatively in the risk assessment. Processes influencing the availability of metals for direct uptake include precipitation, dissolution, adsorption, desorption, and complexation. Currently, most Kp values are expressed in terms of total concentrations in both the aqueous and the solid phase.

When performing a risk assessment, it is of outmost importance that both PEC and PNEC be based on similar levels of bioavailability. What is required is that both exposure and effect assessment, Kp values are expressed in terms of concentrations available for uptake by biota in both the aqueous and the solid phase expressed by Equation 5 outlined below:

Equation 5 Calculation of Kp metal (TGD approach)

$$Kp_{metal} = C_{sol}/C_{aqu}$$

in which:

Csol = Total available concentration in the solid phase [mg-1]*

Caqu = Available concentration in the aqueous phase [mg-1]*

It should be noted that Equation 5 differs from the commonly used expressions for Kp in the sense that instead of total concentrations in both the solid and the aqueous phase, available concentrations are to be used. The reason for this is that part of the metal present in the solid phase may be incorporated in the mineral fraction and is therefore not available. However, until now, the underlying concept for a standardised approach towards partition coefficients representing availability has not been developed sufficiently. The main problem is that there is no widely-accepted method for estimating C_{sol} for a wide variety of metals in different types of sediment matrices.

2.3.4. Degradation – Marine Environment

Degradation values, if available, can be used in risk assessment in order to estimate the environmental concentration and persistence (rate of loss from the environment) of organic chemicals. There are different degradation processes, such as biodegradation, hydrolysis, and photolysis. The rate of biodegradation in the various marine environments depends primarily on the presence of competent microorganisms, environmental conditions (temperature, salinity, light intensity, etc), the concentration and intrinsic properties of the chemical or chemical mixture in question, the concentration of nutrients and organic matter, and the presence of oxygen. These factors vary significantly between freshwater and marine environments, and between estuarine and offshore marine environments. The degradation potential in offshore marine environments is expected, in most cases, to be much lower than the degradation potential in estuaries.

Marine Biodegradation Simulation Tests

As a general rule, degradation rates or half-lives determined in tests simulating the conditions in the actual aquatic environment should be considered for use whenever available. A limited number of standardised simulation tests for the marine compartments are available, including both aerobic and anaerobic degradation (Appendix 8.1). Expert judgment of the validity and the quality of the data is necessary.

Most fine-grained marine sediments are anaerobic below the upper 5-10 mm. The assessment of the biodegradation in marine sediments should ideally be based on results from investigations simulating these conditions. If not available, other approaches may be used (Appendix 8.1).

Biodegradation Screening Test Data

For most organic substances, however, no test data from such simulation tests are available and only data from screening tests are available. When only results from marine or freshwater biodegradation screening tests are available, it is recommended to use the default mineralisation half-lives for the pelagic compartment for use in marine risk assessment as specified in Table 2.1.Both freshwater and marine degradation values are used for calculating the fraction of a chemical degraded in an environmental compartment in a certain time. It is, however, recommended to increase half-lives generated from freshwater/estuarine tests by a factor of three for the marine environment, since the degradation processes are assumed to be slower. The basis for the recommendation is the assumption that degradation of substances in freshwater and estuarine waters can be described by similar degradation rates, whereas the degradation rates are lower in the marine environments more distant from the coastline.

Table 2.1 Recommended mineralisation half-lives for use in marine risk assessment when only screening test data are available.

	Recommended mineralisation half-lives (days)		
Test results	**Freshwater**	**Estuaries** [3)]	**Other marine environments** [4)]
Degradable in marine screening test	NA.	15	50
Readily biodegradable [1)]	15	15	50
Readily biodegradable, but failing 10-d window	50	50	150
Inherently degradable [2)]	150	150	∞
Persistent	∞	∞	∞

1) Pass level >70% DOC removal or > 60% ThOD in 28 days. Not applicable for freshwater.

2) A half-life of 150 days may be used only for those inherently degradable substances that are quickly mineralised in the MITI II or the Zahn Wellens Test (cf. TGD Chapter 2.3.6). The half-life of 150 days is not fully scientifically justifiable (cf. TGD Chapter 2.3.6), but reflects a “guesstimate consensus” between a number of experts.

3) Also including shallow marine water closest to the coastline

4) The half-lives mentioned under this heading are normally to be used in the regional assessment.

The half-lives for the marine environment that are described in Table 2.1 are provisional recommendations, which should be considered, when sufficient data for degradation of different substances in screening tests and simulation tests have been evaluated.

2.4. Environmental Effects Assessment

As stated in the TGD, both freshwater and marine toxicity data can be used for calculating a PNEC. Recently, the TGD was extended with a special section for the marine environment. The principle of the PNEC calculation has not been changed, but justification has been made to account for the greater species distribution (higher biodiversity) of the marine environment compared to freshwater.

2.4.1. Calculation of PNEC for the Marine Water Column Compartment – $\mathrm{PNEC}_{\mathrm{water}}$

Assessment Factors

In principle, the PNEC is determined from the available toxicity data, by applying an assessment factor. PNEC values should be derived from the most sensitive endpoint regardless of the medium. The PNEC is calculated by dividing the lowest LC/EC50 or NOEC value by an appropriate assessment factor in accordance with the TGD as described by the EC (2003). The assessment factor is applied to extrapolate from laboratory single-species toxicity test data to multi-species ecosystem effects. The assessment factor addresses a number of uncertainties:

- Interspecies variation (biological variance);
- Short-term to long-term toxicity extrapolation;
- Laboratory data to field impact extrapolation.

Preferably, toxicity data on at least the three selected taxonomic or trophic levels (e.g., algae, crustaceans, and fish) are required to determine a PNEC for a substance. It is assumed that the marine environment has broader species sensitivity than the freshwater environment because of the greater diversity of taxa in the marine environment. Therefore, higher assessment factors are applied for the marine environment, to reflect the greater uncertainty of extrapolation, as described by the EC in the revised TGD (EC, 2003). However, where data are available for additional marine taxonomic groups, for example rotifers, echinoderms, or mollusks, the uncertainties in the extrapolation are reduced and the magnitude of the assessment factor applied to a dataset can be lowered.

Assessment factors decrease in magnitude from higher values for short-term, acute studies from which L(E)C50 values have been derived to lower values for long-term chronic studies from which NOECs have been derived. For long-term studies, the magnitude of the assessment factors also decreases as information on a wider range of species becomes available. The assessment factors described in Table 2.2 are those that would normally be applied to the datasets available. However, expert judgment may be applied to the interpretation of a dataset, which may result in a lower assessment factor. A full justification must then be provided.

As described by the EC in the revised TGD (EC, 2003), an additional assessment factor of 10 should be applied to account for the greater species sensitivity distribution of the marine environment. It is recognised by the TGD that the assumption of a greater species sensitivity distribution covering the additional marine taxa is based on limited data and is precautionary. The generation of additional toxicity data on marine species may allow this assumption to be further refined such that lower or higher assessment factors may be considered following a systematic review of accumulating evidence.

Table 2.2 Assessment factors proposed for deriving $\text{PNEC}_{\text{seawater}}$ for the marine water column for different data sets (EC, 2003).

Data set	**Assessment factor**
Lowest short-term L(E)C50 from freshwater or saltwater representatives of three taxonomic groups (algae, crustaceans and fish) of three trophic levels	10000
Lowest short-term L(E)C50 from freshwater or saltwater representatives of three taxonomic groups (algae, crustaceans and fish) of three trophic levels, + two additional marine taxonomic groups (e.g. echinoderms, mollusks)	1000
One long-term NOEC (from freshwater or saltwater crustacean reproduction or fish growth studies)	1000
Two long-term NOECs from freshwater or saltwater species representing two trophic levels (algae and/or crustaceans and/or fish)	500
Lowest long-term NOECs from three freshwater or saltwater species (normally algae and/or crustaceans and/or fish) representing three trophic levels	100
Two long-term NOECs from freshwater or saltwater species representing two trophic levels (algae and/or crustaceans and/or fish) + one long-term NOEC from an additional marine taxonomic group (e.g. echinoderms, mollusks)	50
Lowest long-term NOECs from three freshwater or saltwater species (normally algae and/or crustaceans and/or fish) representing three trophic levels + two long-term NOECs from additional marine taxonomic groups (e.g. echinoderms, mollusks)	10

Notes to Table 2.2: Evidence for varying the assessment factor should in general include a consideration of the availability of data from a wider selection of species covering additional feeding strategies/ life forms/ taxonomic groups other than those represented by the algal, crustacean and fish species (such as echinoderms or mollusks). This is especially the case, where data are available for additional taxonomic groups representative of marine species. More specific recommendations as with regard to issues to consider in relation to the data available and the size and variation of the assessment factor are indicated (listed in the TGD). When substantiated evidence exists that the substances may be disrupting the endocrine system of mammals, birds, aquatic or other wildlife species, it should be considered whether the assessment factor would also be sufficient to protect against effects caused by such a mode of action, or whether an increase of the factor would be appropriate. (See more notes to Table 25 in Chapter 4.3.1.3 of the TGD, EC 2003).

Species Sensitivity Distribution (SSD)

If a large data set from long-term tests for different taxonomic groups is available, statistical extrapolation methods may be used to derive a PNEC. In general the method works as follows: long-term toxicity data (NOECs) are log transformed and fitted according to a log-normal distribution. The PNEC is defined as a prescribed percentile of that distribution. In general, it is assumed that sufficient test data for use of statistical extrapolation methods will only be available for relatively few substances, primarily in the form of fresh water data. By using a species sensitivity distribution (SSD) instead of a single PNEC, the PEC/PNEC ratio can be expressed as probabilistic risk.

The method should be applied for all reliable NOECs from chronic/long-term studies, preferably on full life-cycle or multi-generation studies. The minimum species requirements when using the SSD method are at least 10 NOECs (preferably more than 15) for different species covering at least 8 taxonomic groups. Deviations from these recommendations can be made, on a case-by-case basis, through consideration of sensitive endpoints, sensitive species, mode of toxic action, and/or knowledge from structure-activity considerations.

The test data applicable to the most sensitive endpoint should be taken as representative for the species. For equivalent data on the same end-point and species, the geometric mean should be used as the input value for the calculation. If the valid results are considered to be too variable, then grouping into various conditions, should be considered.

For pragmatic reasons, it has been decided that the concentration corresponding to the point in the SSD profile below which 5% of the species occur should be derived as an intermediate value of determination of a PNEC. A 50% confidence interval (c.i.) associated with this concentration should also be derived. The PNEC is then calculated according to Equation 7:

Equation 7: Calculation of PNEC $_{seawater}$ by the SSD method (TGD approach)

$$\mathrm{PNEC}_{water} = \frac{5\%\ \mathrm{SSD}\ (50\%\ \mathrm{c.i.})}{\mathrm{AF}}$$

in which:

c.i. = confidence interval

AF= Assessment factor

AF is an appropriate factor between 5 and 1, reflecting the additional uncertainties identified, such as the overall quality of the database and the endpoints included, knowledge on mode of action of the chemical, etc.

2.4.2. Calculation of PNEC for the Marine Sediment Compartment - PNEC$_{marine\ sediment}$

Substances that are highly hydrophobic or insoluble may be assessed as of low risk for pelagic fauna but can accumulate in sediments to concentrations at which they might exert significant toxic effects. The sediments may act as a permanent sink for highly hydrophobic or insoluble substances that can accumulate in sediments to high concentrations. According to the TGD ‘marine’, the general principles as applied to data on aquatic organisms, also apply to sediment data. It also is acceptable for sediment risk assessment purposes to use freshwater effects data in lieu of or together with saltwater effect data.

Screening/Strategy

The number of toxicity data for most existing substances and infaunal and epibenthic organisms is limited. Normally, no effect data for new substances and sediment dwelling organisms is available. Therefore, the equilibrium partitioning method is proposed as a screening approach to compensate for the lack of toxicity data. Results from this screening can be used as a trigger for determining whether whole-sediment tests with benthic organisms should be conducted. If the PEC/PNEC determined using this method is > 1, the need for testing with benthic organisms should be considered. In the equilibrium partitioning method, the concentration of the chemical in sediment pore water (PEC) is estimated based on its relative affinity for the water and solid organic matter phases of the sediment (expressed as the sediment organic carbon/water partition coefficient: K_{oc}). This PEC is compared to the PNEC for the dissolved chemical.

It is not necessary to apply the equilibrium partitioning method to predicted $PEC_{seawater}$ (as input to $PEC_{marine\ sediment}$) obtained from application of an exposure model when such a model will have used the same K_{oc} or K_{ow} value as that used to predict $PNEC_{sediment}$ by use of the equilibrium partitioning method (EqP). The reason is that the resulting PEC/PNEC ratio of the sediment will have the same value as for the water compartment. In this case no quantitative risk characterisation for marine sediment should be performed. Under these circumstances the assessment conducted for the aquatic compartment will also cover the sediment compartment for chemicals with a log K_{ow} up to 5. For substances with a log $K_{ow} > 5$ (or with a corresponding high K_{oc}, derived from log K_{ow} by Equation 4), the PEC/PNEC ratio for the aquatic/sediment is increased by a factor of 10. The additional factor of 10 on the PEC/PNEC ratio takes into account the possible additional uptake via sediment ingestion.

Four situations can be distinguished for deriving a $PNEC_{sediment}$ and are outlined in Table 2.3:

Table 2.3 Four situations can be distinguished for deriving a PNEC marine sediment.

Situations (available toxicity data)*	**PNEC $_{marinesediment}$ approach tested**	**$PNEC_{marinesediment}$ approach applied in risk characterisation**
1. Only acute data on freshwater species (at least one)	Assessment factor (10000) + EqP method	The lowest $PNEC_{marine\ sediment}$
2. Only acute data on freshwater species + acute data marine species in the same taxonomic group as judged to be the most sensitive in the freshwater tests	Assessment factor (1000) + EqP method	The lowest $PNEC_{marine\ sediment}$
3. Long-term toxicity data on freshwater species	Assessment factor (<1000)	
4. Long-term toxicity data on freshwater species + a minimum of two marine species	Lower assessment factor (10)	

* Toxicity data derived from tests with benthic organisms

Equilibrium Method

In the absence of any ecotoxicological data for sediment-dwelling organisms, the PNEC may provisionally be calculated using the equilibrium partitioning method, provided that measured input data to predict $PEC_{marine\ sediment}$ (measured $PEC_{seawater}$) are available. This approach is considered as a screening level assessment of the risk to sediment dwelling organisms. If a PEC/PNEC ratio > 1 is derived with this method, additional tests with benthic organisms using spiked sediment are required (preferably long-term studies). This method will also be applied with the assessment factor approach when only acute toxicity data are available.

This method uses the $\mathrm{PNEC}_{\mathrm{seawater}}$ for aquatic organisms and the marine suspended matter/water partition coefficient. When using the equilibrium method to calculate the $\mathrm{PNEC}_{\mathrm{marine\ sediment}}$, the $\mathrm{PEC}_{\mathrm{marine\ sediment}}$ should be determined independent of the value of the K_{oc}. If both the PEC and the PNEC for the sediment compartment can only be assessed using the same K_{oc} or K_{ow} values, no quantitative risk characterization for the sediment should be performed because this would only result in the same risk value as for the water compartment. Under these circumstances the calculated risk (PEC/PNEC ratio) for the aquatic environment can also be used for the sediment.

The assumptions that are made in this method are as follows:

- Sediment-dwelling organisms and water column organisms are equally sensitive to the chemical.
- Concentration of the substance in sediment, interstitial water, and benthic organisms are at thermodynamic equilibrium: the concentration in any of these phases can be predicted using the appropriate partition coefficients.
- Sediment/water partition coefficients can either be measured or derived on the basis of a generic partition method from separately measurable characteristics of the sediment and the properties of the chemical.

Based on the equilibrium partitioning the following Equation is applied (Equation 8):

Equation 8 Calculation of $\mathrm{PNEC}_{\mathrm{marine\ sediment}}$ (TGD approach)

$$\mathrm{PNEC}_{\mathrm{marine\ sediment}} = [K_{\mathrm{susp\text{-}water}} / \mathrm{RHO}_{\mathrm{susp}}] * \mathrm{PNEC}_{\mathrm{seawater}} * 1000$$

in which:

$\mathrm{PNEC}_{\mathrm{seawater}}$ = Predicted No Effect Concentration in seawater [$\mathrm{mg.l^{-1}}$]
$\mathrm{RHO}_{\mathrm{susp\ bulk}}$ = density of suspended matter [$\mathrm{kg.m^{-3}}$]
$K_{\mathrm{susp\text{-}water}}$ = partition coefficient suspended matter water [$\mathrm{m^3.m^{-3}}$]
$\mathrm{PNEC}_{\mathrm{marine\_sediment}}$ = Predicted No Effect Concentration in marine sediment [$\mathrm{mg.kg^{-1}}$]

The equilibrium partitioning method considers uptake via the water phase, while uptake may also occur via other exposure pathways such as ingestion of sediment or direct contact with sediment. The TGD notes that direct uptake from marine sediment is observed and may significantly contribute to the uptake of organic contaminants such as PAHs. This may be important, especially for chemicals that have a tendency to adsorb to sediment organic matter. For chemicals with a log K_{ow} up to 5, the uptake of substances through intake of sediment particles is assumed to be low compared to uptake via the water phase. However, not only the log K_{ow} determines the direct uptake from the sediment. It is obvious that feeding mode also influences uptake of substances (via water or ingestion of sediment followed by digestion, e.g. Mayer *et al.*, 1996). No quantitative conclusions have been drawn in the TGD from these studies regarding uptake of substances from sediment. An additional assessment factor of 10 is applied for substances with a log $K_{ow} > 5$ according to the TGD (EC, 2003).

Assessment Factor

If results from whole-sediment tests with benthic organisms are available, the PNEC sediment must be derived using assessment factors.

Only whole sediment tests with infaunal and epibenthic organisms are considered suitable for use in risk assessment of the marine sediments compartment. No fully internationally accepted, standardised test methods for testing the toxicity of whole sediment are currently available. Due to the generally long-term exposure of benthic organisms to sediment-bound substances, long-term tests with sublethal endpoints (like reproduction, growth, emergence, sediment avoidance, and burrowing activity) are regarded as most relevant. The TGD provides an overview of assessment factors applied to acute and chronic whole sediment toxicity tests in Table 2.4 and Table 2.5, respectively.

In contrast to the concept applied to the pelagic marine compartment, it is only necessary to have results from one acute sediment test for the assessment factor of 10000 to apply. Furthermore, if only results from short-term tests with freshwater sediment-dwelling organisms are available (at least one), an assessment factor of 10000 also is applied to the lowest value. The $PNEC_{sediment}$ should also be calculated from the $PNEC_{water}$ using the equilibrium-partitioning method. The lowest PNEC from both approaches is used for further assessment.

Table 2.4 Assessment factors for derivation of PNEC marine sediment, from short-term sediment toxicity tests (TGD approach: EC, 2003).

Available test results	**Assessment factor**	**PNECmarine sediment**
One acute freshwater or marine test	10000	Lowest of LC50 /10000 and equilibrium partitioning method
Two acute tests including a minimum of one marine test with an organism of a sensitive taxa	1000	Lowest of LC50 /1000 and equilibrium partitioning method

If, in addition to the results of tests with freshwater benthic organisms, a result from an acute toxicity test with a marine benthic organism (preferably representative of the same taxon that is most sensitive in aquatic freshwater or saltwater tests) is available, then an assessment factor of 1000 is applicable. A $PNEC_{sediment}$ is derived by application of the following assessment factors to the lowest LC_{50} value from acute tests. Once again a $PNEC_{sediment}$ should also be calculated from the $PNEC_{water}$ using the equilibrium partitioning method.

A further reduction of the assessment factor is only permitted if results from long-term tests with sediment-dwelling organisms are available. A $PNEC_{sediment}$ is derived by application of the following assessment factors to the lowest NOEC/EC10 value from long-term tests (Table 2.5):

Table 2.5 Assessment factors for derivation of $PNEC_{marine\ sediment}$ from long-term sediment toxicity tests (TGD approach: EC, 2003).

Available test results	**Assessment factor ***
One long term freshwater sediment test	1000
Two long term freshwater sediment tests with species representing different living and feeding conditions	500
One long term freshwater and one saltwater sediment test representing different living and feeding conditions	100
Three long term sediment tests with species representing different living and feeding conditions	50
Three long term tests with species representing different living and feeding conditions including a minimum of two tests with marine species	10

* The general principles as applied to data on aquatic organisms, also apply to sediment data. Additionally, where there is convincing evidence that the sensitivity of marine organisms is adequately covered by that available from freshwater species, the assessment factors used for freshwater sediment data may be applied. Such evidence may include data from long-term testing of freshwater and marine aquatic organisms, and must include data on specific marine taxa.

If the PEC/PNEC ratio derived from the results of short-term sediment tests or via the equilibrium partitioning method is a cause for concern (PEC/PNEC >1), performance of long-term testing with sediment organisms should be considered. There are no chronic marine sediment test methods that are internationally accepted. Results from tests should always be carefully evaluated.

2.5. Intermittent Releases

Many substances are released to the environment from industrial sources as a result of batch, rather than continuous, processes. In extreme cases, substances may only be emitted a few times a year. Since the PEC_{local} takes into account the amount released and the number of days of emission, the magnitude of PEC shouldn't be affected. PEC_{local} is always calculated on the basis of a daily release rate, regardless of whether the discharge is intermittent or continuous. It represents the concentration expected on a day when discharge occurs (assumed to be continuous over the 24-hour period).

Intermittent release can be defined as "intermittent when recurring infrequently i.e. less than once per month and for no more than 24 hours". Where the batch process occurs more frequently than above or for a longer duration, protection against short-term effects cannot be guaranteed because different aquatic organisms are more likely to be exposed to the substance on the second and subsequent emissions. The use of this approach needs to be justified or judged on a case-by-case basis.

The likelihood of long-term effects arising from intermittent exposure is low. The risk assessment should generally consider only short-term effects. It is therefore proposed that, to derive a $PNEC_{seawater}$ for such situations, an assessment factor of 100 should be applied to the lowest L(E)C50 value of at least three short-term tests from three trophic levels. The assessment factor is designed to take into account the biological variables of intra and inter-species toxicity, as well as the uncertainties in predicting ecosystem effects from laboratory data.

This extrapolation should be carried out with care. Some substances may be taken up rapidly by aquatic organisms. This can lead to delayed effects even after exposure has ceased. This will generally be taken into account by the lowered assessment factor, but there may be occasions when a higher or lower factor would be appropriate. For substances with a potential to bioaccumulate, the lower assessment factor may not always be sufficient to provide adequate protection. For substances with a known non-specific mode of action, interspecies variations may be low. In such cases, a lower factor may be appropriate. In no case should a factor lower than 10 be applied to a short-term L(E)C50 value.

2.6. Environmental Risk Assessment for Metals

There are a number of fundamental differences between metals and organic substances that must be taken into account when assessing risk to the environment:

- Unlike most organic substances, metals and some organometallic compounds are of natural origin.
- The bioavailability of the metals varies form site to site and is highly dependent on the speciation (physical/chemical form) of the metal; hence it is of outmost importance that both PEC and PNEC are based on a similar level of availability in both exposure and effect assessment, taking speciation into account.

2.6.1. Exposure Assessment

For the assessment of metals, it generally is necessary to take into account all metal species that are discharged to the environment. Since the actual bioavailability of the metal is determined in part by the properties of the receiving media, such as pH and salinity, the precise physico-chemical characteristics of the receiving media must be defined. Processes determining the availability of metals for direct uptake include precipitation, dissolution, adsorption, desorption, and complexation (Chapman et al., 2003).

If it is known that the metal of concern is soluble or can be transformed to a soluble form, the prediction of PEC can be based on the soluble fraction of the metal (metal ion). Then the partitioning behaviour can be based on appropriate K_p values for the soluble ion (see Section 1.2.3). Where possible, information on kinetics of transformation processes should be taken into account (both local and regional PEC). For the aquatic environment, it can be assumed as a first estimate that the substance will dissolve up to its water solubility limit, and that this fraction will be the available form.

It is important to consider the ambient background concentration of metals and the natural background concentration, which may vary from site to site, in the calculation of PEC within a certain area,. In addition to the obvious method of measuring metal concentrations at selected sites, several estimation methods are also included. For surface water and sediments, background concentrations are available from extensive national monitoring programs. For most metals, sufficient reliable monitoring data are available. Preferably, risk assessment should be based on monitoring data (PEC), taking natural and ambient background concentrations into account when interpreting the data. However, these monitoring programs often measure total instead of dissolved or readily exchangeable metal concentrations. For the aquatic environment the dissolved concentrations can be derived from total concentrations by means of the concentrations of dissolved organic matter and suspended particulate matter and partition coefficients between water and either organic or particulate matter. However, this equilibrium approach tends to substantially overestimate concentrations of bioavailable (dissolved) metals in sediment pore water or ambient water if the metal is present as an extremely insoluble mineral with a high solubility product (K_{sp}) in seawater. Barite and most of the metals associated with barite are in this form and PECs for them are difficult to estimate. As indicated before, risk assessment should be performed on the basis of bioavailable fractions; dissolved concentrations should be used if possible, since these indicate the bioavailable metal fraction in the aquatic environment.

2.6.2. Effects Assessment

Results from aquatic toxicity tests usually are expressed as total concentrations of the metals. As a first approach total concentrations have to be recalculated to dissolved concentrations using partition coefficients. Dissolved concentrations can be derived from total concentrations by means of the concentrations of dissolved organic matter and suspended particulate matter and partition coefficients between water and either organic or particulate matter. If this is not possible, the total concentrations can be set equal to the dissolved concentrations. In general ionic metal species are considered to be the dominant metal species bioaccumulated, and thus considered to be the metal species responsible for toxic effects. Ionic and some neutral forms of dissolved metals can move across biological membranes by passive or, sometimes, active processes and accumulate in the cytoplasm of cells. The intracellular metals my bind to different cellular biochemicals, causing pathology. Because ionisable forms of metals are reactive, they do not persist long in ionic forms in cells and tissues.

Fate estimates based on “partitioning” are limited to distribution of a substance in molecular form. For substances that also are distributed in the environment as particles, extrapolation based on partitioning may not be relevant. In such a case the partitioning method may underestimate exposure of sediment environments and overestimate the exposure of water. There are no estimation methods available for particle distribution so this has to be dealt with on case-by-case basis.

2.7. References

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3. SELECTION OF COMPONENTS FOR THE RISK CALCULATION OF DRILLING WASTE DISCHARGES

3.1. Chemicals in Drilling Discharges

Three categories of chemicals associated with drilling waste discharges have been selected for prediction of the possible harm (toxic and non-toxic) to the marine environment of drilling discharges:

- Metals (as ingredients of added chemicals or cuttings)
- Natural organic compounds
- Added chemicals (including drilling fluid chemicals e.g. non-PLONOR, PLONOR chemicals etc.)

The chemicals included in these three categories are summarized in Table 3.1. Many chemicals are included in each of the categories. However, most drilling muds and drill cuttings do not contain environmentally significant amounts (sufficient quantities to cause acute or chronic harm to the marine environment) of all these chemicals.

A limited number of chemicals were selected from Table 3.1 for inclusion in the risk calculation for drilling discharges, based on following criteria:

- The total amount of each chemical used and discharged to the sea from drilling discharges (particularly PLONOR chemicals);
- The potential for the chemical to accumulate in the water column (soluble chemicals) or sediments (low-solubility chemicals) in forms and concentrations that could be toxic (and/or cause other disturbances (burial, oxygen depletion etc.) to marine organisms

Table 3.1 Candidate chemicals for use in the risk calculations (EIF) for drilling discharges.

Chemical	Comment
1. Metals (as ingredients of added chemicals or cuttings)	
Arsenic, Barium, Cadmium, Chromium, Copper, Mercury, Nickel, Lead, and Zinc	Should include consideration of both dissolved and solid species (Table 3.2)
2. Natural Organic Compounds	
BTEX	Unlikely to be present at high concentration in drilling wastes on sea floor. Could be present in the water column following oily cuttings discharge
Naphthalenes	Includes naphthalene and C_1- through C_3-naphthalenes (Table 3.3).
Other 2-3-Ring PAH	Includes 12 analyte groups, including fluorenes, phenanthrenes, and dibenzothiophenes (Table 3.3)
≥ 4-Ring PAH	Includes 10 unalkylated PAH, including benzo(a)pyrene (Table 3.3)
Aliphatic Hydrocarbons	Total petroleum hydrocarbons measured by IR or GC/FID. Sometimes high in cuttings piles
C_0-C_3 Phenols	Unlikely to be present at high concentrations in drilling discharges. Could be present in solution in drilling waste plume in water column
C_4-C_5 Phenols	Unlikely to be present at high concentrations in drilling discharges
≥ C_6 Phenols	Unlikely to be present unless muds contain alkylphenol polyethoxylate detergents. Focus on C_8- & C_9-phenols
3a. Added chemicals (green chemicals)*	
Barite	Barium sulfate: the most frequently used weighting agent in drilling muds. The most abundant solid ingredient in most muds
Carboxymethyl cellulose	Often used instead of lignosulfonate as a clay deflocculent
Bentonite	Montmorillonite clay. Usually, a major solid ingredient in drilling muds
Portland cement class G	Used in setting casing. Usually not discharged intentionally
Quartz	Silica. Generally considered toxicologically inert
Xanthan gum	Natural plant material for viscosity control
3b. Added Chemicals (other chemicals than the green chemicals)**	
Added chemicals to drilling muds	Yellow substances should be evaluated; black or red substances will be evaluated if use is proved to be necessary from a safety or a technical perspective

* These PLONOR List Chemicals are listed for the OSPAR area. The six most frequently discharged PLONOR chemicals on the NCS in 2003 are listed. The PLONOR chemicals evaluated in a literature search are given in appendix 3

** Categorisation and colour code for chemicals used and discharged offshore on the NCS is given in Table 6.3, e,g. OSPAR non-PLONOR chemicals.

3.2. Metals

3.2.1. Metals in Drilling Muds and Cuttings

Several metals are present in most drilling muds (Table 3.2). Concentrations of individual metals may vary depending on the composition of the base ingredients and additives. The metals of greatest concern because of their abundance in drilling muds and cuttings 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). Some of these metals are added intentionally to drilling muds as metal salts and organo-metallic compounds, if approved by local regulations. These metals are included in the added metals category. Most metals in drilling discharges are trace impurities in drill cuttings and major mud ingredients, particularly barite, ilmenite, and clay.

Table 3.2 Concentrations of several metals in drilling muds, drilling mud barite, world sediments, and Norwegian continental shelf (NCS) reference (background) sediments. Ratio of metals concentrations in NCS barite to background sediments is included. Metals with a ratio greater than 1 are highlighted in gray. Data from Bjørgesæter (2006) and Neff (2005). Concentrations are mg/kg dry wt.

Metal	Drilling Muds	U.S. Barite	NCS Barite[a]	World Sediments	NCS Sediments[b]	NCS Barite/Background
Arsenic	1,8 – 2.3	2,2	NV	6,9 – 26	NV	≈ 0,33[c]
Barium	720 – 449 000	523 000	NV	1 – 2000	4,6 – 554	114 000[d]
Cadmium	0,16 – 54,4	0,03	0,7 – 1,7	0,1 – 0,6	0,003 – 0,13	18,9
Chromium	0,10 – 6000	11	9,8 –14,3	36 – 110	2,58 – 39,2	0,90
Copper	0,005 – 307	9,7	76,6 – 104.7	7 – 33	0,3 – 17,2	18,7
Lead	0,40 – 4225	7,8	48,7 – 116	10 – 33	1,92 – 46,5	4,8
Mercury	0,02 – 10,4	0,12	0,31 – 0,69	0,03 – 0,14	0,003 – 0,10	14,8
Nickel	3,8 – 19,9	NV	1,2 – 2,1	13 – 45	NV	≈ 0,09[c]
Vanadium	14 – 28	NV	NV	63 – 238	NV	0,44[e]
Zinc	0,06 – 12 300	8,6	42,9 – 138,9	27 – 88	0,42 – 83,7	2,1

[a] Data for 2001 – 2003; [b] Based on samples from 150 reference stations in North Sea; [c] North Sea background concentration not available, lowest value for world sediments used; [d] Concentration in NCS barite unknown, mean value for U.S. barite used; [e] Ratio of concentration in drilling muds to concentration in world sediments used. NV: no value available.

Weighting agents and clays are the main source of heavy metals in drilling discharges to the ocean on the NCS, because use of additives containing heavy metals is strictly regulated. In 2004, 20,26 kg of lead and copper in pipe dope and 3600 kg of As, Pb, Cd, Cu, Cr and Hg as impurities in weight materials were discharged to the NCS.

The metals most frequently present in drilling muds at concentrations substantially (>100-fold) greater than natural concentrations in soils and sediments are barium, chromium, lead, and zinc (Table 3.2). Mercury sometimes is present at elevated concentrations in US, Canadian, and North Sea drilling muds; it is derived from mercury contamination of drilling mud barite (Neff, 2002b). Impure grades of barite also may contain elevated (compared to natural sediments) concentrations of all the other metals listed in Table 3.2. Because of concern about possible adverse environmental impacts of metal contamination of drilling mud barite, many countries are encouraging or requiring use of cleaner grades of barite for drilling mud formulation, or are recommending use of alternative weighting agents, such as ilmenite, that contain lower concentrations of metals of highest concern. As a result, mean concentrations of mercury and several other metals in ocean discharges of drilling muds and cuttings have decreased in the last decade.

The most abundant metal in most drilling muds is barium (actually an alkaline earth element like calcium and strontium). Nearly all the barium in drilling mud is from barite ($BaSO_4$) added to the mud to increase its density. Barite in drilling muds and sediments has a low solubility in seawater, because of the high natural concentration of sulfate in the ocean. Because it is insoluble in seawater, barite has a low bioavailability and toxicity to marine organisms. Although barite is a PLONOR chemical (not expected to cause harm to the marine environment), it should be included among chemicals used in risk calculations of drilling discharges, because of the large volumes of barite used in many drilling muds and the potential physical disturbance (burial and change in grain size).

Most of the other metals detected in drilling muds are present as trace impurities in barite, clay, or the drill cuttings from the geologic formations. In addition to barium, the most abundant metals in barite are lead, zinc, and iron; some barites also contain elevated concentrations of chromium. Iron usually is present in drilling muds and cuttings at high concentrations; however, because it is present in drilling wastes primarily as highly insoluble oxides or in the matrix of clay particles at concentrations similar to or lower than background concentrations in marine sediments, iron is regarded as of no concern. Five metals, other than barium, are present in a typical North Sea drilling mud barite at concentrations higher than the North Sea sediment background concentrations reported by Bjørgesæter (2006) (Table 3.2). These metals are cadmium, copper, lead, mercury, and zinc.

Frequently in the past, chromium was the only metal other than barium that was detected at elevated concentrations in sediments near drilling discharge locations (Neff et al., 1989). When present at elevated concentrations, compared to concentrations in clean sediment, drilling mud chromium was derived primarily from chrome- or ferrochrome-lignosulfonates or chromate salts added intentionally to the mud for viscosity control. Because of concern about the toxicity of chromium, most operators now use alternative, less toxic viscosifiers for WBM formulation. Chrome lignosulfonates are no longer used in drilling muds on the NCS; they are rarely used in the U.S. Gulf of Mexico. Their use in offshore drilling muds elsewhere in the world is unknown. Clays, the other major source of drilling mud chromium, have been replaced in many modern WBMs by organic polymers, mostly carbohydrates like carboxymethyl cellulose, decreasing the need for chemical viscosity-control chemicals. Thus, the mass of chromium discharged to the ocean in drilling wastes has declined substantially over the last decade. Considering the abundance of chromium in some cuttings piles, attributable to past discharges, the high toxicity of many chromate (CrVI) salts and the presence as a trace impurity in weight materials, chromium should be included among the metals used to model the ecological risks of drilling discharges in sediments.

3.2.2. Summary: Metals to Include in the Risk calculations for Drilling Discharges

Based on the criteria for selection of chemicals; relative concentration in drilling mud and cuttings, potential bioavailability and toxicity or potential for other non-toxic disturbances (burial, oxygen depletion etc.) to marine organisms (based on evidence from field monitoring studies of environmental impacts of the chemicals), the following metals are recommended for inclusion in the EIF calculations for 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 sediments, but will be included for risk calculations in the water column. Barium is used as a tracer of drilling discharges in environmental monitoring, but is not considered toxic and, therefore the contribution to the risk for barium will not be included.

All the metals, except chromium, chosen for inclusion in the toxicity EIF for sediments, also were chosen for inclusion in the toxicity EIF for the water column. Nickel also was selected for inclusion in the toxicity EIF for the water column. As discussed above, slightly soluble chromium compounds are no longer used in WBM discharged to the NCS, Gulf of Mexico, or most other offshore oil development areas. Concentrations of chromium in barite and clays usually are below those in natural marine sediments (Table 3.2). Therefore, chromium was not included in the toxicity EIF for the water column.

Table 3.3 Selection of metals for inclusion in calculation of environmental risk of drilling discharges in the sediment compartment and water compartment. The metals selected are highlighted.

Metal	**Abundant in Mud/Cuttings?**	**Potentially Bioavailable?**	**Aquatic Toxicity Data Adequate?**	**Include in EIF $_{\text{sediment}}$?**	**Include in EIF $_{\text{water}}$?**
Arsenic	No	No	Yes	No	No
Barium	Yes	No	Non-toxic	No	No
Cadmium	**Sometimes**	**Yes**	**Yes**	**Yes**	**Yes**
Chromium	**Yes**	**Yes**	**Yes**	**Yes**	No
Copper	**Sometimes**	**Doubtful**	**Yes**	**Yes**	**Yes**
Lead	**Yes**	**Yes**	**Yes**	**Yes**	**Yes**
Mercury	**Sometimes**	**Doubtful**	**Yes**	**Yes**	**Yes**
Nickel	**No**	**Doubtful**	**Yes**	No	**Yes**
Zinc	**Yes**	**Yes**	**Yes**	**Yes**	**Yes**

3.3. *Natural Organic Compounds*

Natural organic compounds include substances that mainly arise when production oil gets into the drilling mud or completion/reworking fluid system during penetration of a hydrocarbon-bearing reservoir, compounds from cuttings ingredients and from the geologic formations being drilled. An additional source to discharge of natural organic compounds from drilling activities, are ingredients in drilling muds/drilling fluid chemicals (particularly OBM and some SBM) categorised as “added chemicals” in Table 3.1.

The natural organic chemicals of potential interest include polycyclic aromatic hydrocarbons (PAH), aliphatic hydrocarbons, monocyclic aromatic hydrocarbons (BTEX), and alkylated phenols. These components have therefore been evaluated for inclusion in the risk calculation. The PAH usually are divided into three subgroups: naphthalenes, other 2- and 3-ring PAH, and 4- and 5-ring PAH (in accordance to the subdivision in EIF produced water). BTEX are the monocyclic aromatic hydrocarbons, benzene, toluene, ethylbenzene, and xylenes. The alkylated phenols of interest are the more highly alkylated C_8- and C_9-phenols, some of which are toxic; aliphatic hydrocarbons include unbranched and branched chains and rings of carbons joined by single covalent bonds.

3.3.1. BTEX

Benzene, toluene, ethylbenzene, and xylenes (BTEX) are the most abundant monocyclic aromatic hydrocarbons in crude oil and most distillate products (Neff, 2002a). They usually are absent or present at very low concentrations in low-aromatic mineral oil and synthetic base chemicals used in OBM and SBM. However, diesel fuel, formerly widely used in OBM, may contain several percent BTEX. BTEX may get into WBM and SBM by contamination of the mud system with formation oil. However, because of their high volatility and moderate aqueous solubilities, BTEX are not persistent in the drilling mud and cuttings plume. They have a relatively low affinity for the particulate phase of drilling discharges (log K_{ow}s from 2.13 to 3.20) and little or none accumulates in cuttings piles, even when discharges of produced water (often rich in BTEX) and drilling wastes are to shallow coastal waters (Neff, 2002a).

BTEX are unlikely to be present at elevated (above background for seawater and sediments) concentrations in drilling discharges. If these aromatic hydrocarbons are detected in cuttings piles, they probably were derived from produced water discharges. Because of their high volatility, any BTEX aromatic hydrocarbons released to the ocean in drilling discharges are not sufficiently persistent in the water column or sediments to cause toxic effects in resident marine organisms. Therefore, BTEX should not be included in the risk calculations for drilling discharges.

3.3.2. PAHs

PAH from the geological formation

WBM and WBM cuttings usually contain little or no PAH, unless they become contaminated with crude oil from geologic formations encountered during drilling. Sometimes, lubricants, such as gilsonite (a natural asphaltic material), or spotting fluids containing a mineral oil, are added to WBM; they may contain small amounts of PAH. A slug of mud containing mineral oil sometimes may be added in an emergency to the drilling mud system to free stuck pipe. The oil-containing mud usually is kept separate from the general mud system and is recovered and sent to shore for disposal. However, small amounts of the oil, sometimes containing traces of PAH, may get into the WBM and be discharged with the mud and cuttings to the sea. Thus, the small amounts of PAH found in WBM and SBM cuttings come primarily from hydrocarbon-bearing formations penetrated by the drill, as indicated by the increasing concentrations of PAH in cuttings from different depths in a well drilled with WBM offshore California (Table 3.4). The hydrocarbons in cuttings from the surface segments of the well probably are from additives.

Table 3.4 Concentrations of hydrocarbons in drill cuttings from three drilling depths in a well on a platform in the Santa Maria Basin, California. A water based drilling mud was used. Concentrations are mg/kg dry wt (ppm). From Steinhauer et al. (1994).

Chemical	Surface	Mid-well	Bottom	Average
THC[1]	600	95	526	407
Total PAHs[2]	2,3	12	121	45
Naphthalenes[3]	1,2	8,9	96	35
Fluorenes[3]	ND	0,35	8,2	2,8
Phenanthrenes[3]	0,79	0,64	9,3	3,6
Dibenzothiophenes[3]	ND	0,40	8,1	2,8

[1] Total resolved + unresolved petroleum hydrocarbons. [2] Total 2- through 5-Ringed PAHs plus alkyl congeners
[3] Includes parent PAH and alkyl homologues.

PAH in Drilling Muds

The main source of PAH in drilling discharges is from drilling muds (particularly OBM and some SBM) and formation oil in the mud system. Base oils currently in use in the North Sea (non-aqueous phase liquids, including enhanced mineral oil and synthetic base chemicals) by definition contain very low concentrations of PAH, but may contain significant concentrations of aliphatic hydrocarbons and olefins. In 2004, a total of 132 062 tonnes of OBM were used on the NCS, but no mud or cuttings were discharged to the sea. An additional 2298 tonnes of SBM were used in 2003 and 2451 tonnes of SBM cuttings containing 826 tonnes of SBM were discharged. The remainder of the drilling muds and cuttings was reinjected or transported to shore for treatment or disposal (Norwegian Oil Industry

Association, 2004). Most of the "oil" discharged was synthetic base chemical, usually a synthetic olefin, containing little or no PAH. However, historic use of diesel fuel OBM and discharge of OBM cuttings has produced many North Sea cuttings piles that are highly contaminated with PAH.

PAH in Cuttings Piles

Concentrations of total hydrocarbons (THC) often are high in North Sea cuttings piles, particularly those near platforms where OBM or SBM cuttings were discharged (Table 3.5). The hydrocarbons in OBM cuttings are primarily aliphatic petroleum hydrocarbons with trace amounts of PAH and natural biogenic hydrocarbons. Olefins (hydrocarbons with one or more carbon-carbon double bonds) may be present if SBM cuttings were discharged. Most of the THC in SBM cuttings is synthetic chemicals, usually olefins and esters (Neff et al., 2005). These synthetic chemicals have a low toxicity to marine organisms (Neff et al., 2000), but may cause damage to benthic communities by burial and oxygen depletion.

PAH in a cuttings pile may be associated with a distinct nonaqueous liquid (NAPL) phase, such as oil-coated cuttings particles or oil droplets, or they may be adsorbed directly to sediment organic matter (Neff et al., 2005). North Sea cuttings piles often contain elevated concentrations of total hydrocarbons (THC) and sometimes PAH (Table 3.5). The amounts of PAH in the cuttings piles are directly related to the amounts of OBM and SBM cuttings discharged.

Table 3.5 Mean concentrations of several organic contaminants in cuttings piles near 4 multi-well platforms in the central and northern North Sea. Concentrations are mg/kg dry wt. Summarized from Cordah (2001) and Westerlund et al. (2001).

Chemical[a]	**Oil/Gas Platform**			
	Beryl A	**Maureen A**	**Ekofisk 2/4 A**	**Frigg WBM**
Mud Types	OBM/WBM	WBM/OBM/SBM	WBM/SBM	WBM
THC[a]	57,294	16,602	23,673	82
PAH	13	0.82	1.0	0.05
Benzo(a)pyrene	0.07	0.003	0.01	0.0025

[a] THC total hydrocarbons; PAH polycyclic aromatic hydrocarbons (15 analytes).

PAH usually are considered the most toxic hydrocarbons in crude and refined petroleum (Neff, 2002a). Aromatic hydrocarbons, including PAH, also are considered to be major contributors to the toxicity of SBMs and OBMs in sediments (Neff et al., 1987; Kingston, 1992).

PAH are sufficiently toxic and persistent in the marine environment that, if present at concentrations significantly higher than background concentrations in marine sediments, they could contribute to the harm of drilling discharges to sediment dwelling marine organisms. Therefore, PAH should be included in the risk calculations for drilling wastes in the sediments.

3.3.3. Phenols

Phenols are unlikely to be present at high concentrations in drilling wastes. Several phenols, particularly the more highly alkylated forms, are considered moderately to highly toxic, because of their estrogenic effects in aquatic animals. Alkylphenol polyethoxylate detergents containing octylphenol or nonylphenol were used occasionally in the past in drilling muds (Getliff and James, 1996). Because of the potent estrogenicity of octyl- and nonyl-phenols, these detergents are no longer permitted in North Sea drilling muds. However, these detergents still may have limited application in produced water treatment (Jacques et al., 2002).

CEFAS (2001) reported concentrations of 1.5 to 32.7 μg/L alkylphenol polyethoxylate in bottom water over the NW Hutton platform cuttings pile. These concentrations are higher than concentrations frequently reported for river water down-current from wastewater treatment plant discharges and, if real, are probably from rig-wash and produced water effluents, not from drilling discharges. However URS (2002) reported detecting high concentrations of alkylphenol ethoxylate detergents in some cuttings pile samples, though they did not detect any nonylphenol or octylphenol.

Phenol, xylenol, other less alkylated phenols have a low toxicity and are highly soluble and biodegradable (Neff, 2002a). Their concentrations, if present in drilling discharges, are expected to be below toxic levels and should therefore not be included in the risk calculation for drilling discharges. The more highly alkylated phenols, particularly octylphenols and nonylphenols, although toxic, are not expected to be present at toxic concentrations in modern drilling waste discharges and are not expected to accumulate to high concentrations in sediments. There is insufficient information at this time on the presence and concentrations of octyl- and nonyl-phenols in drilling discharges and cuttings piles, to justify inclusion of alkylphenols in the risk calculation for drilling wastes. If monitoring studies show that these highly alkylated phenols are present in drilling discharges and sediments/ cuttings piles or if such components are added in the drilling operations, they should be included in the risk calculation.

3.3.4. Aliphatic hydrocarbons

Low molecular weight aliphatic hydrocarbons, up to about octane, have a solubility that is greater than the aquatic toxicity concentrations and, therefore, may be toxic if present in water or sediments at high concentrations. However, they are volatile and are lost rapidly from petroleum products following exposure to the environment. They rarely accumulate to potentially toxic concentrations in sediments/cuttings piles.

Higher molecular weigh aliphatic hydrocarbons have solubilities well below toxic concentrations. They also are readily metabolized by bacteria, fungi, and marine organisms. They probably make a minor contribution to the toxicity of drilling discharges. However, they do contribute to smothering of benthic organisms and organic enrichment, rendering sediments anoxic. Therefore, aliphatic hydrocarbons should be included in the risk calculations of drilling discharges in sediments.

3.3.5. Summary: Natural Organic Chemicals to Include in the Toxicity Risk Calculation for Drilling Wastes

The natural substances of this type (typically with high sediment organic carbon/water partition coefficient, K_{oc}) may have a large ability to adsorb to organic matter in the sediment or in the water column. They may also have “sticky” properties that cause the compounds to form “agglomerated” particles or be attached to cuttings particles. Therefore, organic compounds with log octanol/water partitions (log K_{ow}) larger than 3 are assumed to be “attached” to particles or to form “agglomerated particles”. Both these processes will bring the chemicals (with log $K_{ow} > 3$) down on the sea floor rather quickly, and the dissolution of these compounds (BTEX, PAHs and aliphatic hydrocarbons) in the water column is assumed to be slow and of minor importance (Rye, 2006). Since naturally occurring substances that might be present in drilling discharges have log Kow greater than 3 (Table 5.4), they are assumed to be attached to cuttings/mud particles and deposited in the sea floor and impact on the sediment, and should therefore be evaluated for inclusion in the risk calculations for the sediments. However, they are recommended excluded from the risk calculation in the water column.

BTEX are unlikely to be present at elevated (above background for seawater and sediments) concentrations in drilling discharges. Because of their high volatility, any BTEX aromatic hydrocarbons released to the ocean in drilling discharges are not sufficiently persistent in the water column or sediments to cause toxic effects in resident marine organisms. Therefore, BTEX should not be included in the risk calculations for drilling discharges.

PAH are sufficiently toxic and persistent in the marine environment that, if present at concentrations significantly higher than background concentrations in marine sediments, they could contribute to the harm of drilling discharges to sediment dwelling marine organisms. Therefore, PAH should be included in the risk calculations for drilling wastes in the sediments.

Less highly alkylated phenols have a low toxicity and are highly soluble and biodegradable (Neff, 2002a). Their concentrations, if present in drilling discharges, are expected to be below toxic levels and should therefore not be included in the risk calculation for drilling discharges. The more highly alkylated phenols, particularly octylphenols and nonylphenols, although toxic, are not expected to be present at toxic concentrations in modern drilling waste discharges and are not expected to accumulate to high concentrations in sediments and are recommended not included in the risk calculation for drilling discharges.

Aliphatic hydrocarbons may cause damage to benthic ecosystems by physical/chemical alteration of sediments (e.g., organic enrichment leading to oxygen depletion) at a high concentration, and should therefore be included in the risk calculations for the sediments.

3.4. Added chemicals

Fates of chemical substances in the water column are included in the present DREAM model. In the former DREAM model (Reed et. al., 2001) added chemical substances in produced water discharge were assumed totally dissolved in the water after discharge. Similarly, the chemical substances in added water based mud (WBM), are mainly expected to dissolve in the water column. Therefore, for chemical substances with low K_{ow} or K_{oc} values (< 1000 or log K_{ow}< 3), the substances are assumed to dissolve (completely) in the water column.

For other types of mud (e.g. OBM) (as well as crude oil from the geological formation), the dissolution of the chemicals in the water column may be slow and limited. The chemical substances of this type (typically with high partition coefficient K_{oc}) may also have a large ability to adsorb to organic matter in the sediment or in the water column. This type of compound may also have “sticky” properties that cause the chemical to form “agglomerated” particles or be attached to cuttings particles. Both these processes will bring the chemicals (with log P_{ow} > 3) down on the sea floor. The “agglomeration” process is a well-known fact for OBM and (most) SBM types of mud. The base fluids in OBM and SBM have usually large partition coefficients. These chemicals tend to form large “clumps” consisting of the chemical, cuttings and other particle matter in the clump (barite). Due to the density of the particles, they will sink down on the sea floor relatively quickly. Therefore, for chemical substances with large K_{ow} or K_{oc} values (1000 or log Kow>3), the chemicals are assumed to deposit on the sea floor.

The agglomerated particles will in general have a relatively high density and sink to the sea floor rapidly (Delvigne, 1996). Because most of the cuttings solids sink down to the sea floor, the chemicals attached to them will experience the same fate.

All chemicals with low P_{ow}, K_{ow} or K_{oc} values (the HOCNF scheme reports the P_{ow} value) are therefore treated as in the produced water discharge, except that the chemical is assumed to spread in the recipient at the depth of trapping (where the near field plume levels out in the recipient). No distinction is made between the three partitioning parameters P_{ow}, K_{ow} or K_{oc}, as discussed in Chapter 2.4.

3.4.1. Green chemicals (PLONOR chemicals)

Most of the chemicals used (> 90%) in normal drilling operations are so called PLONOR chemicals. The PLONOR chemicals are *Substances/Preparations Used and Discharged Offshore which Are Considered to Pose Little or No Risk to the Environment* (OSPAR, 2004).

Until 2003, there were no specific requirements for inclusion of substances on the PLONOR list. The information required for new substances for evaluation as PLONOR candidates is described by OSPAR, 2003. Substances included on the list before 2003 were kept on the PLONOR list, although the requirements for listing were not fulfilled.

During the summer of 2004, Statoil performed a literature search for toxicological information on PLONOR substances. Inorganic salts and sugars were considered non-toxic in sea water and were omitted from further consideration in order to reduce the number of PLONOR substances in the evaluation. Substances discharged by Norsk Hydro, Total E&P Norge and Statoil in 2003 in volumes less than 1 ton also were not considered further. Despite of this selection a large number of PLONOR chemicals were identified for the literature research (Table 3.6).

Table 3.6 Mass discharges (in tonnes/year) of the most common PLONOR substances to the North Sea in drilling discharges by Norsk Hydro, Total E&P Norge, and Statoil in 2003. PLONOR chemicals that will be evaluated most intensively as part of the risk calculations for drilling discharges are highlighted.

PLONOR Substance	Statoil	Total	Norsk Hydro	Total Discharge
Aluminum silicate beads	145	NA	NA	145
Barium sulphate	**21 561**	**1580**	**23 675**	**46 616**
Calcium chloride	372	NA	1975	2347
Calcium carbonate	191	50	3744	3985
Calcium hydroxide	NA	1.2	533	534
Calcium oxide	NA	NA	289	289
Carboxymethyl-cellulose	**307**	**55**	**562**	**924**
Citric acid	NA	NA	121	121
Graphite	NA	NA	128	128
Monoethylene-glycol	432	2.4	NA	434
Montmorillonite (clay)	**1334**	**108**	**1638**	**3080**
Polyanionic cellulose	63	NA	NA	63
Potassium chloride	2241	345	8006	10,592
Portland cement class G	**926**	**43**	**6004**	**6973**
Precipitated amorphous silica	NA	NA	155	155
Quartz (crystalline silica)	**1032**	**64**	**1190**	**2286**
Sodium bromide	58	NA	NA	58
Sodium carbonate	62	4,7	NA	67
Sodium chloride	1590	28	43 840	45 458
Xantham gum	**72**	**14**	**444**	**530**
Cellulose fiber	NA	2,9	NA	2,9
Mica	NA	7,7	NA	7,7
Walnut shell	NA	7,7	NA	7,7

Starch	NA	1,5	NA	1,5
Calcium sulphate dehydrate	NA	45,4	NA	45,4

NA: No data available.

The literature search showed, as expected, that there is little toxicology information available in the literature for most PLONOR chemicals and that the quality of the existing data is poor in many cases. Final quality assurance of the data found in the literature has not been completed at present time.

As a parallel activity to the general literature review, six of the most common (based on amounts discharged and frequency of use among several operators) PLONOR substances were identified for further evaluation. This selection was done by identifying the 15 (approximately) PLONOR chemicals most frequently discharged by the three operators from drilling operations on the NCS in 2003 (Table 3.6). An evaluation of these substances was performed by Battelle and TNO (Memo to I. Nilssen, 2004). The conclusion from the evaluation was that there are limited aquatic toxicity data for the six selected PLONOR substances. These PLONOR chemicals include barite (a drilling mud weighting agent), sodium and potassium chlorides (used in brines and salt muds), Portland cement (for setting casing), montmorillonite (bentonite) clay (to increase the viscosity of the mud), and calcium carbonate (to protect shale formations) (Table 3.1 and 3.6). They will be evaluated as possible contributors to the toxicity in the risk calculations for drilling discharges. Various ethylene glycols are being used with increasing frequency in polyol muds. If discharges from drilling in the North Sea increase, the most frequently used ethylene glycols should also be evaluated for use in the risk calculation, as should all PLONOR chemicals used in higher quantities.

Although the solid PLONOR chemicals, such as weighting agents, barite and ilmenite, bentonite clay, and quartz are expected to contribute little to the toxicity risk from a discharge due to their low solubility and bioavailability, they may cause physical effects in the benthic environment and, therefore, were evaluated as part of the Task 2 with focus on non-toxic, physical disturbances from drilling waste discharges (Smit et al., 2006a, b).

3.4.2. Other chemicals than the green chemicals (non-PLONOR chemicals)

The non-PLONOR chemicals are all chemical additives that are not PLONOR chemicals. *OSPAR Decision 2000/2 on a Harmonised Mandatory Control System for the Use and Reduction of the Discharge of Offshore Chemicals* requires that a suite of aquatic toxicity and biodegradation tests be performed for all offshore chemicals used and discharged from the offshore petroleum activities in the OSPAR area. The information required includes results of biodegradation and bioaccumulation tests and toxicity test results for one or more marine algae, crustaceans, and fish for all substances in a product. A more detailed description of the requirements is presented in Chapter 6 and in the Harmonised Offshore Chemical Notification Format (HOCNF) (OSPAR Recommendation 2000/5).

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4. LITERATURE REVIEW OF MARINE ECOTOXICOLOGY OF METALS AND POLYCYCLIC AROMATIC HYDROCARBONS

The objective of the literature review was to screen the open scientific literature for ecotoxicological studies for selected metals and polycyclic aromatic hydrocarbons (PAHs) in marine sediments. Toxicological endpoints were sought that fit the recommendations laid out in the EU Technical Guidance Document Part II (EU-TGD; EC 2003) for calculation of the Predicted No Effect Concentration (PNEC) for the sediment compartment for these two groups of substances. The principles for calculation of PNEC according to the TGD are outlined in sections 2.4.1 and 2.4.2 in this report. Based on the number of quality assured datapoints retrieved from the literature either the Species Sensitivity Distribution (SSD), assessment factor, or Equilibrium Partitioning (EqP) approach was to be chosen.

4.1. Introduction

The effects of a stressor on an organism can be subdivided into two categories: acute and chronic effects, depending on the level and duration of the exposure. The classification of effects as acute (i.e. giving an effect after a short time of exposure) or chronic (i.e. giving an effect after a prolonged time of exposure) are based on the level and duration of the exposure relative to the expected lifetime of the organism. No established clear-cut criteria for the duration of the exposure exist, as this is highly variable both among as well as within phyla. Organisms in different phyla may have ranges in expected generation times from minutes to hours as in bacteria to several decades in some mammals, as well as from months for some rodents to decades for larger mammals

Acute responses are caused by a level of a toxicant sufficient to cause an effect within a short period of exposure. Associated effects with acute exposures are primarily on the level of survival of the organism. Acute responses are the most powerful in altering the overall structure of benthic communities as they cause rapid adverse effects on single organisms in different populations. Chronic responses often are caused by lower doses (concentration x duration of exposure) of toxicants than those required to cause acute effects, and the observed effects occur after prolonged exposure times. Associated effects with chronic exposures might also be survival of the organism, but focus is primarily on less serious alterations of the physiology of the organism causing poorer ecological fitness, or reproductive success. Effects include changes in the overall energetic status (“Scope for Growth”), somatic growth, reproduction and behaviour. Chronic effects act in a subtler manner on the population than acute effects. They might still be fatal on the individual level, but more random among individuals predisposed for the given toxicant than the acute effects. Chronic effects are often processes with ecological significance, but the time needed for these effects to manifest as a change at the population or community level are often well beyond the duration of a laboratory study. Possible effects on the population and community level have thus to be deduced from the results available from laboratory studies. Dealing with complex multicellular organisms capable of adjusting their physiology to withstand the effect of a given stressor, the results of this deduction might be more or less incorrect dependent on the amount of the information available.

It is generally recognised that the lower levels of biological organisation (molecular, cellular and single organism) respond to environmental stress long before the effects are observed on the higher levels as changes in populations or communities (McKenney 1985). Bioassays involving single species are often performed to assess the possible effects of a toxicant at the population or community level. The majority of these bioassays (Table 4.1) are acute assays with mortality as the endpoint performed under controlled laboratory conditions. The advantage of these studies is the ability to assure the quality of the result obtained through the necessary control of environmental factors and monitoring during the assay. As several of these assays have evolved and been used routinely for evaluation of toxicity over the last few decades, a significant amount of data exist. However, until recently little effort has been put into transforming these laboratory-derived data into predictions of possible ecological effects on the population level *in situ*. (See Long 2000, Long *et al.,* 2001 and Kuhn *et al.,* 2002 for reviews on this issue).

Metals enter marine sediments as a natural part in their geochemical cycling. The organisms living in the sediments are well adapted to the natural concentrations and species of the different metals. Natural concentrations of the different metals in marine sediments vary with sediment grain size and mineralogy. Concentrations of most natural metals co-vary with concentrations of aluminum or iron in sediments on a regional scale and are expressed as the natural background concentration of the metal. Several of the metals are considered essential trace nutrients for maintaining the natural biochemical processes in living organisms. At environmental concentrations of bioavailable forms of the essential metals that are higher or lower than the range where the animal can maintain its steady internal metal levels (homeostasis), symptoms of deficiency or toxicity will become evident. The other metals not utilised in any physiological processes are termed non-essential. Since sediment dwelling animals are not highly mobile, they are adapted to the natural background level of a given metal within a region. Because the sediment plays a role as sink of metals in the ocean, depletion of a given metal is not likely to occur. Elevation of the concentration over the background level on the other hand is possible, and is most likely to originate from either human or geologic activity. Regardless of the metal being essential or not, an elevation of the concentration of a biologically reactive chemical species of the metal in the sediment may lead to more or less severe toxic effects in the biota.

Polycyclic aromatic hydrocarbons (PAHs) are hydrocarbons containing two or more fused benzene rings (Neff, 2002). There are three dominant sources of PAH in the environment. Petrogenic PAHs formed from transformation of fossil organic matter over geologic time periods to produce peat, coal, and petroleum; pyrogenic PAHs formed by combustion of organic matter at high temperature and last biogenic PAHs formed by degradation of certain organic compounds under anoxic conditions in sediments. The most abundant petrogenic PAHs contain two or three benzene rings and multiple alkyl carbons on the benzene rings while the most abundant pyrogenic PAH contain four to six benzene rings and have few alkyl carbons. The most abundant biogenic PAHs in marine sediments are retene (an alkyl-phenanthrene derived from conifer resins) and perylene (from anaerobic degradation of plant pigments).

PAHs are non-ionic, highly hydrophobic chemicals with low aqueous solubility and a high affinity for adsorbtion to solid, organic-rich particles (Neff, 2002). When introduced into the ocean, they tend to adsorb to suspended particles and accumulate in sediments. Petrogenic PAHs enters the ocean primarily associated with crude or refined petroleum or coal dust. PAHs may be released to the ocean from offshore oil and gas operations primarily as dispersed and dissolved oil in produced water discharges and associated with oily drilling muds and cuttings. PAHs entering the ocean from different sources may be degraded slowly in the water column by photo-oxidation and microbial degradation. Those adsorbed to particles eventually settle to and accumulate in bottom sediments, where they may undergo microbial degradation in surface, oxidized layers of sediments. PAHs are biodegraded very slowly in anoxic sediment layers.

Because of the multiple sources of PAHs in the ocean and their slow degradation, nearly all marine sediments, even those in the deep sea, contain some PAHs. These background concentrations of PAHs usually are less than 100 µg/kg dry wt., and values from the Norwegian Continental Shelf are in the range 4-5 µg/kg dry wt. (Bjørgesæter, 2006). Sediment living animals tolerate these concentrations and may bioaccumulate small amounts of PAH from sediment pore water. Sediments near offshore oil and gas platforms may contain elevated concentrations of PAH, mainly from drilling discharges. These excess PAH may be toxic to the bottom dwelling communities and consumers of benthic fauna, including commercially important fish and shellfish.

4.2. Sources for Ecotoxicological Endpoint Data

All the endpoint data reported are obtained from a systematic screening of the open scientific literature for original papers published in scientific journals or well documented scientific reports to regulatory authorities. Open toxicological databases (ECOTOX Database, PAN Pesticides Database) and review papers were only used for identification of studies or papers for further evaluation. No unpublished data or personal communications from individual scientists are evaluated and reported. No discrimination of the identified endpoint data is made between the different routes of uptake in the organism, and only direct effects on the organism were evaluated, ruling out trophic transfer/food chain transfer.

4.3. Criteria for Selection of Representative Organisms

The species commonly used for performing ecotoxicological studies are traditionally chosen based on either ecological relevance or more commonly the availability and ease of maintenance in the laboratory to ensure continuity in testing. Hence they are most likely to originate from harvesting of natural populations or from laboratory cultures if they are easy to keep under laboratory conditions for generations. Some test animals are also commercially available from hatcheries or suppliers of organisms for general laboratory use.

Only studies involving test organisms matching the following criteria were considered as suitable for obtaining valid endpoints representative of the sediment compartment in this literature review:

- The test organisms must be living in close contact with the sediment at least for a significant part of their life-cycle. For species having planktonic developmental stages, or other life stages not in contact with the sediment, studies performed on those stages of the organisms are not included (e.g. in studies involving both planktonic larvae and adult benthic stages, only the endpoints involving the adult stage are reported).
- The organisms in the study should be marine (saltwater) or estuarine species for the metals. For the PAHs, studies with fresh-water species were included in addition to marine and estuarine, but restricted to the species fulfilling the first criterion regarding being a true sediment organism. Studies involving highly mobile larger species were omitted from the evaluation of endpoints since they are capable of moving out of the influenced area during exposure, and are more likely to experience intermittent or highly fluctuating exposures under natural conditions. This excludes primarily the demersal fish species and the larger swimming crustaceans. No geographical limitations were placed on the choice of species to include.

4.4. Quality Criteria for Acceptance of Effect Data

Studies identified as containing relevant endpoint data from the literature were evaluated based on the following criteria:

- The study should be published in a scientific journal or open well documented scientific report. No unpublished data or personal communications from scientists were accepted.
- The test organisms should be well characterised in the study regarding species (scientific name), life stage (egg, juvenile, adult), and origin (laboratory-bred or collected from natural populations) to omit studies involving test organisms collected from known polluted locations.
- 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 paper/publication referred to in the paper, and if applied, reference to international accepted and published guidelines (US-EPA, OECD, OSPAR, ISO, ASTM or similar) if applicable.
- The study should be performed as spiked sediment exposures with controlled and well documented environmental conditions.

- The scale of the study should be documented – whether it is a small-scale laboratory experiment, mesocosm, or field study.
- The endpoint should be of critical concern for the organism. Either as mortality or reduced fitness in form of reduction of realised offspring as a consequence of alteration of the energy status or natural behaviour. This rules out several biomarkers of exposure and for the PAHs also alteration in the organisms immunocompetence, damage to DNA or structural changes in tissue or organs.

4.5. Overview of Available Effects Data for Metals and PAHs in Sediments

Due to a lack of controlled laboratory experiments addressing effects of a single chemical stressor in sediments at the population level, only primary responses at the level of the individual were identified and are reported here. The EU-TGD (EC 2003) does not give specific advice on the recommended duration of studies designed to investigate the effect of a stressor on sediment-dwelling marine organisms. However the recommended standard international guidelines (OECD, US-EPA, OSPAR and ISO) for the different test systems do give specific advice on the duration of exposure. Recommended duration for the different relevant test systems are given in Table 4.1. Please note that not all taxonomic groups are covered by relevant guidelines for either or both acute and/or chronic studies, and the results have to be evaluated on a case-to-case basis.

Table 4.1 European inter-laboratory ringtested draft guidelines for conducting sediment toxicity tests with marine species. Two major marine round-robin tests (RRTs) have been initiated by OSPAR: 1991 and 1993. From these drafted guidelines only the tests with *Corophium* sp. and *Arenicola marina* are finalised into published guidelines (ICES 2001a and 2001b).

Species	**Phyla/Taxon**	**Duration**	**Acute/ Chronic**	**Reference**
Abra alba	Mollusca: Bivalvia	5 days	Acute	RRT, OSPAR 1991[1]. Bjørnestad and Petersen 1992
Echinocordatum cordatum	Echinodermata: Echinoidea	21 days	Acute	RRT, OSPAR 1991[1]. Bjørnestad and Petersen 1992
Nereis virens.	Annelida: Polychaeta	10 days.	Acute	RRT, OSPAR 1991[1]. Bjørnestad and Petersen 1992
Echinocordatum cordatum	Echinodermata: Echinoidea	21 days	Acute	RRT, OSPAR 1993[2]. Parcom 1993
Corophium sp.	Crustacea: Amphipoda	10 days	Acute	RRT, OSPAR 1993[2]. Parcom 1993
Arenicola marina.	Annelida: Polychaeta	10 days	Acute	RRT, OSPAR 1993[2]. Parcom 1993

[1] Tested chemicals: 3,5-dichlorophenol, Bioban P-1487 (microbiocide) and Vantocil 1B (microbiocide).
[2] Tested chemicals: Fluoranthene (PAH), Servo CK337 (corrosion inhibitor) and Bioban (microbiocide).

As seen in Table 4.2 there is a substantial imbalance between the phyla naturally represented in marine sediments and the phyla covered by the available guidelines for testing of sediments. This can be attributed to the fact that there are relatively few naturally-occurring species in the sediments that are sufficiently abundant and tolerant to laboratory maintenance and culture conditions to be suitable as test organisms for routine tests in the laboratory. Some of the listed guidelines have been adjusted in some studies to fit other phyla. There seems to be a general lack in the literature reviewed of information on effects of metals on some major benthic phyla such as cnidaria (hydroids), echinodermata (echinoderms) and mollusca (bivalves and gastropods).

Table 4.2 Published international guidelines for conducting sediment toxicity tests with marine species.

Species	**Phylum/Taxon**	**Duration**	**Acute/ Chronic**	**Institution/Code/ Reference**
Rhepoxynius abronius, *Eohaustorius washingtonianus*, *Eohaustorius estuarius*, *Amphiporeia virginiana*	Crustacea: Amphipoda	10 days	Acute	Environment Canada, EPS 1/RM/26, 1992
Vibrio fischeri	Bacteria	5-15 min.	Acute	Environment Canada, EPS 1/RM/24, 1992
Polydora cornuta	Annelida: Polychaeta	14 days.	Acute	Environment Canada, EPS 1/RM/41E, 2001
Ampelisca abdita, *Eohaustorius estuarius*, *Leptocheirus plumulosus*, *Rhepoxynius abronius*	Crustacea: Amphipoda	10 days	Acute	US-EPA, 600-R-94-022, 1994
Ampelisca abdita, *Eohaustorius estuarius*, *Rhepoxynius abronius*, *Leptocheirus plumulosus*	Crustacea: Amphipoda	10 days	Acute	US-EPA, OPPTS 850.1740. (EPA 712-C-96-355), 1996
Corophium sp.	Crustacea: Amphipoda	10 days	Acute	ICES, ICES 2001a
Corophium sp.	Crustacea: Amphipoda	28 days	Chronic	OECD, OECD 1998
Arenicola marina	Annelida: Polychaeta	10 days	Acute	ICES, ICES 2001b
Arenicola marina	Annelida: Polychaeta	28 days	Chronic	OECD, OECD 1998
Arenicola marina	Annelida: Polychaeta	10 days	Subacute (Casting rate)	ICES, ICES 2001b
Echinocardium cordatum	Echinodermata: Echinoidea	14 days	Acute/ subacute	OECD, OECD 1998
Leptocheirus plumulosus, *Ampelisca abdita*, *Eohaustorius estuarius*, *Rhepoxynius abronius*	Crustacea: Amphipoda	10 days	Acute	ASTM, E1367-03e1, 2003
Leptocheirus plumulosus	Crustacea: Amphipoda	28 days	Chronic	US-EPA, 600-R-01-020, 2001
Leptocheirus plumulosus	Crustacea: Amphipoda	28 days	Chronic	ASTM, E1367-03e1, 2003
Neanthes arenaceodentata, *Neanthes virens*	Annelida: Polychaeta	10 days	Acute	ASTM, E1611-00, 2000
Neanthes arenaceodentata	Annelida: Polychaeta	20-28 days	Chronic	ASTM, E1611-00, 2000

The distribution of the identified and quality assured toxicity endpoints for the different metals are summarised in Table 4.3 and on trophic levels in Table 4.5. If not stated otherwise, the effect concentrations are bulk concentrations. The distribution of species for each endpoint is given in detail for the different metals in Tables 4.7 to 4.18 and in Appendix 4.1 to 4.12. Similar data for PAHs are summarised in Table 4.4 and 4.6. The distribution of species for each endpoint is given in detail for the different PAHs in Tables 4.20 to 4.23 and in Appendix 4.13 to 4.17.

Table 4.3 Distribution of identified and quality assured endpoints for the different metals with corresponding indicator of effect.

Endpoint	**Acute/Chronic**	**Effect**	**Cd**	**Cr sed.**	**Cr. aq.**	**Cu**	**Hg**	**Pb**	**Zn**	**Total**
Behaviour:										
- Emergence from sediment	Acute/Chronic[1]	EC_{50}	1							1
	Acute/Chronic[1]	NOEC	1			1			1	3
- Number of casts	Acute/Chronic[1]	NOEC	1			1			1	3
- Size of casts	Acute/Chronic[1]	NOEC	1			1			1	3
Reproductive effects:										
- Fertility (reduction in brood size)	Chronic	EC_{50}			1					1
	Chronic	NOEC			1					1
	Chronic	LOEC			1					1
	Chronic	SChV[2]			1					1
- [SEM]- AVS data	Chronic	-[3]	4							4
Minor physiological effects:										
- Inhibition of growth	Acute/Chronic[1]	EC_{50}	1			1		1		3
- [SEM]- AVS data	Chronic	-[3]	4							4
Mortality:										
- [SEM]- AVS data	Acute/Chronic[1]	-[3]	21	13		12		12	12	64
- Bulk concentration data	Acute/Chronic[1]	LC_{50}	16	2	44	22	1	1	4	96
	Acute/Chronic[1]	NOEC	1		1	1			1	4
	Acute/Chronic[1]	LOEC			1					1
	Chronic	SChV[2]			1					1
Post-exposure reburial:		EC_{50}	4			1			1	6
Total number of responses:			**55**	**15**	**51**	**40**	**1**	**14**	**21**	**197**

[1] Classification of an endpoint as acute or chronic is dependent on the species and duration of the study.

[2] Subchronic value is described by Hutchinson *et al.* (1994) as the geometric mean of the highest NOEC and the lowest LOEC values determined, termed the sub-chronic value (SChV). The SChV is an estimate of the chronic value (termed the ChV and historically was referred to as the maximum acceptable threshold concentration or 'MATC'). The ChV or SChV represents the hypothetical toxic threshold between the NOEC and LOEC for a given biological endpoint.

[3] Endpoints from studies recording corresponding data on SEM and AVS are recorded as discrete endpoints in the table rather than single LC/EC-values.

Table 4.4 Distribution of identified and quality assured endpoints for the different PAHs with corresponding indicator of effect (Ace: Acenaphthene, Fuel: Diesel Fuel, Flu: Fluoranthene, Phe: Phenanthrene and Pyr: Pyrene).

Endpoint	**Acute/Chronic**	**Effect**	**Ace**	**Fuel**	**Flu**	**Phe**	**Pyr**	**Total**
Behaviour:								
- Emergence from sediment	Acute/Chronic[1]	EC_{50}					1	1
- Egestion	Acute/Chronic[1]	LOEC				1	1	2
		NOEC				1	1	2
- Grazing	Acute/Chronic[1]	IC_{50}		1	3	1		5
		LOEC			2			2
		NOEC			2			2
Reproductive effects:								
- Fertility (reduction in brood size)	Chronic	EC_{50}		1	3	1		5
	Chronic	LOEC			1	3		4
	Chronic	NOEC			2	3		5
- Developmental time of eggs	Chronic	LOEC				2		2
	Chronic	NOEC				2		2
- Hatching success of eggs	Chronic	LOEC				2		2
	Chronic	NOEC				2		2
Mortality:								
	Acute/Chronic[1]	LC_{50}	7	1	55	22	3	88
	Acute/Chronic[1]	LOEC			4	12		16
	Acute/Chronic[1]	NOEC			3	12		15
Total number of responses:			**7**	**3**	**75**	**64**	**6**	**155**

[1] Classification of an endpoint as acute or chronic is dependent on the species and duration of the study.

4.6. Trophic Levels

Trophic levels define the general flow of energy (nutrients) and hence also the possible flow of contaminants within the communities in an ecosystem. The bottom part - first level - of the system consists of producers, organisms that can synthesise and accumulate organic matter from inorganic precursors. The primary consumers or herbivores make the second level, and the following levels of consumers (carnivores and omnivores) make up the rest of the levels. None of the consumers are capable of building organic substances from inorganic precursors, and hence are ultimately dependent on the energy from the primary producers. The decomposers are working within all levels to transform dead organic debris into inorganic compounds to be recycled again into the food web. Organisms for routine studies of ecotoxicity are often chosen from different trophic levels to elucidate the possible effects of a chemical stressor on the different levels.

4.6.1. Producers (P)

Producers are organisms that can synthesise and hence build organic matter from inorganic precursors by the energy derived from either sunlight (photo-autotrophs) or gained by chemical modification of inorganic substances (chemo-autotrophs). The main exposure routes for toxic substances on this level are direct exposure from the sediment or water, either by direct contact or passive or active uptake across membranes from the water. The most important primary producers in surface waters and marine sediments are bacteria and microscopic and macroscopic plants.

4.6.2. Primary Consumers (PC)

Primary consumers are organisms that are not able to synthesise organic matter from inorganic precursors and have to feed on living or detrital organic matter to gain energy to support the life functions. Primary consumers are herbivores and get their energy by feeding on the primary producers on the previous trophic level. Some primary consumers are omnivorous and act both as herbivores and carnivores, placing them in both categories. They feed opportunistically on plants and animals in their environment. Some animals shift from primary to secondary consumers during their life cycle; some aquatic crustaceans or other animals with planktonic life-stages shift from herbivory to carnivory during metamorphosis. The main exposure routes for toxic substances on this level are direct exposure from the sediment or water, either to the exterior by contact or interior by ingestion of contaminated water, sediment, or food.

4.6.3. Secondary Consumers (SC)

Secondary consumers resemble the primary consumers in their way of gaining energy to support life functions, but the secondary producers are carnivores, and get their energy by feeding on the other consumers in the food-web. They feed most often on the previous trophic level (primary consumers) because the primary consumers usually are much more abundant than secondary consumers. However, they may also feed on organisms within their own trophic level or from higher levels. Some primary consumers are omnivorous and act both as herbivores and carnivores, placing them in both categories, or they shift from primary to secondary consumers during their life cycle as with some aquatic crustaceans. The main exposure routes for toxic substances on this level are the same as for the primary consumers.

4.6.4. Decomposers (D)

Decomposers are saprophytic organisms gaining energy from degrading complex organic matter to simpler organic or inorganic forms, and utilising some of the available energy in this process for growth and propagation. Many bacteria and fungi are decomposers. They are essential for cycling nutrients in ecosystems. Effects of chemicals on marine decomposers usually are not investigated. They usually are considered more tolerant to chemical pollution than other trophic levels.

Table 4.5 Distribution of identified and quality assured endpoints for metals distributed on different trophic levels. P: Producers, PC: Primary consumers and SC: Secondary consumers.

Endpoint	**Acute/Chronic**	**Effect**	**P**	**PC**	**PC/SC**	**SC**
Behaviour:						
- Emergence from sediment	Acute/Chronic[1]	EC_{50}			1	
	Acute/Chronic[1]	NOEC			3	
- Number of casts	Acute/Chronic[1]	NOEC			3	
- Size of casts	Acute/Chronic[1]	NOEC			3	
Reproductive effects:						
- Fertility (reduction in brood size)	Chronic	EC_{50}			1	
	Chronic	NOEC			1	
	Chronic	LOEC			1	
	Chronic	SChV[2]			1	
- [SEM]- AVS data	Chronic	-[3]			4	
Minor physiological effects:						
Inhibition of growth	Acute/Chronic[1]	EC_{50}	3			
- [SEM]- AVS data	Chronic	-[3]			4	
Mortality:						
- [SEM]- AVS data	Acute/Chronic[1]	-[3]			64	
- Bulk concentration data	Acute/Chronic[1]	LC_{50}		22	61	13
	Acute/Chronic[1]	NOEC			4	
	Acute/Chronic[1]	LOEC			1	
	Chronic	SChV[2]			1	
Post-exposure reburial:		EC_{50}			6	
Total number of responses:			**3**	**22**	**159**	**13**

[1] Classification of an endpoint as acute or chronic is dependent on the species and duration of the study.

[2] Subchronic value is described by Hutchinson *et al.,* (1994) as the geometric mean of the highest NOEC and the lowest LOEC values determined, termed the sub-chronic value (SChV). The SChV is an estimate of the chronic value (termed the ChV and historically was referred to as the maximum accepTable threshold concentration or 'MATC'). The ChV or SChV represents the hypothetical toxic threshold between the NOEC and LOEC for a given biological endpoint.

[3] Endpoints from studies recording corresponding data on SEM and AVS are recorded as discrete endpoints in the table rather than single LC/EC-values.

Table 4.6 Distribution of identified and quality assured endpoints for PAHs distributed on different trophic levels. P: Producers, PC: Primary consumers and SC: Secondary consumers.

Endpoint	**Acute/Chronic**	**Effect**	**P**	**PC**	**PC/SC**	**SC**
Behaviour:						
- Emergence from sediment	Acute/Chronic[1]	EC_{50}			1	
- Egestion	Acute/Chronic[1]	LOEC			2	
		NOEC			2	
- Grazing	Acute/Chronic[1]	IC_{50}			5	
		LOEC			2	
		NOEC			2	
Reproductive effects:						
- Fertility (reduction in brood size)	Chronic	EC_{50}			5	
	Chronic	LOEC			4	
	Chronic	NOEC			5	
- Developmental time of eggs	Chronic	LOEC			2	
	Chronic	NOEC			2	
- Hatching success of eggs	Chronic	LOEC			2	
	Chronic	NOEC			2	
Mortality:						
	Acute/Chronic[1]	LC_{50}		16	72	
	Acute/Chronic[1]	LOEC		4	12	
	Acute/Chronic[1]	NOEC		4	11	
Total number of responses:				**24**	**131**	

[1] Classification of an endpoint as acute or chronic is dependent on the species and duration of the study.

4.7. Identified and Quality Assured Endpoint-Data for the Different Metals

The identified and quality assured endpoint data from exposure studies with cadmium, chromium, copper, lead and zinc are presented in two separate Tables in which the effect concentrations are reported as bulk metal or simultaneously extracted metal concentrations ([SEM]). This separation is based on an operational definition, and is dependent on the method of extraction of the metal from the sediment samples prior to analysis. Extraction for bulk metal analysis is performed under conditions expected to bring all the metal in the sample into solution. The metal making up the SEM in a sample is the fraction extracTable with cold diluted acid (0.5 – 1 M). The concentration of each metal listed in the Tables is the concentration of that metal in the SEM fraction and not the molar difference between SEM and AVS (“SEM – AVS”), as described in Section 4.8.1. The SEM – AVS is considered to be the potentially bioavailable fraction and, as such, represents the fraction of the metal in sediment that poses a potential risk to benthic organisms. Endpoints based on bulk metal analysis are reported either as LC/EC_{50}, NOEC or subchronic values (SChV) calculated from the observed data. The endpoints based on the SEM analysis are listed in the Tables as discrete datapoints where each value for the SEM concentration is listed with the corresponding observed biological effect and other relevant data. Recalculating these data to single LC/EC$_{50}$-values will cause some loss of information, as the observed effects are dependent on the SEM-values, which are ultimately under control of the concentration of AVS as well as other metal binding factors in the sediment.

The endpoint data are presented in the following Tables with a bare minimum of supporting data. Extended Tables with experimental and analytical conditions are listed in Appendix 4.1 to 4.12. References to the cited literature are listed after each metal. Please note that the numbering of the references is not interchangeable between the Tables in the report and the appendix.

4.7.1. Cadmium

Bulk Metal Effect Concentration data

After quality assurance of the identified endpoints a total of 26 unique data points were identified that met the recommendations for inclusion. These endpoints were obtained from eight different studies describing responses in eight different species from four different taxonomic groups, annelida, crustacea, mollusca and algae, covering the trophic levels of producers as well as primary and secondary consumers. None of the secondary consumers were considered strict carnivores and are listed as combined primary/secondary consumers in the Table. All the data sets were acute data; eight datapoints were associated with behavioural responses, one with inhibition of algal growth and the remaining 17 with lethality.

Table 4.7 Bulk metal effect concentration data for cadmium. Extended Tables with experimental and analytical conditions are listed in Appendix 4.1. References to the cited literature are listed at the end of this section (cadmium).

Taxonomic Group	Species	Trophic Level	End-point Parameter	Effect conc. (µg/g dw)	Ref.	Comments
Annelida: Polychaeta	*Arenicola marina*	PC/SC	NOEC $_{\text{Mortality 10 days}}$ /Acute	Between 9 and 25	{1}	Sediment TOC: 1,58%. Effect concentration estimated from figure 2, p. 227 in the paper.
Annelida: Polychaeta	*Arenicola marina*	PC/SC	NOEC $_{\text{Zero emergence 10 days}}$ /Acute	< 25	{1}	Sediment TOC: 1,58%. Effect concentration estimated from figure 3, p. 229 in the paper.
Annelida: Polychaeta	*Arenicola marina*	PC/SC	NOEC $_{\text{Number of casts 10 days}}$ /Acute	< 9	{1}	Sediment TOC: 1,58%. Effect concentration estimated from figure 4, p. 231 in the paper.
Annelida: Polychaeta	*Arenicola marina*	PC/SC	NOEC $_{\text{size of casts 10 days}}$ /Acute	< 9	{1}	Sediment TOC: 1,58%. Effect concentration estimated from figure 5, p. 232 in the paper.
Crustacea: Amphipoda	*Rhepoxinius abronius*	PC/SC	LC$_{50\text{ 10 days}}$ /Acute	6,9	{2}	
Crustacea: Amphipoda	*Rhepoxinius abronius*	PC/SC	LC$_{50\text{ 4 days}}$ /Acute	25,9	{2}	
Crustacea: Amphipoda	*Rhepoxinius abronius*	PC/SC	EC$_{50\text{ 1hr. Reburial}}$ /Acute [1]	6,5	{2}	
Crustacea: Amphipoda	*Rhepoxinius abronius*	PC/SC	EC$_{50\text{ 1hr. Reburial}}$ / Acute [1]	20,8	{2}	Effect endpoint: reburial in clean sediment within 1 hour after 4 days exposure to Cd in sediment.
Mollusca: Bivalvia	*Ruditapes philippinarum*	PC	LC$_{50\text{ 48 hour}}$ /Acute	4,52	{3}	
Mollusca: Bivalvia	*Ruditapes philippinarum*	PC	LC$_{50\text{ 48 hour}}$ /Acute	1,26	{3}	
Algae: Bacillariophyceae	*Cylindrotheca closterium*	P	EC$_{50\text{ 72hour}}$ /Acute	79	{4}	
Crustacea: Amphipoda	*Rhepoxinius abronius*	PC/SC	LC$_{50\text{ 10 days}}$ /Acute	9,8	{5}	
Crustacea: Amphipoda	*Rhepoxinius abronius*	PC/SC	EC$_{50\text{ 10 days emergence}}$ /Acute	9,72	{5}	Effect endpoint: animals emerged from the sediment after 10 days exposure to Cd in sediment.
Crustacea: Amphipoda	*Rhepoxinius abronius*	PC/SC	EC$_{50\text{ 1hr. Reburial}}$ /Acute [1]	9,07	{5}	
Crustacea: Amphipoda	*Corophium volutator*	PC/SC	LC$_{50\text{ 10 days}}$/Acute	14,42	{1}	Sediment TOC: 2,1%.

Table 4.7 Bulk metal effect concentration data for cadmium continued

Taxonomic Group	Species	Trophic Level	End-point Parameter	Effect conc. (µg/g dw)	Ref.	Comments
Crustacea: Amphipoda	*Corophium volutator*	PC/SC	$EC_{50\ 1hr.\ Reburial}$/Acute [1]	9,3	{1}	
Annelida: Polychaeta	*Arenicola marina*	PC/SC	$LC_{50\ 10\ days}$/Acute	35	{1}	Sediment TOC: 1,58%
Crustacea: Copepoda	*Amphiascus tenuiremis*	PC	$LC_{50\ 96\ hour}$/Acute	37,9	{6}	
Crustacea: Copepoda	*Amphiascus tenuiremis*	PC	$LC_{50\ 96\ hour}$/Acute	52,5	{6}	
Crustacea: Amphipoda	*Ampelisa abdita*	PC/SC	$LC_{50\ 10\ days}$/Acute	2580	{7}	
Crustacea: Amphipoda	*Ampelisa abdita*	PC/SC	$LC_{50\ 10\ days}$/Acute	2850	{7}	
Crustacea: Amphipoda	*Ampelisa abdita*	PC/SC	$LC_{50\ 10\ days}$/Acute	1070	{7}	
Crustacea: Amphipoda	*Rhepoxynius hudsoni*	PC/SC	$LC_{50\ 10\ days}$/Acute	290	{7}	
Crustacea: Amphipoda	*Ampelisa abdita*	PC/SC	$LC_{50\ 10\ days}$/Acute [2]	2608	{8}	
Crustacea: Amphipoda	*Ampelisa abdita*	PC/SC	$LC_{50\ 10\ days}$/Acute [2]	1866	{8}	1)
Crustacea: Amphipoda	*Ampelisa abdita*	PC/SC	$LC_{50\ 10\ days}$/Acute [2]	1664	{8}	1)

[1] Effect endpoint: reburial in clean sediment within 1 hour after 10 days exposure to Cd in sediment.

[2] LC_{50}-value calculated by non-linear regression based on the number of survivors vs. exposure concentrations in Table 1, p. 2071 in the paper {8}.

SEM effect concentrations

Two different studies met the quality criteria for inclusion of the endpoints. These two studies dealt with two species in one taxonomic group, crustacea, and only one trophic level. None of the consumers were considered strict carnivores and are listed as combined primary/secondary consumers in Table 4.8. A total of 29 corresponding SEM-effect concentration sets of data were identified along with six data sets for unspiked controls. Of the 29 data sets 15 were acute data and 14 chronic data. Of the chronic data six were associated with lethality, four with growth, and the last four with reproduction.

Table 4.8 SEM effect concentration data for cadmium. SEM concentrations are the measured concentration of Cd in the total SEM extract. Extended Tables with experimental and analytical conditions are listed in Appendix 4.2. References to the cited literature are listed at the end of this section (cadmium).

Taxonomic Group	Species	Trophic Level	AVS (µmol/g dw)	Effect endpoint/ type/ Test duration	Effect size	[SEM] (µmol/ g dw)	[SEM]/ AVS-ratio	Ref	Comments
Crustacea: Amphipoda	*Leptocheirus plumulosus*	PC/SC	6,25	Mortality/Chronic/ 28 days	5 %	0,0	0,00	{9}	Unspiked control
Crustacea: Amphipoda	*Leptocheirus plumulosus*	PC/SC	5,09	Mortality/Chronic/ 28 days	0 %	1,6	0,34	{9}	
Crustacea: Amphipoda	*Leptocheirus plumulosus*	PC/SC	5,22	Mortality/Chronic/ 28 days	5 %	3,2	0,74	{9}	
Crustacea: Amphipoda	*Leptocheirus plumulosus*	PC/SC	5,84	Mortality/Chronic/ 28 days	0 %	6,6	1,55	{9}	
Crustacea: Amphipoda	*Leptocheirus plumulosus*	PC/SC	10,28	Mortality/Chronic/ 28 days	5 %	12,2	1,31	{9}	
Crustacea: Amphipoda	*Leptocheirus plumulosus*	PC/SC	8,55	Mortality/Chronic/ 28 days	100 %	17,4	2,23	{9}	
Crustacea: Amphipoda	*Leptocheirus plumulosus*	PC/SC	7,00	Mortality/Chronic/ 28 days	100 %	22,5	4,82	{9}	
Crustacea: Amphipoda	*Leptocheirus plumulosus*	PC/SC	6,25	Growth/Chronic/ 28 days	5,24 mm	0,0	0,00	{9}	Unspiked control
Crustacea: Amphipoda	*Leptocheirus plumulosus*	PC/SC	5,09	Growth/Chronic/ 28 days	5,73 mm	1,6	0,34	{9}	

Table 4.8 SEM effect concentration data for cadmium continued

Taxonomic Group	Species	Trophic Level	AVS (µmol/g dw)	Effect endpoint/ type/ Test duration	Effect size	[SEM] (µmol/ g dw)	[SEM]/ AVS-ratio	Ref	Comments
Crustacea: Amphipoda	*Leptocheirus plumulosus*	PC/SC	5,22	Growth/Chronic/ 28 days	5,74 mm	3,2	0,74	{9}	
Crustacea: Amphipoda	*Leptocheirus plumulosus*	PC/SC	5,84	Growth/Chronic/ 28 days	5,73 mm	6,6	1,55	{9}	
Crustacea: Amphipoda	*Leptocheirus plumulosus*	PC/SC	10,28	Growth/Chronic/ 28 days	5,87 mm	12,2	1,31	{9}	
Crustacea: Amphipoda	*Leptocheirus plumulosus*	PC/SC	6,25	Fertility/Chronic/ 28 days [1]	7,47	0,0	0,00	{9}	Unspiked control
Crustacea: Amphipoda	*Leptocheirus plumulosus*	PC/SC	5,09	Fertility/Chronic/ 28 days [1]	15,71	1,6	0,34	{9}	
Crustacea: Amphipoda	*Leptocheirus plumulosus*	PC/SC	5,22	Fertility/Chronic/ 28 days [1]	12,85	3,2	0,74	{9}	
Crustacea: Amphipoda	*Leptocheirus plumulosus*	PC/SC	5,84	Fertility/Chronic/ 28 days [1]	10,65	6,6	1,55	{9}	
Crustacea: Amphipoda	*Leptocheirus plumulosus*	PC/SC	10,28	Fertility/Chronic/ 28 days [1]	14,71	12,2	1,31	{9}	
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	14,9	Mortality/Acute/ 10 days	1,7 %	0	0,00	{8}	Unspiked control Sediment TOC: 0,88%.
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	14,9	Mortality/Acute/ 10 days	8,4 %	1,57	0,10	{8}	Sediment TOC: 0,88%.
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	14,9	Mortality/Acute/ 10 days	16,7 %	4,85	0,33	{8}	Sediment TOC: 0,88%.
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	14,9	Mortality/Acute/ 10 days	10 %	16,7	1,12	{8}	Sediment TOC: 0,88%.
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	14,9	Mortality/Acute/ 10 days	100 %	51,7	3,50	{8}	Sediment TOC: 0,88%.
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	14,9	Mortality/Acute/ 10 days	88,4 %	177	11,90	{8}	Sediment TOC: 0,88%.
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	1,31	Mortality/Acute/ 10 days	5 %	0	0,00	{8}	Unspiked control Sediment TOC: 0,15%.
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	1,31	Mortality/Acute/ 10 days	12,5 %	0,15	0,12	{8}	Sediment TOC: 0,15%.
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	1,31	Mortality/Acute/ 10 days	12,5 %	0,64	0,50	{8}	Sediment TOC: 0,15%.
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	1,31	Mortality/Acute/ 10 days	40 %	2,57	1,95	{8}	Sediment TOC: 0,15%.
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	1,31	Mortality/Acute/ 10 days	95 %	5,9	4,34	{8}	Sediment TOC: 0,15%.
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	1,31	Mortality/Acute/ 10 days	100 %	24,3	18,50	{8}	Sediment TOC: 0,15%.
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	4,34	Mortality/Acute/ 10 days	16,7 %	0	0,00	{8}	Unspiked control
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	4,34	Mortality/Acute/ 10 days	11,7 %	0,3	0,10	{8}	
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	4,34	Mortality/Acute/ 10 days	23,4 %	1,75	0,40	{8}	
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	4,34	Mortality/Acute/ 10 days	46,7 %	9,64	2,22	{8}	
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	4,34	Mortality/Acute/ 10 days	100 %	20,7	4,80	{8}	
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	4,34	Mortality/Acute/ 10 days	85 %	48,4	11,20	{8}	

[1] Fertility as average number of offspring pr. surviving female.

Cadmium Toxicity References

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{9} DeWitt, T.H., R.C. Swartz, D.J. Hansen, D. McGovern and W.J. Berry (1996). Bioavailiability and chronic toxicity of cadmium in sediment to the estuarine amphipod *Leptocheirus plumulosus*. Environ. Toxicol. Chem., 15: 2095-2101.

4.7.2. Chromium

Due to the lack of spiked sediment exposure studies with datapoints identified to meet the criteria for inclusion, the data sets for chromium were expanded to include water-only exposures as well. However the criteria regarding selection of relevant test species was not altered, and the test species were chosen according to “Criteria for Selection of Representative Organisms” in the introduction to this section.

Bulk metal effect concentrations

After quality assurance of the identified endpoints for chromium in sediments, only a single study was identified that met the criteria for inclusion. The effect concentrations in this study were calculated by a non-linear regression analysis based on the observed data reported in the study before they were entered into Table 4.9. The study reported responses in one species, the benthic crustacean *Ampelisca abdita*, listed as a combined primary/secondary consumer in the Table. All the data sets were acute data (10-day tests) associated with lethality.

Table 4.9 Bulk metal effect concentration data for chromium. Extended Tables with experimental and analytical conditions are listed in Appendix 4.3. References to the cited literature are listed at the end of this section (chromium).

Taxonomic Group	Species	Trophic Level	End-point Parameter	Effect conc. (µg/g dw)	Ref.	Comments
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	$LC_{50\ 10\ days}$ /Acute	1227[1]	{1}	Sediment TOC: 1,6%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	$LC_{50\ 10\ days}$ /Acute	147[1]	{1}	Sediment TOC: 0,13%

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[1] Effect-concentration value calculated by non-linear regression based on data in the paper.

SEM effect concentrations

After quality assurance of the identified endpoints, only a single study was identified to meet the criteria for inclusion. This study was the same study as identified for the bulk metal effect concentration data listed in Table 4.10. The study described responses in one species, the crustacean *Ampelisca abdita*, considered a combined primary/secondary consumer. A total of 13 corresponding SEM-effect concentration sets of data were identified along with three data sets for unspiked controls (Table 4.8). All the data sets were acute data associated with lethality.

Table 4.10 SEM effect concentration data for chromium. Extended Tables with experimental and analytical conditions are listed in Appendix 4.4. References to the cited literature are listed at the end of this section (chromium).

Taxonomic Group	**Species**	**Trophic Level**	**Effect endpoint/ type/ Test duration**	**AVS (µmol/g dw)**	**Effect size (%)**	**[SEM] (µmol/g dw)**	**Ref.**	**Comments**
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/ 10 days	19,2	10	0,2 Cr total/ 0,0 Cr(VI)	{1}	Unspiked control. Sediment TOC: 1,6%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/ 10 days	5,3	5,0	329 Cr total/ 0,0 Cr(VI)	{1}	Sediment TOC: 1,6%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/ 10 days	5,9	7,5	0,2 Cr total/ 0,0 Cr(VI)	{1}	Unspiked control. Sediment TOC: 1,6%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/ 10 days	6,1	7,5	1,2 Cr total/ 0,0 Cr(VI)	{1}	Sediment TOC: 1,6%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/ 10 days	5,5	2,5	2,8 Cr total/ 0,0 Cr(VI)	{1}	Sediment TOC: 1,6%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/ 10 days	4,5	0	6,0 Cr total/ 0,0 Cr(VI)	{1}	Sediment TOC: 1,6%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/ 10 days	1,5	7,5	13,7 Cr total/ 0,0 Cr(VI)	{1}	Sediment TOC: 1,6%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/ 10 days	0,6	67,5	28,2 Cr total/ 0,4 Cr(VI)	{1}	Sediment TOC: 1,6%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/ 10 days	0,05	100	53,0 Cr total/ 8,1 Cr(VI)	{1}	Sediment TOC: 1,6%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/ 10 days	1,4	0	0,0 Cr/ total 0,0 Cr(VI)	{1}	Unspiked control. Sediment TOC: 0,13%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/ 10 days	1,3	0	0,2 Cr/ total 0,0 Cr(VI)	{1}	Sediment TOC: 0,13%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/ 10 days	1,3	0	0,5 Cr total/ 0,0 Cr(VI)	{1}	Sediment TOC: 0,13%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/ 10 days	0,9	5	1,3 Cr total/ 0,0 Cr(VI)	{1}	Sediment TOC: 0,13%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/ 10 days	0,6	2,5	2,1 Cr total/ 0,0 Cr(VI)	{1}	Sediment TOC: 0,13%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/ 10 days	0,01	72,5	3,7 Cr total/ 1,0 Cr(VI)	{1}	Sediment TOC: 0,13%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/ 10 days	0	97,5	6,5 Cr total/ 4,1 Cr(VI)	{1}	Sediment TOC: 0,13%

Water only exposure effect concentration data

The solubility and toxicity of chromium in seawater is dependent on the valence of the chromium ion. Trivalent chromium (Cr-III) is the most prevalent form in the environment, because hexavalent chromium (Cr-VI) in seawater and sediments is rapidly reduced to the trivalent state, particularly under reducing conditions (Neff, 2002).

Hexavalent chromium is a strong oxidizing agent and is very reactive and toxic. Mearns *et al.*, (1976) did a short-term study with the polychaetous annelid *Neanthes arenoceodentata* and trivalent chromium administered as $CrCl_3$ in a nominal concentration range of 0.195 – 50.0 mg/l. No mortality was reported after 14 days of exposure to nominal concentrations of 0.195, 0.78, 3.12 and 12.5 mg/l at pH values ranging from 7.0 to 7.8. At the nominal concentration of 50.0 mg/l, the pH was 4.5, and 100 % mortality was observed within the first 24 hours of exposure. In all exposure solutions, chromium precipitated as chromium-hydroxide, and the effects observed at 50.0 mg/l might as well be caused by the abnormal pH-values as an observed effect of chromium-III as noted by Berry *et al.*, (2004). A second long term reproduction and survival experiment with *A. arenoceodentata* performed by Mearns *et al.*, (1976) supports further the observed low toxicity of chromium-III as $CrCl_3$ in seawater. At a nominal concentration of 50.4 mg/l, the worms behaved normally and no significant effects on mean time for spawning, mean brood size, and total number of offspring was observed after an exposure period of 165 days. However measurements of dissolved chromium did indicate that less than 0.02 mg/l was actually dissolved and the rest 99.96% was precipitated primarily as insoluble blue-gray hydroxides as the pH of the exposure solution was adjusted by adding sodium hydroxide (NaOH). During exposure, the worms built their burrows in the precipitate and the characteristic colour of the precipitate was seen in the gut of the animals and in the faecal pellets.

After quality assurance of the identified endpoints a total of 51 unique effects concentrations for hexavalent chromium met the criteria for inclusion. These endpoints were obtained from nine different studies reporting responses in 13 species from four taxonomic groups, annelida, crustacea, mollusca and echinodermata, covering the trophic levels of primary- and/or secondary consumers. The consumers considered either strict herbivores or carnivores are listed as primary or secondary consumers in Table 4.11. Consumers not strictly herbivores or carnivores are listed as combined primary/secondary consumers in the Table. Of the 51 data sets five were chronic data; four of these were associated with effects on fertility, and one with lethality. The remaining 41 data sets were acute data associated with lethality.

Table 4.11 Water only exposure effect concentration data for hexavalent chromium salts. Extended Tables with experimental and analytical conditions are listed in Appendix 4.5. References to the cited literature are listed at the end of this section (chromium).

Taxonomic Group	**Species**	**Trophic Level**	**End-point Parameter**	**Effect conc. (mg/l)**	**Ref.**	**Comments**
Annelida: Polychaeta	*Neanthes arenaceodentata*	PC/SC	LC$_{50\text{ 96 hours}}$ /Acute	2,22	{2}	
Annelida: Polychaeta	*Neanthes arenaceodentata*	PC/SC	LC$_{50\text{ 7 days}}$ /Acute	1,89	{2}	
Annelida: Polychaeta	*Neanthes arenaceodentata*	PC/SC	LC$_{50\text{ 7 days}}$ /Acute	1,15	{2}	
Annelida: Polychaeta	*Neanthes arenaceodentata*	PC/SC	LC$_{50\text{ 96 hours}}$ /Acute	3,23	{2}	
Annelida: Polychaeta	*Neanthes arenaceodentata*	PC/SC	LC$_{50\text{ 7 days}}$ /Acute	1,48	{2}	
Annelida: Polychaeta	*Neanthes arenaceodentata*	PC/SC	LC$_{50\text{ 96 hours}}$ /Acute	3,45	{2}	
Annelida: Polychaeta	*Neanthes arenaceodentata*	PC/SC	LC$_{50\text{ 7 days}}$ /Acute	1,78	{2}	
Annelida: Polychaeta	*Neanthes arenaceodentata*	PC/SC	LC$_{50\text{ 7 days}}$ /Acute	1,77	{2}	Test animals F$_1$ of parents exposed to 0,0125 mg/L Cr(VI) throughout their life cycle in a prev. study.
Annelida: Polychaeta	*Neanthes arenaceodentata*	PC/SC	LC$_{50\text{ 96 hours}}$ /Acute	3,63	{2}	Test animals F$_1$ of parents exposed to 0,025 mg/L Cr(VI) throughout their life cycle in a prev. study.
Annelida: Polychaeta	*Neanthes arenaceodentata*	PC/SC	LC$_{50\text{ 7 days}}$ /Acute	1,7	{2}	Test animals F$_1$ of parents exposed to 0,025 mg/L Cr(VI) throughout their life cycle in a prev. study.
Annelida: Polychaeta	*Neanthes arenaceodentata*	PC/SC	LC$_{50\text{ 7 days}}$ /Acute	1,67	{2}	Test animals F$_1$ of parents exposed to 0,05 mg/L Cr(VI) throughout their life cycle in a prev. study.
Annelida: Polychaeta	*Neanthes arenaceodentata*	PC/SC	EC$_{50\text{ Reduction in brood size}}$ /Chronic	0,025	{2}	Test animals F$_1$ of parents exposed to 0,025 mg/L Cr(VI) throughout their life cycle in a prev. study. F$_1$ exposed for > 153 days.
Crustacea: Amphipoda	*Allorchestes compressa*	PC/SC	LC$_{50\text{ 96 hours}}$ /Acute	5,56	{3}	Test animals from Middle Spit, Australia.
Crustacea: Amphipoda	*Allorchestes compressa*	PC/SC	LC$_{50\text{ 96 hours}}$ /Acute	6,34	{3}	Test animals from from Somers, Australia.
Crustacea: Decapoda	*Callinectes sapidus*	SC	LC$_{50\text{ 24 hours}}$ /Acute	171	{4}	

Table 4.11 Water only exposure effect concentration data for hexavalent chromium salts continued

Taxonomic Group	**Species**	**Trophic Level**	**End-point Parameter**	**Effect conc. (mg/l)**	**Ref.**	**Comments**
Crustacea: Decapoda	*Callinectes sapidus*	SC	LC$_{50\ 48\ hours}$ /Acute	130	{4}	
Crustacea: Decapoda	*Callinectes sapidus*	SC	LC$_{50\ 72\ hours}$ /Acute	114	{4}	
Crustacea: Decapoda	*Callinectes sapidus*	SC	LC$_{50\ 96\ hours}$ /Acute	98	{4}	
Mollusca: Bivalvia	*Rangia cuneata*	PC	LC$_{50\ 48\ hours}$ /Acute	86	{5}	Salinity 22 ppt.
Mollusca: Bivalvia	*Rangia cuneata*	PC	LC$_{50\ 72\ hours}$ /Acute	73	{5}	Salinity 22 ppt.
Mollusca: Bivalvia	*Rangia cuneata*	PC	LC$_{50\ 96\ hours}$ /Acute	35	{5}	Salinity 22 ppt.
Annelida: Polychaeta	*Neanthes arenaceodentata*	PC/SC	LC$_{50\ 28\ days}$ /Chronic	0,7	{6}	
Annelida: Polychaeta	*Neanthes arenaceodentata*	PC/SC	LC$_{50\ 28\ days}$ /Chronic	0,55	{6}	
Annelida: Polychaeta	*Neanthes arenaceodentata*	PC/SC	LC$_{50\ 96\ hours}$ /Acute	5	{6}	
Annelida: Polychaeta	*Neanthes arenaceodentata*	PC/SC	LC$_{50\ 28\ days}$ /Chronic	0,28	{6}	
Annelida: Polychaeta	*Capitella capitata*	PC/SC	LC$_{50\ 5\ months}$ /Chronic	0,26 [1]	{7}	
Crustacea: Copepoda	*Tisbe battagliai*	PC/SC	LC$_{50\ 96\ hours}$ /Acute	5,9	{8}	
Crustacea: Copepoda	*Tisbe battagliai*	PC/SC	NOEC $_{8\ days\ Reproduction}$ /Chronic	0,32	{8}	
Crustacea: Copepoda	*Tisbe battagliai*	PC/SC	LOEC $_{8\ days\ Reproduction}$ /Chronic	0,56	{8}	
Crustacea: Copepoda	*Tisbe battagliai*	PC/SC	SChV $_{8\ days\ Reproduction}$ /Chronic [2]	0,42	{8}	
Crustacea: Copepoda	*Tisbe battagliai*	PC/SC	LC$_{50\ 96\ hours}$ /Acute	1,6	{8}	
Crustacea: Copepoda	*Tisbe battagliai*	PC/SC	NOEC $_{8\ days\ Survival}$ /Chronic	0,32	{8}	
Crustacea: Copepoda	*Tisbe battagliai*	PC/SC	LOEC $_{8\ days\ Survival}$ /Chronic	0,56	{8}	
Crustacea: Copepoda	*Tisbe battagliai*	PC/SC	SChV $_{8\ days\ Survival}$ /Chronic [2]	0,42	{8}	
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	LC$_{50\ 10\ days}$ /Acute	1,98	{1}	
Annelida: Polychaeta	*Nereis virens*	PC/SC	LC$_{50\ 24\ hours}$ /Acute	80	{9}	
Annelida: Polychaeta	*Nereis virens*	PC/SC	LC$_{50\ 96\ hours}$ /Acute	2	{9}	
Annelida: Polychaeta	*Nereis virens*	PC/SC	LC$_{50\ 168\ hours}$ /Acute	0,7	{9}	
Crustacea: Decapoda	*Pagurus longicarpus*	SC	LC$_{50\ 24\ hours}$ /Acute	31	{9}	
Crustacea: Decapoda	*Pagurus longicarpus*	SC	LC$_{50\ 96\ hours}$ /Acute	10	{9}	
Crustacea: Decapoda	*Pagurus longicarpus*	SC	LC$_{50\ 168\ hours}$ /Acute	2,7	{9}	
Mollusca: Bivalvia	*Mya arenaria*	PC	LC$_{50\ 24\ hours}$ /Acute	225	{9}	
Mollusca: Bivalvia	*Mya arenaria*	PC	LC$_{50\ 96\ hours}$ /Acute	57	{9}	
Mollusca: Bivalvia	*Mya arenaria*	PC	LC$_{50\ 168\ hours}$ /Acute	8	{9}	
Echinodermata : Asteroidea	*Asterias forbesi*	SC	LC$_{50\ 24\ hours}$ /Acute	540	{9}	
Echinodermata : Asteroidea	*Asterias forbesi*	SC	LC$_{50\ 96\ hours}$ /Acute	32	{9}	
Echinodermata : Asteroidea	*Asterias forbesi*	SC	LC$_{50\ 168\ hours}$ /Acute	10	{9}	

Table 4.11 Water only exposure effect concentration data for hexavalent chromium salts continued

Taxonomic Group	Species	Trophic Level	End-point Parameter	Effect conc. (mg/l)	Ref.	Comments
Mollusca: Gastropoda	*Nassarius obsoletus*	SC	LC$_{50\ 24\ hours}$ /Acute	390	{9}	
Mollusca: Gastropoda	*Nassarius obsoletus*	SC	LC$_{50\ 96\ hours}$ /Acute	105	{9}	
Mollusca: Gastropoda	*Nassarius obsoletus*	SC	LC$_{50\ 168\ hours}$ /Acute	10	{9}	
Annelida: Polychaeta	*Ctenodrilus serratus*	PC/SC	LC$_{50\ 96\ hours}$ /Acute	4,4 $^{1)}$	{9}	

[1] Effect-concentration value calculated by non-linear regression based on data in the paper.

[2] According to Hutchinson *et al.,* {8} the geometric mean of the highest NOEC and the lowest LOEC values were determined, termed the subchronic value (SChV). The SChV is an estimate of the chronic value (termed the ChV and historically was referred to as the maximum accepTable threshold concentration or 'MATC'). The ChV or SChV represents the hypothetical toxic threshold between the NOEC and LOEC for a given biological endpoint ({10}, {11}).

Chromium Toxicity References

{1} Berry, W.J., W.S. Boothman, J.R. Serbst and P.A. Edwards (2004). Predicting the toxicity of chromium in sediments. Environ. Toxicol. Chem., 23: 2981-2992.

{2} Mearns, A.J., P.S. Oshida, M.J. Sherwood, D.R. Young and D.J. Reish (1976). Chromium effects on coastal organisms. J. Water Control Pollut. Fed., 48: 1929-1939.

{3} Ashnullah, A. (1982). Acute toxicity of chromium, mercury, molybdenum and nickel to the amphipod *Allorchestes compressa*. Aust. J. Mar. Fresh. Res., 33: 465-474.

{4} Frank, P.M. and P.B. Robertson (1979). The influence of salinity on toxicity of cadmium and chromium to the blue crab, *Callinectes sapidus*. Bull. Env. Contam. Toxicol., 21: 74-78.

{5} Olson, K.R. and R.C. Harrel (1973). Effect of salinity on acute toxicity of mercury, copper, and chromium for *Rangia cuneata* (Pelecypoda:Mactridae). Contributions in Marine Science, 17: 9-13.

{6} Reish, D.J. and J.M. Martin (1976). The effect of heavy metals on laboratory populations of two polychaetes with comparisons to the water quality conditions and standards in southern California marine waters. Water Res., 10: 299-302

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{9} Eisler, R. and R.J. Hennekey (1977). Acute toxicities of Cd^{2+}, Cr^{6+}, Hg^{2+}, Ni^{2+}, and Zn^{2+} to estuarine macrofauna. Arch. Environ. Con. Tox., 6: 315-323.

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{11} Norberg-King, T. J. (1989). An evaluation of the fathead minnow seven-day subchronic test for estimating chronic toxicity. Environ. Toxicol. Chem., 8: 1075-89.

4.7.3. Copper

Bulk metal effect concentration

After quality assurance of the identified endpoints a total of 28 unique endpoints met the recommendations for inclusion. These endpoints were obtained from seven different studies presenting responses in seven different species from four different taxonomic groups, annelida, crustacea, mollusca and algae, covering the trophic levels of producers as well as primary- and/or secondary consumers. The consumers considered strict herbivores are listed as primary consumers in Table 4.12.

Consumers not strictly herbivores or carnivores are listed as combined primary/secondary consumers in the Table. All the data sets were acute data; four datapoints were associated with behavioural responses, one with inhibition of algal growth and the remaining 23 with lethality.

Table 4.12 Bulk metal effect concentration data for copper. Extended Tables with experimental and analytical conditions are listed in Appendix 4.6. References to the cited literature are listed at the end of this section (copper).

Taxonomic Group	**Species**	**Trophic Level**	**End-point Parameter**	**Effect conc. (µg/g dw.)**	**Ref.**	**Comments**
Crustacea: Amphipoda	*Gammarus locusta*	PC/SC	$LC_{50\ \text{10 days}}$ /Acute	18	{1}	Sediment with 0,5% size-fraction < 0,063mm and sediment TOC: 1%
Crustacea: Amphipoda	*Gammarus locusta*	PC/SC	$LC_{50\ \text{10 days}}$ /Acute	159	{1}	Sediment with 25% size-fraction < 0,063mm and sediment TOC: 2%
Crustacea: Amphipoda	*Gammarus locusta*	PC/SC	$LC_{50\ \text{10 days}}$ /Acute	> 402	{1}	Sediment with 75% size-fraction < 0,063mm and sediment TOC: 4%
Algae: Bacillariophyceae	*Cylindrotheca closterium*	P	$EC_{50\ \text{72 hours}}$ /Acute	26	{2}	
Crustacea: Amphipoda	*Corophium volutator*	PC/SC	$LC_{50\ \text{10 days}}$ /Acute	36,85	{3}	Sediment TOC: 2,1%.
Crustacea: Amphipoda	*Corophium volutator*	PC/SC	$EC_{50\ \text{1hr. Reburial}}$ /Acute[1]	31,66	{3}	Effect endpoint: The ability of the test animals to rebury within 1 hour after 10 days exposure to copper-spiked sediment
Annelida: Polychaeta	*Arenicola marina*	PC/SC	$LC_{50\ \text{10 days}}$ /Acute	20	{3}	Sediment TOC: 1,58%
Annelida: Polychaeta	*Arenicola marina*	PC/SC	$NOEC_{\text{Mortality 10 days}}$ /Acute	Between 7 and 14	{3}	Value estimated from figure 2, p. 227 in the paper. Sediment TOC: 1,58%
Annelida: Polychaeta	*Arenicola marina*	PC/SC	$NOEC_{\text{Zero emergence 10 days}}$ /Acute	< 14	{3}	Value estimated from figure 3, p. 229 in the paper. Sediment TOC: 1,58%
Annelida: Polychaeta	*Arenicola marina*	PC/SC	$NOEC_{\text{Number of casts 10 days}}$ /Acute	< 7	{3}	Value estimated from figure 4, p. 231 in the paper. Sediment TOC: 1,58%
Annelida: Polychaeta	*Arenicola marina*	PC/SC	$NOEC_{\text{Size of casts 10 days}}$ /Acute	Between 7 and 14	{3}	Value estimated from figure 5, p. 232 in the paper. Sediment TOC: 1,58%
Crustacea: Amphipoda	*Paracorophium excavatum*	PC/SC	$LC_{50\ \text{10 days}}$ /Acute	43	{4}	
Crustacea: Amphipoda	*Gammarus locusta*	PC/SC	$LC_{50\ \text{10 days}}$ /Acute	6,8	{5}	Sediment with 0,5% size-fraction < 0,063mm and sediment TVS: 0,9%
Crustacea: Amphipoda	*Gammarus locusta*	PC/SC	$LC_{50\ \text{10 days}}$ /Acute	56,7	{5}	Sediment with 25% size-fraction < 0,063mm and sediment TVS: 1,9%
Crustacea: Amphipoda	*Gammarus locusta*	PC/SC	$LC_{50\ \text{10 days}}$ /Acute	Over 160	{5}	Sediment with 75% size-fraction < 0,063mm and sediment TVS: 7,1%
Crustacea: Amphipoda	*Corophium volutator*	PC/SC	$LC_{50\ \text{10 days}}$ /Acute	129	{6}	
Mollusca: Bivalvia	*Mulinia lateralis*	PC	$LC_{50\ \text{96 hours}}$ /Acute	44,5	{7}	Test animals 35 days old at start of exposure
Mollusca: Bivalvia	*Mulinia lateralis*	PC	$LC_{50\ \text{96 hours}}$ /Acute	53,4	{7}	Test animals 42 days old at start of exposure
Mollusca: Bivalvia	*Mulinia lateralis*	PC	$LC_{50\ \text{96 hours}}$ /Acute	23,5	{7}	Test animals 56 days old at start of exposure
Mollusca: Bivalvia	*Mulinia lateralis*	PC	$LC_{50\ \text{96 hours}}$ /Acute	19,9	{7}	Test animals 49 days old at start of exposure
Mollusca: Bivalvia	*Mulinia lateralis*	PC	$LC_{50\ \text{96 hours}}$ /Acute	21,3	{7}	Test animals 63 days old at start of exposure
Mollusca: Bivalvia	*Mulinia lateralis*	PC	$LC_{50\ \text{96 hours}}$ /Acute	29,5	{7}	Test animals 77 days old at start of exposure
Mollusca: Bivalvia	*Mulinia lateralis*	PC	$LC_{50\ \text{96 hours}}$ /Acute	31,2	{7}	Test animals 70 days old at start of exposure
Mollusca: Bivalvia	*Mulinia lateralis*	PC	$LC_{50\ \text{96 hours}}$ /Acute	57,1	{7}	Test animals 84 days old at start of exposure
Mollusca: Bivalvia	*Mulinia lateralis*	PC	$LC_{50\ \text{96 hours}}$ /Acute	29	{7}	Test animals 91 days old at start of exposure
Mollusca: Bivalvia	*Mulinia lateralis*	PC	$LC_{50\ \text{96 hours}}$ /Acute	48,9	{7}	Test animals 98 days old at start of exposure
Mollusca: Bivalvia	*Mulinia lateralis*	PC	$LC_{50\ \text{96 hours}}$ /Acute	38,2	{7}	Test animals 112 days old at start of exposure
Mollusca: Bivalvia	*Mulinia lateralis*	PC	$LC_{50\ \text{96 hours}}$ /Acute	14,6	{7}	Test animals 105 days old at start of exposure

[1] Effect endpoint: reburial in clean sediment within 1 hour after 10 days exposure to Cd in sediment.

SEM effect concentrations

After quality assurance of the identified endpoints for copper in sediments, only a single study met the criteria for inclusion. The study reported responses in one species, the crustacean *Ampelisca abdita*, considered a combined primary/secondary consumer. A total of 12 corresponding SEM-effect concentration sets of data were identified along with two data sets for unspiked controls (Table 4.13). All the data sets were acute data associated with lethality.

Table 4.13 SEM effect concentration data for copper. Extended Tables with experimental and analytical conditions are listed in Appendix 4.7. References to the cited literature are listed at the end of this section (copper).

Taxonomic Group	**Species**	**Trophic Level**	**Effect endpoint/ type/ Test duration**	**AVS (µmol/ g dw)**	**Effect size (%)**	**[SEM] (µmol/ g dw)**	**[SEM]/ AVS-ratio**	**Ref.**	**Comments**
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/ Acute/ 10 days	13,3	12,5	0,27	0,02	{8}	Unspiked control. Sediment TOC: 0,88%,
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/ Acute/ 10 days	12,2	7,5	1,00	0,10	{8}	Sediment TOC: 0,88%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/ Acute/ 10 days	4,44	17,5	1,57	0,35	{8}	Sediment TOC: 0,88%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/ Acute/ 10 days	1,21	100,0	11,6	9,6	{8}	Sediment TOC: 0,88%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/ Acute/ 10 days	1,94	100,0	47,0	24,3	{8}	Sediment TOC: 0,88%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/ Acute/ 10 days	1,67	100,0	176,0	105,0	{8}	Sediment TOC: 0,88%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/ Acute/ 10 days	1,84	100,0	306,0	166,0	{8}	Sediment TOC: 0,88%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/ Acute/ 10 days	1,22	22,5	0,00	0,00	{8}	Unspiked control. Sediment TOC: 0,15%,
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/ Acute/ 10 days	1,42	5,0	0,05	0,04	{8}	Sediment TOC: 0,15%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/ Acute/ 10 days	1,08	15,0	0,09	0,08	{8}	Sediment TOC: 0,15%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/ Acute/ 10 days	0,635	30,0	0,43	0,68	{8}	Sediment TOC: 0,15%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/ Acute/ 10 days	0,323	100,0	2,08	6,46	{8}	Sediment TOC: 0,15%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/ Acute/ 10 days	0,345	100,0	5,40	15,67	{8}	Sediment TOC: 0,15%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/ Acute/ 10 days	0,63	100,0	10,40	16,58	{8}	Sediment TOC: 0,15%

Copper Toxicity References

{1} Correia, A.D. and M.H. Costa (2000). Effects of sediment geochemical properties on the toxicity of copper-spiked sediments to the marine amphipod *Gammarus locusta*. Sci. Total Environ., 247: 99-106.

{2} Moreno-Garrido, I., M. Hampel, L.M. Lubián and J. Blasco (2003). Sediment toxicity tests using benthic marine microalgae *Cylindrotheca closterium* (Ehremberg) Lewin and Reimann (Bacillariophyceae). Ecotox. Environ. Safety, 54: 290-295.

{3} Bat, L. and D. Raffaelli (1998). Sediment toxicity testing: a bioassay approach using the amphipod *Corophium volutator* and the polychaete *Arenicola marina*. J. Exp. Mar Biol. Ecol., 226: 217-239.

{4} Marsden, I. D., and C.H.T. Wong (2001). Effects of sediment copper on a tube-dwelling estuarine amphipod, *Paracorophium excavatum*. Marine and Freshwater Research, 52: 1007-1014.

{5} Costa, F.O., A.D. Correia and M.H. Costa (1996). Sensitivity of a marine amphipod to non-contaminant variables and to copper in the sediment. Écologie, 27: 269-276.

{6} Briggs, A.D., N. Greenwood and A. Grant (2003). Can turbidity caused by *Corophium volutator* (Pallas) activity be used to assess sediment toxicity rapidly? Mar. Environ. Res., 55: 181-192.

{7} Burgess, R.M., B.A. Rogers, S.A. Rego, J.M. Corbin and G.E. Morrison (1994). Sand spiked with copper as a reference toxicant material for sediment toxicity testing: A preliminary evaluation. Arch. Environ. Contam. Toxicol., 26: 163-168.

{8} Berry, W.J., J.D. Hansen, J.D. Mahony, D.L. Robson, D.M. Di Toro, B.P. Shipley, B. Rogers, J.M. Corbin and W.S. Bootman (1996). Predicting the toxicity of metal-spiked laboratory sediments using acid-volatile sulphide and interstitial water normalizations. Environ. Toxicol. Chem., 15: 2067-2079.

4.7.4. Mercury

Only effects of inorganic forms of mercury were included in the literature review.

Bulk metal effect concentrations

After quality assurance of the identified endpoints for mercury, only a single study met the criteria for inclusion. The study reported the responses in one species, the crustacean *Rhepoxynius abronius*, considered a combined primary/secondary consumer. The data set were acute data associated with lethality (Table 4.14).

Table 4.14 Bulk metal effect concentration data for mercury. Extended Tables with experimental and analytical conditions are listed in Appendix 4.8. References to the cited literature are listed at the end of this section (mercury).

Taxonomic Group	**Species**	**Trophic Level**	**End-point Parameter**	**Effect conc. (µg/g dw)**	**Ref.**	**Comments**
Crustacea: Amphipoda	*Rhepoxynius abronius*	PC/SC	$LC_{50\ 10\ days}$ /Acute	15,2	{1}	Sediment TVS: 1,4%.

Mercury Toxicity References

{1} Swartz, R.C., P.F. Kemp, D.W. Scults and J.O. Lamberson (1988). Effects of mixtures of sediment contaminants on the marine infaunal amphipod, *Rhepoxynius abronius*. Environ. Toxicol. Chem., 7: 1013-1020.

4.7.5. Lead

Bulk metal effect concentrations

After quality assurance of the identified endpoints for lead in sediments, two unique points met the recommendations for inclusion. These endpoints were obtained from two different studies presenting responses in two different species from two different taxonomic groups, crustacea and algae, covering the trophic levels of producers and consumers. The crustacean, *Amphiascus tenuiremis*, is considered a combined primary/secondary consumer. All the data sets were acute data; one associated with inhibition of algal growth and one with lethality (Table 4.15).

Table 4.15 Bulk metal effect concentration data for lead. Extended Tables with experimental and analytical conditions are listed in Appendix 4.9. References to the cited literature are listed at the end of this section (lead).

Taxonomic Group	**Species**	**Trophic Level**	**End-point Parameter**	**Effect conc. (µg/g dw)**	**Ref.**	**Comments**
Algae: Bacillariophyceae	*Cylindrotheca closterium*	P	$EC_{50\ 72\ hours}$ /Acute	29	{1}	
Crustacea: Copepoda	*Amphiascus tenuiremis*	PC/SC	$LC_{50\ 96\ hours}$ /Acute	2462	{2}	Sediment TOC: 2,77%

SEM effect concentrations

After quality assurance of the identified endpoints for lead, only a single study met the criteria for inclusion. The study reported responses in one species, the crustacean *Ampelisca abdita*, considered a combined primary/secondary consumer. A total of 12 corresponding SEM-effect concentration sets of data were identified along with two data sets for unspiked controls (Table 4.16). All the data sets were acute data associated with lethality.

Table 4.16 SEM effect concentration data for lead. Extended Tables with experimental and analytical conditions are listed in Appendix 4.10. References to the cited literature are listed at the end of this section (lead).

Taxonomic Group	**Species**	**Trophic Level**	**Effect endpoint/ type/ Test duration**	**AVS (µmol/ g dw)**	**Effect size (%)**	**[SEM] (µmol/ g dw)**	**[SEM]/ AVS-ratio**	**Ref.**	**Comments**
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/ 10 days	19,9	10,0	0,23	0,01	{3}	Sediment TOC: 0,88%. Unspiked control
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/ 10 days	18,6	5,0	1,25	0,07	{3}	Sediment TOC: 0,88%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/ 10 days	12,8	12,5	4,14	0,32	{3}	Sediment TOC: 0,88%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/ 10 days	16,4	7,5	14,50	0,89	{3}	Sediment TOC: 0,88%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/ 10 days	14,9	22,5	28,30	1,90	{3}	Sediment TOC: 0,88%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/ 10 days	15,5	42,5	67,90	4,38	{3}	Sediment TOC: 0,88%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/ 10 days	14,2	100,0	78,20	5,49	{3}	Sediment TOC: 0,88%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/ 10 days	1,2	10,0	0,02	0,02	{3}	Sediment TOC: 0,15%. Unspiked control
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/ 10 days	1,92	17,5	0,20	0,09	{3}	Sediment TOC: 0,15%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/ 10 days	2,23	15,0	0,60	0,26	{3}	Sediment TOC: 0,15%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/ 10 days	3,1	5,0	1,70	0,60	{3}	Sediment TOC: 0,15%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/ 10 days	5,75	17,5	7,10	1,24	{3}	Sediment TOC: 0,15%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/ 10 days	4,08	55,0	16,60	4,08	{3}	Sediment TOC: 0,15%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/ 10 days	3,37	92,5	20,20	5,97	{3}	Sediment TOC: 0,15%

Lead Toxicity References

{1} Moreno-Garrido, I., M. Hampel, L.M. Lubián and J. Blasco (2003). Sediment toxicity tests using benthic marine microalgae *Cylindrotheca closterium* (Ehremberg) Lewin and Reimann (Bacillariophyceae). Ecotox. Environ. Safety, 54: 290-295.

{2} Hagiopan-Schlekat, T., G.T. Chandler and T.J. Shaw (2001). Acute toxicity of five sediment-associated metals, individually and in a mixture, to the estuarine meiobenthic harpactoid copepod *Amphiascus tenuiremis*. Marine Environmental Research, 51: 247-264.

{3} Berry, W.J., J.D. Hansen, J.D. Mahony, D.L. Robson, D.M. Di Toro, B.P. Shipley, B. Rogers, J.M. Corbin and W.S. Bootman (1996). Predicting the toxicity of metal-spiked laboratory sediments using acid-volatile sulphide and interstitial water normalizations. Environ. Toxicol. Chem., 15: 2067-2079.

4.7.6. Zinc

Bulk metal effect concentrations

After quality assurance of the identified endpoints for zinc in sediments, a total of nine unique endpoints met the recommendations for inclusion. These endpoints were obtained from three different studies reporting responses in different species from two taxonomic groups, crustacea and annelida, covering only the consumer trophic level. None of the consumers were strictly herbivores or carnivores and are listed as combined primary/secondary consumers in the Table 4.17. All the data sets were acute data; four datapoints were associated with behavioural responses and the remaining five with lethality.

Table 4.17 Bulk metal effect concentration data for zinc. Extended Tables with experimental and analytical conditions are listed in Appendix 4.11. References to the cited literature are listed at the end of this section (zinc).

Taxonomic Group	Species	Trophic Level	End-point Parameter	Effect conc. (µg/g dw)	Ref.	Comments
Crustacea: Amphipoda	*Corophium volutator*	PC/SC	$\mathrm{LC_{50\ 10\ days}}$ /Acute	31,9	{1}	Sediment TOC: 2,1%
Crustacea: Amphipoda	*Corophium volutator*	PC/SC	$\mathrm{EC_{50\ 1hr.\ Reburial}}$ /Acute	28,6	{1}	Effect endpoint: The ability of the test animals to rebury within 1 hour after 10 days exposure to copper-spiked sediment
Annelida: Polychaeta	*Arenicola marina*	PC/SC	$\mathrm{LC_{50\ 10\ days}}$ /Acute	50	{1}	Sediment TOC: 1,58%
Annelida: Polychaeta	*Arenicola marina*	PC/SC	$\mathrm{NOEC_{Mortality\ 10\ days}}$ /Acute	Between 23 and 52	{1}	Value estimated from figure 2, p. 227 in the paper. Sediment TOC: 1,58%
Annelida: Polychaeta	*Arenicola marina*	PC/SC	$\mathrm{NOEC_{Zero\ emergence\ 10\ days}}$ /Acute	Between 23 and 52	{1}	Value estimated from figure 3, p. 229 in the paper. Sediment TOC: 1,58%
Annelida: Polychaeta	*Arenicola marina*	PC/SC	$\mathrm{NOEC_{Number\ of\ casts\ 10\ days}}$ /Acute	< 23	{1}	Value estimated from figure 4, p. 231 in the paper. Sediment TOC: 1,58%
Annelida: Polychaeta	*Arenicola marina*	PC/SC	$\mathrm{NOEC_{Size\ of\ casts\ 10\ days}}$ /Acute	Between 23 and 52	{1}	Value estimated from figure 5, p. 232 in the paper. Sediment TOC: 1,58%
Crustacea: Amphipoda	*Rhepoxynius abronius*	PC/SC	$\mathrm{LC_{50\ 10\ days}}$ /Acute	270	{2}	Sediment TVS: 1,4%
Crustacea: Copepoda	*Amphiascus tenuiremis*	PC/SC	$\mathrm{LC_{50\ 96\ hours}}$ /Acute	671,3	{3}	Sediment TOC: 2,77%

SEM effect concentrations

After quality assurance of the identified endpoints for zinc, only a single study met the criteria for inclusion. The study reported responses in one species, the crustacean *Ampelisca abdita*, considered a combined primary/secondary consumer. A total of 12 corresponding SEM-effect concentration sets of data were identified along with two data sets for unspiked controls (Table 4.18). All the data sets were acute data associated with lethality.

Table 4.18 SEM effect concentration data for zinc. Extended Tables with experimental and analytical conditions are listed in Appendix 4.12. References to the cited literature are listed at the end of this section (zinc).

Taxonomic Group	Species	Trophic Level	Effect endpoint/ type/ Test duration	AVS (µmol/ g dw)	Effect size (%)	[SEM] (µmol/ g dw)	[SEM]/ AVS-ratio	Ref.	Comments
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/10 days	11,2	15,0	1,20	0,10	{4}	Sediment TOC: 0,88%. Unspiked control
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/10 days	11,7	7,5	2,80	0,24	{4}	Sediment TOC: 0,88%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/10 days	13,4	17,5	5,50	0,41	{4}	Sediment TOC: 0,88%

Table 4.18 SEM effect concentration data for zinc continued

Taxonomic Group	Species	Trophic Level	Effect endpoint/ type/ Test duration	AVS (µmol/ g dw)	Effect size (%)	[SEM] (µmol/ g dw)	[SEM]/ AVS-ratio	Ref.	Comments
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/10 days	15,1	15,0	20,30	1,34	{4}	Sediment TOC: 0,88%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/10 days	18,2	77,5	74,30	4,09	{4}	Sediment TOC: 0,88%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/10 days	15	100,0	155,00	10,30	{4}	Sediment TOC: 0,88%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/10 days	14	100,0	140,00	9,96	{4}	Sediment TOC: 0,88%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/10 days	2,25	5,0	0,01	0,00	{4}	Sediment TOC: 0,15%. Unspiked control
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/10 days	2,48	12,5	0,30	0,11	{4}	Sediment TOC: 0,15%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/10 days	3	12,5	0,70	0,23	{4}	Sediment TOC: 0,15%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/10 days	2,73	5,0	1,50	0,54	{4}	Sediment TOC: 0,15%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/10 days	1,82	35,0	2,00	1,09	{4}	Sediment TOC: 0,15%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/10 days	1,31	95,0	4,13	3,15	{4}	Sediment TOC: 0,15%
Crustacea: Amphipoda	*Ampelisca abdita*	PC/SC	Mortality/Acute/10 days	1,94	100,0	8,82	4,54	{4}	Sediment TOC: 0,15%

Zinc Toxicity References

{1} Bat, L. and D. Raffaelli (1998). Sediment toxicity testing: a bioassay approach using the amphipod *Corophium volutator* and the polychaete *Arenicola marina*. J. Exp. Mar Biol. Ecol., 226: 217-239.

{2} Swartz, R.C., P.F. Kemp, D.W. Scults and J.O. Lamberson (1988). Effects of mixtures of sediment contaminants on the marine infaunal amphipod, *Rhepoxynius abronius*. Environ. Toxicol. Chem., 7: 1013-1020.

{3} Hagiopan-Schlekat, T., G.T. Chandler and T.J. Shaw (2001). Acute toxicity of five sediment-associated metals, individually and in a mixture, to the estuarine meiobenthic harpactoid copepod *Amphiascus tenuiremis*. Marine Environmental Research, 51: 247-264.

{4} Berry, W.J., J.D. Hansen, J.D. Mahony, D.L. Robson, D.M. Di Toro, B.P. Shipley, B. Rogers, J.M. Corbin and W.S. Bootman (1996). Predicting the toxicity of metal-spiked laboratory sediments using acid-volatile sulphide and interstitial water normalizations. Environ. Toxicol. Chem., 15: 2067-2079.

4.8. Sediment Physiochemical Factors Mediating Metal Bioavailability and Toxicity

Metals enter the marine environment from many natural and human activity sources and in many physical or chemical forms. These different forms of metals undergo complex chemical and physical changes, called speciation, when they enter the marine environment or when there are physical or chemical changes in the environmental compartment where they reside. Although many aspects of chemical speciation of most metals of environmental concern in the marine environment are known, kinetics (reaction rates) of these changes and influence of environmental variables are yet poorly understood. Since the physical or chemical species of a metal in seawater or sediments has a marked effect on its bioavailability and toxicity to marine organisms, an understanding of metal speciation is essential for understanding the effects of metals in marine ecosystems.

Metal ions are labile and reactive; they tend to form more or less stable complexes with anions with available electrons for bonding. These complexes can be both free hydrated forms remaining in solution, as well as aggregates, precipitates and particle-adsorbed metals. Some metals, such as many of those associated with drilling discharges, are introduced into the ocean in solid, insoluble forms. These metals are inert, unless they can be transformed to more labile, reactive forms by physical or biological processes in the ocean. Depending on the stability of these different metallic forms, there will be an exchange of metals among the different forms or species as the surrounding physical and chemical conditions change.

The bioavailable, and hence biologically active forms of metals with potential to harm marine organisms, are restricted to the chemical species that can cross the membranes of the organism and enter the interior of the cells. The permeable, bioavailable forms of metals are according to Simkiss and Taylor (1995):

- Free metal ions (e.g., M^{2+})
- Hydrated ions (e.g., $M(H_2O)_6{}^{2+}$)
- Charged metal complexes (e.g., $MCl(H_2O)_5{}^{+}$)
- Uncharged inorganic complexes (e.g., $MCl_2{}^{0}$)
- Some organometallic complexes (e.g., CH_3M^{n+})

These forms are only a fraction of the total metal pool in the sediments. There are few, if any, techniques for sampling and chemical analysis that maintains the chemical integrity of the samples and clearly discriminates among the bioavailable and non-bioavailable fractions of metals. The extraction of sediments with cold, weak acid (1M HCl) and analysis of the supernatant for metals has been used for the last 15 years as an operational definition of the bioavailable fraction of metals in sediment (Luoma, 1989; Di Toro *et al.*, 1990).

Prediction of the metal concentrations in, and toxicity to sediment-dwelling organisms in apparent equilibrium with the sediments is improved when the concentrations of trace metals extracted from the sediments are normalised with respect to concentrations of iron (as hydrous oxides) and total organic carbon in sediments and to co-extracted sulfide in sediments (Tessier and Campbell, 1987; Di Toro *et al.*, 1990; Ankley, 1996). ExtracTable iron (from amorphous and poorly crystalline iron oxy-hydroxides) tends to inhibit the bioavailability of silver, arsenic, copper, mercury, lead, and zinc in sediments; suggesting that these metals sorb preferentially to the reducible fraction of oxidized layers of sediment (Campbell *et al.*, 1988). By normalising metals concentrations to co-extracted iron concentrations, an estimate can be obtained of the most bioavailable fraction of the metals (the fraction in excess of that sorbed to iron oxides). A similar approach has been taken to estimate metal bioavailability based on the ratio of metals to acid-volatile sulfide (AVS) concentrations in sediment (Ankley *et al.*, 1996).

4.8.1. Acid Volatile Sulfide (AVS)

Introduction

Since 1990, there has been a growing attention on the importance of the acid volatile sulfide pool (AVS) as a factor mediating the bioavailability, and hence acute toxicity, of several metals with possible adverse effects on aquatic biota (DiToro *et al.,* 1990, 1992 Ankley *et al.,* 1991, Casas and Crecelius, 1994). AVS is defined operationally as the sulfide liberated from wet sediment by treatment with 1 M HCl (Ankley *et al.,* 1996). Because of the high natural concentration of Fe^{2+} in most sediment, the AVS pool in most uncontaminated marine sediments consists primarily of ferrous sulfides (Kersten and Förstner, 1986, 1991). Several metals of environmental concern form more stable, less soluble metal sulfides than the iron sulfides. These metals include copper, cadmium, lead, nickel, zinc (Ankley, 1996; Ankley *et al.*, 1996), silver, arsenic, and mercury (Luoma, 1989; Allen *et al.*, 1993; Hare *et al.*, 1994; Ankley *et al.*, 1996; Neff, 2002; Berry *et al.*, 1999). In the presence of AVS in sediments, these metals precipitate as their respective metal sulfides. These sulfides precipitate on the surface of sediment particles, are of low solubility, rendering the metals biologically inert as long as the conditions in the sediments are kept suboxic.

Theory behind the SEM/AVS-approach

Sulphate-ions (SO_4^{2-}) are the second most abundant anion in natural seawater next to chloride (Cl^-) with an average of 2,65 ‰ (2.65 g/kg) by weight (Brown *et al.,* 1995). Under hypoxic or suboxic conditions, sulphate is reduced to sulfide (S^{2-}), primarily by sulfide reducing bacteria. In the presence of iron or manganese-ions, the sulfide-ions precipitate as iron monosulfide (mackinawite - $(Fe,Ni)_9S_8$ and greigite - $FeFe_2S_4$), or manganese monosulfide (alabandite – MnS). At lower Eh of anoxic sediments, these slightly labile monosulfides are reduced further to more sTable, insoluble iron disulfide (pyrite – FeS_2) or manganese disulfide (hauerite - MnS_2). The sediment sulfides can be divided into three classes based on their chemical and analytical properties. The sulfides that can be extracted from the sediments by cold weak acid (0.5-1 M HCl, Di Toro *et al.,* 1990) make up the AVS and are mainly iron and manganese monosulfides. The second sulfide pool is made up mainly of pyrite and hauerite (because of the abundance of iron and manganese in marine sediments), and the third pool from organic sulfides. The second and third sulfide pools are not extracted by cold weak acid and are not included in the analysis of AVS. The metal cations mentioned above that are not associated with AVS, adsorbed to iron oxide coatings or organic films on clay particles are present in sediments mainly as stable metal sulfides or metal organic complexes, or in the mineral lattice of sediment minerals. These metals are not bioavailable. The metals co-extracted with AVS are considered to be bioavailable under some conditions.

Iron monosulfide (FeS_{solid}) is in equilibrium with aqueous sulfide ions in the surrounding water phase according to the Equation:

$$\text{“}FeS_{solid}\text{”} \leftrightarrow Fe^{2+}_{aq} + S^{2-}_{aq} \quad (4\text{-}1)$$

When another divalent metal ion (Me^{2+}_{aq}), which is able to form a sulfide with lower solubility than the Mn/Fe monosulfides is introduced in this system, a new equilibrium will be established:

$$Me^{2+}_{aq} + \text{“}FeS_{solid}\text{”} \leftrightarrow \text{“}FeS_{solid}\text{”}\ Me^{2+}_{aq} + Fe^{2+}_{aq} + S^{2-}_{aq} \quad (4\text{-}2)$$

If the concentration of the divalent metal ion Me^{2+}_{aq} exceeds the solubility for the “MeS_{solid}”-sulfide, precipitation will begin:

$$Me^{2+}_{aq} + \text{“}FeS_{solid}\text{”} \rightarrow \text{“}MeS_{solid}\text{”} + Me^{2+}_{aq} + Fe^{2+}_{aq} + S^{2-}_{aq} \quad (4\text{-}3)$$

The divalent metals nickel (Ni), zinc (Zn), cadmium (Cd), lead (Pb), copper (Cu), mercury (Hg), silver (Ag) and arsenic (probably as $FeAs^{2+}$) are all able to form sulfides of lower solubility than the sulfides in the AVS-pool. Solubility products of selected sulfides are listed in Table 4.19. Each metal forming a sulfide with a lower (more negative) solubility product ($\log_{10} K_{sp}$) is able to displace the metal ions in the sulfides with the higher (less negative) solubility product. Hence all the listed metals in Table 4.17 are able to displace manganese and iron from the sulfides in the AVS-pool.

Table 4.19 Solubility for selected divalent metal sulfides. Data from Van den Hoop *et al.*, (1997).

Sulfide	**$\log_{10} K_{sp}$**	**Sulfide**	**$\log_{10} K_{sp}$**
MnS (alabandite)	-13.33	PbS (galena)	-28,04
FeS (mackinawite)	-18,80	CdS (greenocktite)	-28,85
NiS (millerite)	-20,97	CuS (covellite)	-35,90
ZnS (wurtzite)	-24,53	HgS (metacinnabar)	-52,19

Sulfide-ions (S^{2-}) can bind equi-molar amounts of divalent metal-ions. When the binding capacity of the sulfide-pool in the sediment is exceeded, the excess metal ions or adsorbed metals will theoretically exist in exchangeable, labile forms on sediment particles or in pore water. The free ions of metals are the most biologically available forms, and may cause adverse effects in organisms. If the sulfide-pool was the only factor mediating the concentration of free metal ions in the pore water, the concentration of free ions should rise when the moles of metal ions exceed the moles of available, labile sulfide ions (AVS). As the difference between the molar concentration of the "simultaneously extracted metal"[1] (SEM) and AVS increases above 0, the concentration of free metal ions in the pore water should rise.

If the molar concentration of AVS in sediments is higher than the sum of the molar concentrations of the cationic metals in the 1 M HCl extract (the simultaneously extracted metals [SEM]) of the sediment, all of the metals are in insoluble, non-bioavailable forms in the sediments. As the AVS concentration decreases or the SEM concentration increases, the fraction of SEM that is in solution in sediment pore water in potentially bioavailable forms increases. These relationships can be summarised as follows:

SEM:AVS<1, metals are not likely to be bioavailable
SEM:AVS >1, metals are likely to be present in bioavailable forms

Thus, at equilibrium, the molar ratio of SEM to AVS ("SEM/AVS") may be a good predictor of the fraction of total metal in sediments that is bioavailable. If molar SEM/AVS < 1 in sediments, the sediment-associated metals are not bioavailable and toxic; if SEM/AVS > 1, some of the metals may be present in pore water in bioavailable forms and, if bioavailable metals concentrations are high enough, may be toxic to sediment-dwelling organisms (Ankley *et al.*, 1996).

If the SEM:AVS>1, SEM:AVS data can be used to calculate the available fraction of metals for use as a sediment PEC. It is important to note that each of the metals evaluated has a different binding affinity for sulfides (EPA, 1994). Currently there is considerable debate regarding the relative affinities of each of the metals. Relative affinities of metals for sulfide increase as the log K_{sp} decreases. Mercury and copper have the lowest log K_{sp} values (Table 4.19) indicating that the affinity of these metals for AVS is higher than that of the other metal cations.

The Hg concentration in sediments nearly always is much lower than concentrations of all other metals, so it doesn't usually compete with other metals for complexation with AVS.

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[1] The concentration of the metal ion(s) that can be extracted with weak cold acid as used for extracting the AVS and termed SEM or EM for short. Often considered the biological available fraction of the metal in the sediment.

It usually is assumed that, at equilibrium, copper preferentially reacts with AVS, displacing all other metals. If the available AVS is not completely saturated by copper, then the remaining metals react in the following order: lead, cadmium, zinc, and nickel. In this model, the fraction of copper in the sediment that is potentially bioavailable and toxic is considered to be defined as follows:

(4-4) $$Cu_b = ([Cu_{SEM}] - [AVS]) \times (MW_{Cu})$$

where,

Cu_b = fraction of copper that is bioavailable
$[Cu_{SEM}]$ = molar concentration of Cu as defined by simultaneous extraction with diluted acid
[AVS] = molar concentration of AVS
MW_{Cu} = molecular weight of copper (mg/moles).

The concentration (mg/kg sediment) of bioavailable copper in sediments is:

(4-5) $$Cu_{bioavailable} = [Cu_{sediment}] \times Cu_b$$

where,

$[Cu_{sediment}]$ is the molar concentration of total copper in sediment.

The bioavailable fraction of the other metals in sediment may be determined in the same manner, following the order described above. For each successive metal, the molar concentration of AVS applied should be decreased according to the molar concentration of the preceding chemical in the SEM fraction; when the concentration of AVS is zero, all remaining metals are assumed to be bioavailable.

Several studies have been performed to elucidate the link between AVS in the sediment, the SEM, and the corresponding biological effects. Because the exposure concentration expressed as SEM co-varies with the AVS at the different exposure concentrations, a good fit to a theoretical dose-response curve rarely is achieved and an EC/LC_{50} value is difficult to calculate. In section 4.7, data for each effect concentration in the studies reviewed that included corresponding concentration data for AVS and SEM are listed in separate Tables for those metals. These studies include both controlled laboratory experiments as well as data generated from field-based sampling and monitoring.

For the SEM/AVS-approach to be applicable for predicting metal toxicity in sediments a given set of criteria has to be met (US EPA, 2000):

- The different metals and the corresponding chemical species are at equilibrium both chemically (speciation) and with the sediment compartments (physical interactions with surfaces).
- The toxic effects of the different metals in the sediments are no more than additive.
- Toxic effects can be predicted from the interstitial pore-water concentration of the metals.

One of the major limitations with the SEM/AVS-approach is the instability of AVS under shifting oxidation state of the sediment. Under normal conditions the surface 2-5 mm of the sediment usually is kept aerobic by the diffusion processes alone, giving a sufficient gradient of oxygen to facilitate the diffusion. The depth of oxygen penetration by diffusion is controlled mainly by the sediment grain size, and fine silt or clay with low permeability and a high organic carbon concentration to fuel the microbial respiration will have only a thin aerobic layer of sediment. The opposite can be found in coarse sand with low organic carbon concentration where the aerobic layer may be several centimetres thick because of fairly good diffusion and low oxygen consumption in the sediment. AVS occurs at low concentration in surface, oxidised layers of sediment and concentration increases with depth below the sediment surface (Boothman *et al.*, 2001).

The majority of the biological activity caused by macro-organisms (a process called bioturbation) is in the aerobic part of the sediment. Either in the naturally aerobic top layer of the sediment or in vented burrows in the suboxic part. Under these conditions the metal-sulfides are re-oxidised, becoming potentially bioavailable, and the SEM/AVS will not be a suitable approach for assessing the bioavailability and toxicity of the metals in the sediment. The concentration of SEM is then most likely to exceed AVS in the biologically active oxidised surface layers of sediments if no other physical phases bind the reactive species of the metal. This re-distribution of SEM and AVS may increase the fraction of total metal cations that is in exchangeable, potentially bioavailable forms. However, under oxidising conditions metals tend to adsorb strongly to surface organic coatings on solid iron oxide and clay particles, limiting bioavailability. Because of the high concentrations of iron and sulfur in marine sediments, much of the metals in all but the most heavily contaminated sediments are complexed to sulfides or iron oxides and little is bioavailable to benthic organisms.

Laboratory derived data supporting the approach.

An early work by Swartz and others (1985) demonstrated a correlation between sediment interstitial (pore) water concentrations of cadmium and toxicity to the marine amphipod *Rhepoxynius abronius* indicating that the acute toxicity was controlled by the concentration in the interstitial water rather than the total bulk concentration in the sediment. Thus, the interstitial water concentrations represent the bioavailable part of the metal, but no apparent binding phase for cadmium in the sediment was identified.

DiToro and others (1990) published the first experimental work showing the link between observed acute toxicity in marine amphipods, corresponding SEM/AVS-ratios and interstitial water concentrations of cadmium. Since then, several studies have confirmed this using both freshwater and marine sediments spiked with cadmium, nickel, lead, copper and zinc (Carlson *et al.,* 1991, DiToro *et al.,* 1992, Green *et al.,* 1993, Casas and Creselius 1994, Berry *et al.,* 1996, Lee and Lee, 2005). The technical basis for transforming this approach into a Sediment Quality Criterion (SQC) is reviewed by Ankley and others (1996). The approach has also been tested and proven promising for sediment silver (Crecelius *et al.,* 1997) and recently chromium (Berry *et al.,* 2004).

Field application of the approach

Parallel to being elucidated in spiked sediment exposures under laboratory conditions, the approach was also applied to field conditions for selected metals. One early study by Moore and others (1988) was focused solely on the physiochemical partitioning processes in sediments rich in sulfide. Thus no ecotoxicological effects were recorded, but valuable data on partitioning of arsenic, copper and zinc in suboxic sediment was obtained. Several studies have tested the approach under field conditions for different metals: cadmium (Hare *et al.,* 1994), cadmium and nickel (Pesch *et al.,* 1995) and mercury (Sferra *et al.,* 1999).

Hansen and others (1996) did a comparison between the bulk metal concentration in field collected sediments and the acute response of amphipods (70 sediments from five saltwater locations) and polychaetes (16 sediments from one salt-water location). Cadmium, copper, lead, nickel and zinc were extracted by ultrasonic treatment of the sediment with cold 2M nitric acid. This extraction protocol is assumed to remove the majority of the metals from the bulk sediment phase. The results are summarised in Figure 4.1. No causal relation between metal concentration (µmol/g dw.) and acute response as percent mortality was apparent. Sediments with metal concentrations ranging from 9,50 to 885 µmol/g were acutely toxic (> 24% mortality, 10 days exposure) and sediments with concentrations in the range 0,20 to 885 µmol/g were not toxic (≤ 24% mortality, 10 days exposure).

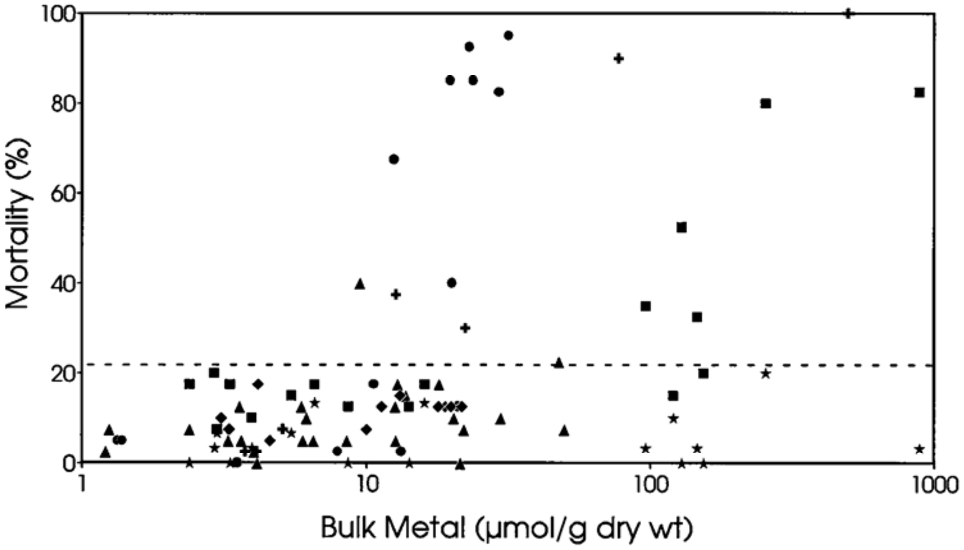

Figure 4.1. Percent mortality of the amphipod *Ampelisca albida* (*A.a*) and the polychaete *Neanthes arenaecodentata* (*N.a.*) in sediments from saltwater locations in a salt mash (▲= *A.a.*), Belledune Harbour (♦ = *A.a.*), Bear Creek, (● = *A.a.*), Foundry Cove (■ = *A.a.*; * = *N.a.*), and Jinzou Bay (+ = *A.a.*) as a function of the sum of the concentrations of cadmium, copper, lead, nickel and zinc in micromoles divalent metal per. gram dry weight sediment. (From Hansen et al., 1996).

Normalising these data by the simultaneously extracted metal/acid-volatile sulfide (SEM/AVS) ratio instead of bulk concentration yields better agreement between the observed mortality and the theoretical bioavailable pool of reactive metal ions in the sediments, as illustrated in Figure 4.2. The sediments from Bear Creek and Jinzou Bay were found to contain toxic substances in addition to metals, and were excluded in this figure (Hansen *et al.,* 1996). All sediments (42 samples) with SEM/AVS-ratio ≤ 1,0 were not toxic. Of the 32 sediment samples with SEM/AVS > 1,0 only 6 were acutely toxic and the remaining 26 samples were not acutely toxic (24% effect threshold, 10 days exposure). This indicates the presence of binding factors in these samples in addition to the AVS-pool that kept the metals biologically inert.

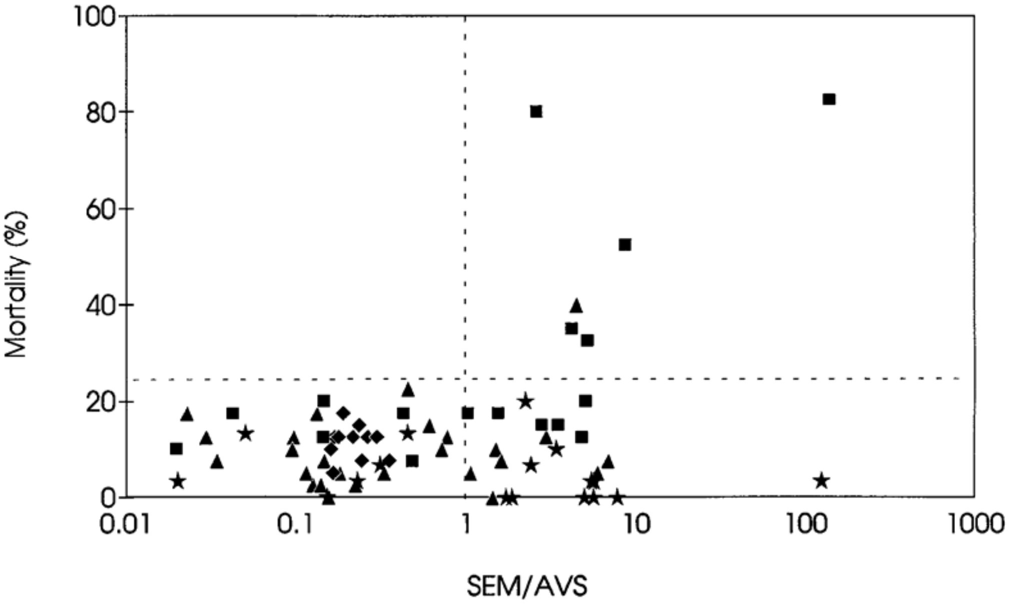

Figure 4.2. Percent mortality of the amphipod *Ampelisca albida* (*A.a*) and the polychaete *Neanthes arenaecodentata* (*N.a.*) in sediments from three saltwater field locations in a salt mash (▲=

A.a.), Belledune Harbour (♦ = *A.a.*), Foundry Cove (■ = *A.a.*; * = *N.a.*) as a function of the SEM/AVS ratio. (From Hansen et al., 1996).

Long and others (1998) did a critical comparison between normalising the effect data (as mortality) on dry weight or SEM/AVS using the same data as Hansen and others (1996). They compared it with the effects range low (ERL) and effects range median (ERM) of Long and others (1995) as well as apparent effects thresholds (AET) of Washington state (Washington Department of Ecology, 1995). Long and others (1998) concluded that "...these data suggest that in comparison with the SEM:AVS criteria, the SQGs based upon total dry weight-normalized metals concentrations were equally, if not more, accurate in correctly predicting both nontoxicity and toxicity in these selected data sets"... They also found that the same SQGs were considerably more sensitive than the SEM/AVS-ratios used in the dataset by Hansen and others (1996).

One of the reasons why the SEM/AVS-approach is not that conclusive on field collected samples may be that the concept was derived based on laboratory experiments with metal-spiked sediments under controlled conditions (DiToro *et al.,* 1990, 1992). Field samples are likely to be a more complex mixture of chemical stressors where only the contributions from the sulfide-forming metals are under control by the SEM/AVS-approach.

4.8.2. Other Binding phases.

Although AVS is an important binding phase for reactive metal species in the sediments, it is evident that other physio-chemical factors may play important roles. Under oxidising conditions and in areas with low productivity (i.e. low input of organic carbon into the sediment to fuel the generation of AVS), AVS has little to no effect on controlling the bioavailable fraction of the metals. Under these conditions, the metals tend to adsorb strongly to surface organic coatings on solid iron oxide and clay particles thus limiting bioavailability. Because of the high concentrations of iron and sulfur in marine sediments, much of the metals in all but the most heavily contaminated sediments are complexed to sulfides or iron oxides and little remains reactive and is bioavailable to benthic organisms.

Correia and Costa (2000) investigated the effects of sediment grain size and organic content on the toxicity of copper in a laboratory based study with the amphipod *Gammarus locusta*. In this study sediment with three different levels of grain size and organic content was spiked with different loading of copper and a 10-day standard amphipod bioassay was performed according to ASTM protocols (1992). By increasing the amount of particles < 0,063 mm (Fine Fraction – FF) in the sediment from 0,5% to 25%, and the total organic carbon (TOC) from 1% to 2%, a 9-fold decrease in the toxicity expressed as median LC_{50} value calculated from bulk concentrations were observed. In sediments with 75% FF and 4% TOC the amphipods were not significantly affected even at the highest exposure concentrations. The difference between SEM_{Cu} and AVS, were calculated to be 0,3 µmol/g for the 0,5% FF / 1% TOC- sediment, 3,4 µmol/g for the 25% FF / 2% TOC- sediment and 8,9 µmol/g for the 75% FF / 4% TOC- sediment at end of exposure. This indicates an effect, of either or both grain size and organic carbon in the sediment, in addition to the AVS-pool, for binding copper. Analysis of copper in the overlying water at the end of exposure did confirm the same pattern. In the 75% FF / 4% TOC – sediment the concentration of free copper in the water approached 38 µg Cu/l, whilst for 0,5% FF / 1% TOC and 25% FF / 2% TOC – sediments the concentrations at the end of exposure were 92 and 63 µg Cu/l, respectively, indicating a lower binding capacity in the sediment.

4.9. Recommendations for application of the SEM/AVS-approach in Drilling Discharges EIF

The SEM/AVS-approach belongs to the family of theoretically derived Sediment Quality Guidelines and it is to be considered an "equilibrium partitioning"-approach. It is in part derived from the same theories as the EqP for non-ionic organic contaminants derived by US-EPA (1993a-f) following the suggestions by MacKay (1982) that a single chemical potential determines the equilibrium between an organism and its environment. The toxicity of a given metal to a sediment dwelling organism could then be explained by the concentrations in the interstitial (pore) water. This will be the assumed main route for exposure for sediment dwelling organisms, and is demonstrated in laboratory studies for cadmium by Swartz and others (1985) and Kemp and Swartz (1988) with single-species studies with the amphipod *Rhepoxynius abronius* in spiked sediment environments.

The SEM/AVS-approach will most likely add strength and support to the chosen approach for calculation of the PEC and PNEC. Regional SEM/AVS data from the NCS should be provided as a test-case to evaluate if the approach should be included in the regular surveys as supportive data for interpreting the chemical data from metal analysis and corresponding calculated $\text{PNEC}_{\text{marine sediment}}$. Considering the potential for local variability in the AVS-concentration with the vertical redox-discontinuity depth in the sediment, care must be taken both in designing the scheme for sampling as well as the way the sub-samples are taken within each sample to ensure the integrity of the samples. Rather than sampling at fixed depths in the sediment core, sub-sampling should be performed based on previous data and good science. Sampling at fixed depth-intervals will not apply to all samples in a region due to the variability in the redox-discontinuity depth. As demonstrated in both laboratory experiments with spiked sediments and with field-collected sediments, the SEM/AVS-approach has proved its potential for explaining the acute effects observed for selected metals. According to US-EPA (2000a), normalising the SEM/AVS to organic carbon in the sediment could further strengthen the approach.

The SEM/AVS-approach can help answer questions like ”*Can this metal contaminant at this concentration in sediment with these characteristics contribute to toxicity to benthic life?*”, and the approach may be used in support to other SQGs for evaluation of possible adverse effects to benthic organisms. However as discussed above, because of the variability in the nature of the AVS (both in time and with shifting sediment physical and chemical characteristics), care has to be taken during planning, sampling, analysis and interpretation of the analytical data.

4.10. Identified and Quality Assured Endpoint-data for the Different PAHs and Diesel Fuel

The endpoint data are presented in the following Tables with a bare minimum of supporting data. Extended Tables with experimental and analytical conditions are listed in Appendices 4.13 to 4.17. Identified biological effect concentrations from the litterature are listed in the Tables as either or both bulk concentration data as microgram contaminant pr. gram sediment (µg/g dw.) or data normalised to organic carbon in the sediment as microgram contaminant pr. gram organic carbon (µg/g oc dw.). Both concentrations calculated on a dry weight basis. References to the cited literature are listed after each Table. Please note that the numbering of the references is not interchangeable between the Tables in the report and the Appendices.

4.10.1. Acenaphthene

After quality assurance of the identified endpoints a total of 7 unique data points were identified that met the recommendations for inclusion. These endpoints were obtained from two different studies describing responses in three different species from the same taxonomic group, crustacea, covering the trophic levels of primary and secondary consumers. None of the consumers were considered strict carnivores and are listed as combined primary/secondary consumers in the Table. All the data were acute and associated with lethality and were from marine studies.

Table 4.20 Effect concentration data for acenaphthene. Extended Tables with experimental and analytical conditions are listed in Appendix 4.13. References to the cited literature are listed at the end of this section (acenaphthene).

Taxonomic Group	**Species M/F[1]**	**Trophic Level**	**End-point Parameter**	**Effect conc. (μg/g dw)**	**Effect conc. (μg/g dw oc)**	**Ref.**	**Comments**
Crustacea: Amphipoda	*Eohaustorius estuarius* (M)	PC/SC	$LC_{50\ 10\ days}$ /Acute	43,3	4180	{1}	Sediment TOC: 1,23%
Crustacea: Amphipoda	*Eohaustorius estuarius* (M)	PC/SC	$LC_{50\ 10\ days}$ /Acute	47,8	1920	{1}	Sediment TOC: 2,49%
Crustacea: Amphipoda	*Eohaustorius estuarius* (M)	PC/SC	$LC_{50\ 10\ days}$ /Acute	68,4	1630	{1}	Sediment TOC: 4,21%
Crustacea: Amphipoda	*Leptocheirus plumulosus* (M)	PC/SC	$LC_{50\ 10\ days}$ /Acute	209,3	8450	{1}	Sediment TOC: 2,52%
Crustacea: Amphipoda	*Leptocheirus plumulosus* (M)	PC/SC	$LC_{50\ 10\ days}$ /Acute	373,0	10890	{1}	Sediment TOC: 3,66%
Crustacea: Amphipoda	*Rhepoxynius abronius* (M)	PC/SC	$LC_{50\ 10\ days}$ /Acute		2110	{2}	Sediment TOC: 3%
Crustacea: Amphipoda	*Rhepoxynius abronius* (M)	PC/SC	$LC_{50\ 10\ days}$ /Acute		2310	{2}	Sediment TOC: 3%

1. M: Marine, F: Freshwater.

Acenaphthene Toxicity References

{1} Swartz, R.C., T.H. DeWitt, D.W. Schults, G.R. Ditsworth, J.O. Lamberson, J.E. Sewall and R.J. Ozretich. 1991. Toxicity of sediment-associated acenaphtene and phenanthrene to marine benthic amphipods. Data Report. Pacific Ecosystems Branch, Environmental Research Laboratory, Narraganset, Office of Research and Development, U.S. EPA, Newport, Oregon. (Marked "Incomplete Draft"). Data also cited in: US-EPA. 1993. Sediment Quality Criteria for the Protection of Benthic Organisms: Acenapthene. United States Environmental Protection Agency, Office of Science and Technology, EPA-822-R-93-013 and US-EPA. 1992. Development of a Chronic Sediment Toxicity Test for Marine Benthic Amphipods. United States Environmental Protection Agency, EPA's Environmental Research Laboratory, Narragansett. EPA 903-R-92-002.

{2} Swartz, R.C., S.P. Ferraro, J.O. Lamberson, F.A. Cole, R.J. Ozretich, B.L. Boese, D.W. Schults, M. Behrenfield and G.T. Ankley. 1997. Photoactivation and toxicity of mixtures of polycyclic aromatic hydrocarbon compounds in marine sediment. Environ. Toxicol. Chem., 16(10): 2151-2157.

4.10.2. Diesel Fuel

As a representative of a hydrocarbon source diesel fuel were chosen. However relevant data in the literature were scarse. Diesel fuel is a mix of several distillation fractions of hydrocarbons, and composition and biological effects are likely to vary within the group dependent on the actual composition. For the identified study little information regarding the source and composition of the actual fuel were available.

After quality assurance of the identified endpoints a total of 3 unique data points were identified that met the recommendations for inclusion. These endpoints were obtained from one study describing responses in the crustacean *Schizopera knabeni*, a marine harpactiod copepod, considered a combined primary/secondary consumer. Two of the data were considered acute and associated with either lethality or inhibition of grazing activity. A third and chronic datapoint were associated with reproduction. All the data were from a marine study. For the identified study little information regarding the source and composition of the actual fuel were available. Data for diesel fuel is presented in tabular form in Appendix 4.14 only.

4.10.3. Fluoranthene

After quality assurance of the identified endpoints a total of 75 data points were identified that met the recommendations for inclusion. These endpoints were obtained from 16 different studies reporting responses in 10 species from three taxonomic groups, annelida, crustacea, and insecta, covering the trophic levels of primary- and/or secondary consumers. The consumers considered either strict herbivores or carnivores are listed as either primary or secondary consumers in the table; consumers not strictly herbivores or carnivores are listed as combined primary/secondary consumers. Of the 75 data points 12 were chronic data; six of these were associated with effects on reproduction and six with lethality. The remaining 63 acute data points were associated with lethality (56) and inhibition of grazing (7).

Table 4.21 Effect concentration data for fluoranthene. Extended Tables with experimental and analytical conditions are listed in Appendix 4.15. References to the cited literature are listed at the end of this section (fluoranthene).

Taxonomic Group	**Species M/F^1**	**Trophic Level**	**End-point Parameter**	**Effect conc. (µg/g dw)**	**Effect conc. (µg/g dw oc)**	**Ref.**	**Comments**
Crustacea: Amphipoda	*Rhepoxynius abronius* (M)	PC/SC	$LC_{50\ 10\ days}$ /Acute	3,4		{1}	Sediment TOC: 0,18%
Crustacea: Amphipoda	*Rhepoxynius abronius* (M)	PC/SC	$LC_{50\ 10\ days}$ /Acute	6,5		{1}	Sediment TOC: 0,31%
Crustacea: Amphipoda	*Rhepoxynius abronius* (M)	PC/SC	$LC_{50\ 10\ days}$ /Acute	10,7		{1}	Sediment TOC: 0,48%
Crustacea: Amphipoda	*Corophium spinicorne* (M)	PC/SC	$LC_{50\ 10\ days}$ /Acute	5,1		{1}	Sediment TOC: 0,18%
Crustacea: Amphipoda	*Corophium spinicorne* (M)	PC/SC	$LC_{50\ 10\ days}$ /Acute		3600	{1}	Sediment TOC: 0,18%
Crustacea: Amphipoda	*Corophium spinicorne* (M)	PC/SC	$LC_{50\ 10\ days}$ /Acute		2100	{1}	Sediment TOC: 0,18%
Crustacea: Amphipoda	*Rhepoxynius abronius* (M)	PC/SC	$LC_{50\ 10\ days}$ /Acute	3,1		{2}	Sediment TOC: 0,22/0,26% (Data pooled)
Crustacea: Copepoda	*Schizopera knabeni* (M)	PC/SC	$IC_{50\ 30hours\ Grazing}$ /Acute	94		{3}	Sediment SOC: 1,5%
Crustacea: Copepoda	*Schizopera knabeni* (M)	PC/SC	$EC_{50\ 14\ days\ Reproduction}$ /Chronic	38		{3}	Sediment SOC: 1,5%
Crustacea: Amphipoda	*Hyalella azteca* (F)	PC/SC	$LC_{50\ 10\ days}$ /Acute	2,3	500	{4}	Sediment TOC: 0,46%
Insecta:Diptera	*Chironomus tetans* (F)	PC	$LC_{50\ 10\ days}$ /Acute	7,3	1587	{4}	Sediment TOC: 0,46%
Crustacea: Amphipoda	*Hyalella azteca* (F)	PC/SC	$LC_{50\ 10\ days}$ /Acute	7,4	1480	{4}	Sediment TOC: 0,50%
Insecta:Diptera	*Chironomus tetans* (F)	PC	$LC_{50\ 10\ days}$ /Acute	8,7	1740	{4}	Sediment TOC: 0,50%
Crustacea: Amphipoda	*Hyalella azteca* (F)	PC/SC	$LC_{50\ 10\ days}$ /Acute	5,5	1250	{4}	Sediment TOC: 0,50%
Insecta:Diptera	*Chironomus tetans* (F)	PC	$LC_{50\ 10\ days}$ /Acute	3,0	682	{4}	Sediment TOC: 0,50%
Crustacea: Amphipoda	*Eohaustorius estuarius* (M)	PC/SC	$LC_{50\ 10\ days}$ /Acute	9,3		{5}	Sediment TOC: Not stated.
Crustacea: Amphipoda	*Eohaustorius estuarius* (M)	PC/SC	$LC_{50\ 10\ days}$ /Acute	10,7		{5}	Sediment TOC: Not stated.
Crustacea: Amphipoda	*Eohaustorius estuarius* (M)	PC/SC	$LC_{50\ 10\ days}$ /Acute	11,8		{5}	Sediment TOC: Not stated.
Crustacea: Amphipoda	*Rhepoxynius abronius* (M)	PC/SC	$LC_{50\ 10\ days}$ /Acute	5,1		{5}	Sediment TOC: Not stated.
Crustacea: Amphipoda	*Hyalella azteca* (F)	PC/SC	$LC_{50\ 10\ days}$ /Acute	15,4		{5}	Sediment TOC: Not stated.
Crustacea: Amphipoda	*Rhepoxynius abronius* (M)	PC/SC	$LC_{50\ 10\ days}$ /Acute	16,0	7400	{6}	Sediment TOC: 0,2%. Spiked sediment eq. for 13 days.
Crustacea: Amphipoda	*Rhepoxynius abronius* (M)	PC/SC	$LC_{50\ 10\ days}$ /Acute	22,1	10200	{6}	Sediment TOC: 0,2%. Spiked sediment eq. for 27 days.
Crustacea: Amphipoda	*Rhepoxynius abronius* (M)	PC/SC	$LC_{50\ 10\ days}$ /Acute	22,1	10200	{6}	Sediment TOC: 0,2%. Spiked sediment eq. for 41 days.
Crustacea: Amphipoda	*Rhepoxynius abronius* (M)	PC/SC	$LC_{50\ 10\ days}$ /Acute	25,5	11800	{6}	Sediment TOC: 0,2%. Spiked sediment eq. for 55 days.

Table 4.21 Effect concentration data for fluoranthene continued

Taxonomic Group	**Species M/F^1**	**Trophic Level**	**End-point Parameter**	**Effect conc. (µg/g dw)**	**Effect conc. (µg/g dw oc)**	**Ref.**	**Comments**
Crustacea: Amphipoda	*Rhepoxynius abronius* (M)	PC/SC	LC$_{50\ 10\ days}$ /Acute	22,6	10500	{6}	Sediment TOC: 0,2%. Spiked sediment eq. for 69 days.
Crustacea: Amphipoda	*Rhepoxynius abronius* (M)	PC/SC	LC$_{50\ 10\ days}$ /Acute	23,1	10700	{6}	Sediment TOC: 0,2%. Spiked sediment eq. for 83 days.
Crustacea: Amphipoda	*Rhepoxynius abronius* (M)	PC/SC	LC$_{50\ 10\ days}$ /Acute	52,2	24200	{6}	Sediment TOC: 0,2%. Spiked sediment eq. for 121 days.
Crustacea: Amphipoda	*Rhepoxynius abronius* (M)	PC/SC	LC$_{50\ 10\ days}$ /Acute	59,4	27600	{6}	Sediment TOC: 0,2%. Spiked sediment eq. for 170 days.
Crustacea: Amphipoda	*Rhepoxynius abronius* (M)	PC/SC	LC$_{50\ 10\ days}$ /Acute	31,8	5300	{6}	Sediment TOC: 0,6%. Spiked sediment eq. for 13 days.
Crustacea: Amphipoda	*Rhepoxynius abronius* (M)	PC/SC	LC$_{50\ 10\ days}$ /Acute	37,2	6200	{6}	Sediment TOC: 0,6%. Spiked sediment eq. for 27 days.
Crustacea: Amphipoda	*Rhepoxynius abronius* (M)	PC/SC	LC$_{50\ 10\ days}$ /Acute	36,2	6100	{6}	Sediment TOC: 0,6%. Spiked sediment eq. for 41 days.
Crustacea: Amphipoda	*Rhepoxynius abronius* (M)	PC/SC	LC$_{50\ 10\ days}$ /Acute	38,7	6500	{6}	Sediment TOC: 0,6%. Spiked sediment eq. for 55 days.
Crustacea: Amphipoda	*Rhepoxynius abronius* (M)	PC/SC	LC$_{50\ 10\ days}$ /Acute	36,6	6100	{6}	Sediment TOC: 0,6%. Spiked sediment eq. for 69 days.
Crustacea: Amphipoda	*Rhepoxynius abronius* (M)	PC/SC	LC$_{50\ 10\ days}$ /Acute	32,2	5400	{6}	Sediment TOC: 0,6%. Spiked sediment eq. for 83 days.
Crustacea: Amphipoda	*Rhepoxynius abronius* (M)	PC/SC	LC$_{50\ 10\ days}$ /Acute	38,8	6500	{6}	Sediment TOC: 0,6%. Spiked sediment eq. for 170 days.
Annelida: Polychaeta	*Streblospio benedicti* (M)	PC/SC	LC$_{50\ 10\ days}$ /Acute	65,6		{7}	Sediment TOC: 2,04%.
Annelida: Polychaeta	*Streblospio benedicti* (M)	PC/SC	LC$_{50\ 10\ days}$ /Acute	39,9		{7}	Sediment TOC: 2,04%.
Crustacea: Amphipoda	*Rhepoxynius abronius* (M)	PC/SC	LC$_{50\ 10\ days}$ /Acute	16,6		{8}	Sediment TOC: 0,34%
Crustacea: Amphipoda	*Rhepoxynius abronius* (M)	PC/SC	LC$_{50\ 10\ days}$ /Acute		2320	{9}	Sediment TOC: 3%
Crustacea: Amphipoda	*Rhepoxynius abronius* (M)	PC/SC	LC$_{50\ 10\ days}$ /Acute		3310	{9}	Sediment TOC: 3%
Insecta:Diptera	*Chironomus riparius* (F)	PC	LC$_{50\ 10\ days}$ /Acute	14,69		{10}	Sediment TOC: 2%
Insecta:Diptera	*Chironomus riparius* (F)	PC	LC$_{50\ 10\ days\ LOEC}$ /Acute	3		{10}	Sediment TOC: 2%
Insecta:Diptera	*Chironomus riparius* (F)	PC	LC$_{50\ 14\ days}$ /Acute	5,2		{10}	Sediment TOC: 2%
Insecta:Diptera	*Chironomus riparius* (F)	PC	LC$_{50\ 14\ days\ LOEC}$ /Acute	3		{10}	Sediment TOC: 2%
Insecta:Diptera	*Chironomus riparius* (F)	PC	LC$_{50\ 11\ days}$ /Acute	31,7		{11}	Sediment TOC: 0,53%
Insecta:Diptera	*Chironomus riparius* (F)	PC	LC$_{50\ 11\ days}$ /Acute	29,7		{11}	Sediment TOC: 0,53%
Insecta:Diptera	*Chironomus riparius* (F)	PC	LC$_{50\ 11\ days}$ /Acute	31,9		{11}	Sediment TOC: 0,53%
Insecta:Diptera	*Chironomus riparius* (F)	PC	LC$_{50\ 11\ days}$ /Acute	41,5		{11}	Sediment TOC: 0,53%
Insecta:Diptera	*Chironomus tetans* (F)	PC	LC$_{50\ 10\ days}$ /Acute	7,3	1587	{12}	Sediment TOC: 0,46%
Insecta:Diptera	*Chironomus tetans* (F)	PC	LC$_{50\ 10\ days}$ /Acute	3,0	682	{12}	Sediment TOC: 0,50%
Insecta:Diptera	*Chironomus tetans* (F)	PC	LC$_{50\ 10\ days}$ /Acute	8,7	1740	{12}	Sediment TOC: 0,44%
Insecta:Diptera	*Chironomus tetans* (F)	PC	LC$_{50\ 10\ days}$ /Acute	2,3	500	{12}	Sediment TOC: 0,46%
Crustacea: Amphipoda	*Hyalella azteca* (F)	PC/SC	LC$_{50\ 10\ days}$ /Acute	5,5	1250	{12}	Sediment TOC: 0,50%.
Crustacea: Amphipoda	*Hyalella azteca* (F)	PC/SC	LC$_{50\ 10\ days}$ /Acute	7,4	1480	{12}	Sediment TOC: 0,44%.
Crustacea: Copepoda	*Schizopera knabeni* (M)	PC/SC	LC$_{50\ 10\ days}$ /Chronic	213		{13}	Sediment SOC: 1,5%
Crustacea: Copepoda	*Schizopera knabeni* (M)	PC/SC	LC$_{50\ 10\ days\ LOEC}$ /Chronic	334		{13}	Sediment SOC: 1,5%
Crustacea: Copepoda	*Schizopera knabeni* (M)	PC/SC	LC$_{50\ 10\ days\ NOEC}$ /Chronic	132		{13}	Sediment SOC: 1,5%

Table 4.21 Effect concentration data for fluoranthene continued

Taxonomic Group	Species M/F[1]	Trophic Level	End-point Parameter	Effect conc. (µg/g dw)	Effect conc. (µg/g dw oc)	Ref.	Comments
Crustacea: Copepoda	*Schizopera knabeni* (M)	PC/SC	$EC_{50\text{ 10 days Reproduction}}$ /Chronic	55		{13}	Sediment SOC: 1,5%
Crustacea: Copepoda	*Schizopera knabeni* (M)	PC/SC	$EC_{50\text{ 10 days Reproduction LOEC}}$ /Chronic	47		{13}	Sediment SOC: 1,5%
Crustacea: Copepoda	*Schizopera knabeni* (M)	PC/SC	$EC_{50\text{ 10 days Reproduction NOEC}}$ /Chronic	18		{13}	Sediment SOC: 1,5%
Crustacea: Copepoda	*Schizopera knabeni* (M)	PC/SC	$IC_{50\text{ 3hours Grazing}}$ /Acute	34		{13}	Sediment SOC: 1,5%
Crustacea: Copepoda	*Schizopera knabeni* (M)	PC/SC	$IC_{50\text{ 3hours Grazing LOEC}}$ /Acute	18		{13}	Sediment SOC: 1,5%
Crustacea: Copepoda	*Schizopera knabeni* (M)	PC/SC	$IC_{50\text{ 3hours Grazing NOEC}}$ /Acute	5		{13}	Sediment SOC: 1,5%
Crustacea: Copepoda	*Coullana sp* (M)	PC/SC	$LC_{50\text{ 10 days}}$ /Chronic	132		{13}	Sediment SOC: 1,5%
Crustacea: Copepoda	*Coullana sp* (M)	PC/SC	$LC_{50\text{ 10 days LOEC}}$ /Chronic	132		{13}	Sediment SOC: 1,5%
Crustacea: Copepoda	*Coullana sp* (M)	PC/SC	$LC_{50\text{ 10 days NOEC}}$ /Chronic	47		{13}	Sediment SOC: 1,5%
Crustacea: Copepoda	*Coullana sp* (M)	PC/SC	$EC_{50\text{ 10 days Reproduction LOEC}}$ /Chronic	132		{13}	Sediment SOC: 1,5%
Crustacea: Copepoda	*Coullana sp* (M)	PC/SC	$EC_{50\text{ 10 days Reproduction NOEC}}$ /Chronic	47		{13}	Sediment SOC: 1,5%
Crustacea: Copepoda	*Coullana sp* (M)	PC/SC	$IC_{50\text{ 3hours Grazing}}$ /Acute	35		{13}	Sediment SOC: 1,5%
Crustacea: Copepoda	*Coullana sp* (M)	PC/SC	$IC_{50\text{ 3hours Grazing LOEC}}$ /Acute	47		{13}	Sediment SOC: 1,5%
Crustacea: Copepoda	*Coullana sp* (M)	PC/SC	$IC_{50\text{ 3hours Grazing NOEC}}$ /Acute	18		{13}	Sediment SOC: 1,5%

1. M: Marine, F: Freshwater.

Fluoranthene Toxicity References

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4.10.4. Phenanthrene

After quality assurance of the identified endpoints a total of 64 data points were identified that met the recommendations for inclusion. These endpoints were obtained from seven different studies reporting responses in seven species from three taxonomic groups, annelida, crustacea, and insecta, covering the trophic levels of primary- and/or secondary consumers. The consumers considered either strict herbivores or carnivores are listed as either primary or secondary consumers in the Table, and consumers not strictly herbivores or carnivores are listed as combined primary/secondary consumers. Of the 64 data points 39 were chronic data; 15 of these were associated with effects on reproduction and 24 with lethality. The remaining 25 acute data points were associated with lethality (22), inhibition of grazing (1) and egestion (2).

Table 4.22 Effect concentration data for phenanthrene. Extended Tables with experimental and analytical conditions are listed in Appendix 4.16. References to the cited literature are listed at the end of this section (phenanthrene).

Taxonomic Group	**Species M/F**[1]	**Trophic Level**	**End-point Parameter**	**Effect conc. (µg/g dw)**	**Effect conc. (µg/g dw oc)**	**Ref.**	**Comments**
Crustacea: Copepoda	*Schizopera knabeni* (M)	PC/SC	$\text{LC}_{50\text{ 96 hours}}$ /Acute	524		{1}	Sediment SOC: 1,5%
Crustacea: Copepoda	*Schizopera knabeni* (M)	PC/SC	$\text{IC}_{50\text{ 3hours Grazing}}$ /Acute	51		{1}	Sediment SOC: 1,5%
Crustacea: Copepoda	*Schizopera knabeni* (M)	PC/SC	$\text{EC}_{50\text{ 14 days Reproduction}}$ /Chronic	952		{1}	Sediment SOC: 1,5%
Crustacea: Copepoda	*Schizopera knabeni* (M)	PC/SC	$\text{LC}_{50\text{ 10 days}}$ /Chronic	84	5600	{2}	Sediment SOC: 1,5%. Test initiated with nauplius stage.
Crustacea: Copepoda	*Schizopera knabeni* (M)	PC/SC	$\text{LC}_{50\text{ 10 days LOEC}}$ /Chronic	45		{2}	Sediment SOC: 1,5%. Test initiated with nauplius stage.
Crustacea: Copepoda	*Schizopera knabeni* (M)	PC/SC	$\text{LC}_{50\text{ 10 days NOEC}}$ /Chronic	22		{2}	Sediment SOC: 1,5%. Test initiated with nauplius stage.
Crustacea: Copepoda	*Schizopera knabeni* (M)	PC/SC	$\text{LC}_{50\text{ 10 days}}$ /Chronic	172		{2}	Sediment SOC: 1,5%. Test initiated with copepodite stage.
Crustacea: Copepoda	*Schizopera knabeni* (M)	PC/SC	$\text{LC}_{50\text{ 10 days LOEC}}$ /Chronic	177		{2}	Sediment SOC: 1,5%. Test initiated with copepodite stage.
Crustacea: Copepoda	*Schizopera knabeni* (M)	PC/SC	$\text{LC}_{50\text{ 10 days NOEC}}$ /Chronic	90		{2}	Sediment SOC: 1,5%. Test initiated with copepodite stage.
Crustacea: Copepoda	*Schizopera knabeni* (M)	PC/SC	$\text{LC}_{50\text{ 10 days}}$ /Chronic	349	26800	{2}	Sediment SOC: 1,5%. Test initiated with adult males.
Crustacea: Copepoda	*Schizopera knabeni* (M)	PC/SC	$\text{LC}_{50\text{ 10 days LOEC}}$ /Chronic	492		{2}	Sediment SOC: 1,5%. Test initiated with adult males.
Crustacea: Copepoda	*Schizopera knabeni* (M)	PC/SC	$\text{LC}_{50\text{ 10 days NOEC}}$ /Chronic	217		{2}	Sediment SOC: 1,5%. Test initiated with adult males.
Crustacea: Copepoda	*Schizopera knabeni* (M)	PC/SC	$\text{LC}_{50\text{ 10 days}}$ /Chronic	345		{2}	Sediment SOC: 1,5%. Test initiated with adult females.
Crustacea: Copepoda	*Schizopera knabeni* (M)	PC/SC	$\text{LC}_{50\text{ 10 days LOEC}}$ /Chronic	492		{2}	Sediment SOC: 1,5%. Test initiated with adult females.
Crustacea: Copepoda	*Schizopera knabeni* (M)	PC/SC	$\text{LC}_{50\text{ 10 days NOEC}}$ /Chronic	217		{2}	Sediment SOC: 1,5%. Test initiated with adult females.
Crustacea: Copepoda	*Schizopera knabeni* (M)	PC/SC	$\text{EC}_{50\text{ 10 days Reproduction NOEC}}$ /Chronic	11		{2}	Sediment SOC: 1,5%.
Crustacea: Copepoda	*Schizopera knabeni* (M)	PC/SC	$\text{EC}_{50\text{ 10 days Reproduction LOEC}}$ /Chronic	22		{2}	Sediment SOC: 1,5%.

Table 4.22 Effect concentration data for phenanthrene continued

Taxonomic Group	Species M/F^1	Trophic Level	End-point Parameter	Effect conc. (µg/g dw)	Effect conc. (µg/g dw oc)	Ref.	Comments
Crustacea: Copepoda	*Schizopera knabeni* (M)	PC/SC	$EC_{50\text{ 10 days Development time of eggs LOEC}}$ /Chronic	22		{2}	Sediment SOC: 1,5%.
Crustacea: Copepoda	*Schizopera knabeni* (M)	PC/SC	$EC_{50\text{ 10 days Development time of eggs NOEC}}$ /Chronic	11		{2}	Sediment SOC: 1,5%.
Crustacea: Copepoda	*Schizopera knabeni* (M)	PC/SC	$EC_{50\text{ 10 days Hatching success of eggs NOEC}}$ /Chronic	22		{2}	Sediment SOC: 1,5%.
Crustacea: Copepoda	*Schizopera knabeni* (M)	PC/SC	$EC_{50\text{ 10 days Hatching success of eggs LOEC}}$ /Chronic	45		{2}	Sediment SOC: 1,5%.
Crustacea: Copepoda	*Nitocra lacustris* (M)	PC/SC	$LC_{50\text{ 10 days}}$ /Chronic	71	2867	{2}	Sediment SOC: 1,5%. Test initiated with nauplius stage.
Crustacea: Copepoda	*Nitocra lacustris* (M)	PC/SC	$LC_{50\text{ 10 days LOEC}}$ /Chronic	45		{2}	Sediment SOC: 1,5%. Test initiated with nauplius stage.
Crustacea: Copepoda	*Nitocra lacustris* (M)	PC/SC	$LC_{50\text{ 10 days NOEC}}$ /Chronic	22		{2}	Sediment SOC: 1,5%. Test initiated with nauplius stage.
Crustacea: Copepoda	*Nitocra lacustris* (M)	PC/SC	$LC_{50\text{ 10 days}}$ /Chronic	43		{2}	Sediment SOC: 1,5%. Test initiated with copepodite stage.
Crustacea: Copepoda	*Nitocra lacustris* (M)	PC/SC	$LC_{50\text{ 10 days LOEC}}$ /Chronic	22		{2}	Sediment SOC: 1,5%. Test initiated with copepodite stage.
Crustacea: Copepoda	*Nitocra lacustris* (M)	PC/SC	$LC_{50\text{ 10 days NOEC}}$ /Chronic	11		{2}	Sediment SOC: 1,5%. Test initiated with copepodite stage.
Crustacea: Copepoda	*Nitocra lacustris* (M)	PC/SC	$LC_{50\text{ 10 days}}$ /Chronic	72	7000	{2}	Sediment SOC: 1,5%. Test initiated with adult males.
Crustacea: Copepoda	*Nitocra lacustris* (M))	PC/SC	$LC_{50\text{ 10 days LOEC}}$ /Chronic	90		{2}	Sediment SOC: 1,5%. Test initiated with adult males.
Crustacea: Copepoda	*Nitocra lacustris* (M)	PC/SC	$LC_{50\text{ 10 days NOEC}}$ /Chronic	45		{2}	Sediment SOC: 1,5%. Test initiated with adult males.
Crustacea: Copepoda	*Nitocra lacustris* (M)	PC/SC	$LC_{50\text{ 10 days}}$ /Chronic	105		{2}	Sediment SOC: 1,5%. Test initiated with adult females.
Crustacea: Copepoda	*Nitocra lacustris* (M)	PC/SC	$LC_{50\text{ 10 days LOEC}}$ /Chronic	177		{2}	Sediment SOC: 1,5%. Test initiated with adult females.
Crustacea: Copepoda	*Nitocra lacustris* (M)	PC/SC	$LC_{50\text{ 10 days NOEC}}$ /Chronic	90		{2}	Sediment SOC: 1,5%. Test initiated with adult females.
Crustacea: Copepoda	*Nitocra lacustris* (M)	PC/SC	$EC_{50\text{ 10 days Reproduction NOEC}}$ /Chronic	45		{2}	Sediment SOC: 1,5%.
Crustacea: Copepoda	*Nitocra lacustris* (M)	PC/SC	$EC_{50\text{ 10 days Reproduction LOEC}}$ /Chronic	90		{2}	Sediment SOC: 1,5%.
Crustacea: Copepoda	*Nitocra lacustris* (M)	PC/SC	$EC_{50\text{ 10 days Development time of eggs LOEC}}$ /Chronic	45		{2}	Sediment SOC: 1,5%.
Crustacea: Copepoda	*Nitocra lacustris* (M)	PC/SC	$EC_{50\text{ 10 days Development time of eggs NOEC}}$ /Chronic	22		{2}	Sediment SOC: 1,5%.
Crustacea: Copepoda	*Nitocra lacustris* (M)	PC/SC	$EC_{50\text{ 10 days Hatching success of eggs NOEC}}$ /Chronic	45		{2}	Sediment SOC: 1,5%.
Crustacea: Copepoda	*Nitocra lacustris* (M)	PC/SC	$EC_{50\text{ 10 days Hatching success of eggs LOEC}}$ /Chronic	90		{2}	Sediment SOC: 1,5%.
Annelida: Oligochaeta	*Limnodrilus hoffmeisteri* (F)	PC/SC	$LC_{50\text{ 10 days}}$ /Acute	297,5	42500	{3}	Sediment TOC: 0,7%
Annelida: Oligochaeta	*Limnodrilus hoffmeisteri* (F)	PC/SC	$EC_{50\text{ 5 days Egestion LOEC}}$ /Acute	47		{3}	Sediment TOC: 0,7%
Annelida: Oligochaeta	*Limnodrilus hoffmeisteri* (F)	PC/SC	$EC_{50\text{ 5 days Egestion NOEC}}$ /Acute	20		{3}	Sediment TOC: 0,7%
Annelida: Oligochaeta	*Limnodrilus hoffmeisteri* (F)	PC/SC	$EC_{50\text{ 10 days Reproduction LOEC}}$ /Chronic	102		{3}	Sediment TOC: 0,7%
Annelida: Oligochaeta	*Limnodrilus hoffmeisteri* (F)	PC/SC	$EC_{50\text{ 10 days Reproduction NOEC}}$ /Chronic	47		{3}	Sediment TOC: 0,7%

Table 4.22 Effect concentration data for phenanthrene continued

Taxonomic Group	Species M/F[1]	Trophic Level	End-point Parameter	Effect conc. (µg/g dw)	Effect conc. (µg/g dw oc)	Ref.	Comments
Crustacea: Amphipoda	*Eohaustorius estuarius* (M)	PC/SC	$LC_{50\ 10\ days}$ /Acute	39,2	4060	{4}	Sediment TOC: 1,02%
Crustacea: Amphipoda	*Eohaustorius estuarius* (M)	PC/SC	$LC_{50\ 10\ days}$ /Acute	92,6	3760	{4}	Sediment TOC: 2,47%
Crustacea: Amphipoda	*Eohaustorius estuarius* (M)	PC/SC	$LC_{50\ 10\ days}$ /Acute	134,1	4210	{4}	Sediment TOC: 3,33%
Crustacea: Amphipoda	*Leptocheirus plumulosus* (M)	PC/SC	$LC_{50\ 10\ days}$ /Acute	170,1	6870	{4}	Sediment TOC: 2,5%
Crustacea: Amphipoda	*Leptocheirus plumulosus* (M)	PC/SC	$LC_{50\ 10\ days}$ /Acute	91,9	8080	{4}	Sediment TOC: 1,96%
Crustacea: Amphipoda	*Leptocheirus plumulosus* (M)	PC/SC	$LC_{50\ 10\ days}$ /Acute	254,8	8180	{4}	Sediment TOC: 3,6%
Crustacea: Amphipoda	*Rhepoxynius abronius* (M)	PC/SC	$LC_{50\ 10\ days}$ /Acute		3080	{5}	Sediment TOC: 3%
Crustacea: Amphipoda	*Rhepoxynius abronius* (M)	PC/SC	$LC_{50\ 10\ days}$ /Acute		2220	{5}	Sediment TOC: 3%
Insecta:Diptera	*Chironomus riparius* (F)	PC	$LC_{50\ 10\ days}$ /Acute	14,7		{6}	Sediment TOC: 2%
Insecta:Diptera	*Chironomus riparius* (F)	PC	$LC_{50\ 11\ days\ LOEC}$ /Acute	30		{6}	Sediment TOC: 2%
Insecta:Diptera	*Chironomus riparius* (F)	PC	$LC_{50\ 11\ days\ NOEC}$ /Acute	15,83		{6}	Sediment TOC: 2%
Insecta:Diptera	*Chironomus riparius* (F)	PC	$LC_{50\ 10\ days}$ /Acute	10		{6}	Sediment TOC: 2%
Insecta:Diptera	*Chironomus riparius* (F)	PC	$LC_{50\ 11\ days\ LOEC}$ /Acute	30		{6}	Sediment TOC: 2%
Insecta:Diptera	*Chironomus riparius* (F)	PC	$LC_{50\ 11\ days\ NOEC}$ /Acute	10		{6}	Sediment TOC: 2%
Insecta:Diptera	*Chironomus riparius* (F)	PC	$LC_{50\ 10\ days}$ /Acute	13,63		{6}	Sediment TOC: 2%
Insecta:Diptera	*Chironomus riparius* (F)	PC	$LC_{50\ 11\ days\ LOEC}$ /Acute	30		{6}	Sediment TOC: 2%
Insecta:Diptera	*Chironomus riparius* (F)	PC	$LC_{50\ 11\ days\ NOEC}$ /Acute	10		{6}	Sediment TOC: 2%
Insecta:Diptera	*Chironomus riparius* (F)	PC	$LC_{50\ 10\ days}$ /Acute	20,54		{6}	Sediment TOC: 2%
Insecta:Diptera	*Chironomus riparius* (F)	PC	$LC_{50\ 11\ days\ LOEC}$ /Acute	30		{6}	Sediment TOC: 2%
Insecta:Diptera	*Chironomus riparius* (F)	PC	$LC_{50\ 11\ days\ NOEC}$ /Acute	10		{6}	Sediment TOC: 2%

1. M: Marine, F: Freshwater.

Phenanthrene Toxicity References

{1} Lotufo, G.R. 1997. Toxicity of sediment-associated PAHs to an estuarine copepod: Effects on survival, feeding, reproduction and behaviour. Marine Environmental Research, 44(2) 149-166.

{2} Lotufo, G.R. and J.W. Fleeger. 1997. Effects of sediment-associated phenanthrene on survival, development and reproduction of two species of meiobenthic copepods. Marine Ecology Process Series, 151:91-102.

{3} Lotufo, G.R. and J.W. Fleeger. 1996. Toxicity of sediment-associated pyrene and phenanthrene to *Limnodrilus hoffmeisteri* (Oligochaeta:Tubificidae). Environmental Toxicology and Chemistry, 15(9): 1508-1516.

{4} Swartz, R.C., T.H. DeWitt, D.W. Schults, G.R. Ditsworth, J.O. Lamberson, J.E. Sewall and R.J. Ozretich. 1991. Toxicity of sediment-associated acenaphtene and phenanthrene to marine benthic amphipods. Data Report. Pacific Ecosystems Branch, Environmental Research Laboratory, Narragansett, Office of Research and Development, U.S. EPA, Newport, Oregon. (Marked "Incomplete Draft"). Data also cited in: US-EPA. 1993. Sediment Quality Criteria for the Protection of Benthic Organisms: Phenanthrene. United States Environmental Protection Agency, Office of Science and Technology, EPA-822-R-93-014 and US-EPA. 1992.

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{5} Swartz, R.C., S.P. Ferraro, J.O. Lamberson, F.A. Cole, R.J. Ozretich, B.L. Boese, D.W. Schults, M. Behrenfield and G.T. Ankley. 1997. Photoactivation and toxicity of mixtures of polycyclic aromatic hydrocarbon compounds in marine sediment. Environ. Toxicol. Chem., 16(10): 2151-2157.

{6} Verrhiest, G., B. Clement and G. Blake. 2001. Single and combined effects of sediment-associated PAHs on three species of freshwater macroinvertebrates. Ecotoxicology, 10: 363-372.

4.10.5. Pyrene

After quality assurance of the identified endpoints a total of six data points were identified that met the recommendations for inclusion. These endpoints were obtained from three different studies reporting responses in four species from two different taxonomic groups, annelida and crustacea, covering the trophic levels of primary- and/or secondary consumers. Consumers not strictly herbivores or carnivores are listed as combined primary/secondary consumers. Of the six data points one was chronic data associated with lethality. The remaining five acute data points were associated with lethality (2), sediment avoidance (1) and egestion (2).

Table 4.23 Effect concentration data for pyrene. Extended Tables with experimental and analytical conditions are listed in Appendix 4.17. References to the cited literature are listed at the end of this section (pyrene).

Taxonomic Group	Species M/F[1]	Trophic Level	End-point Parameter	Effect conc. (µg/g dw)	Effect conc. (µg/g dw oc)	Ref.	Comments
Crustacea: Amphipoda	*Diporeia spp.* (F)	PC/SC	$LC_{50\ 28\ days}$ /Chronic	147		{1}	Sediment TOC: 0,46%
Annelida: Oligochaeta	*Lumbriculus variegatus* (F)	PC/SC	$EC_{50\ 7\ days\ Sediment\ avoidance}$ /Acute	226		{2}	Sediment TOC: Not reported?
Annelida: Oligochaeta	*Limnodrilus hoffmeisteri* (F)	PC/SC	$EC_{50\ 5\ days\ Egestion\ LOEC}$ /Acute	91		{3}	Sediment TOC: 0,7%
Annelida: Oligochaeta	*Limnodrilus hoffmeisteri* (F)	PC/SC	$EC_{50\ 5\ days\ Egestion\ NOEC}$ /Acute	46		{3}	Sediment TOC: 0,7%
Crustacea: Amphipoda	*Rhepoxynius abronius* (M)	PC/SC	$LC_{50\ 10\ days}$ /Acute		1220	{3}	Sediment TOC: 3%
Crustacea: Amphipoda	*Rhepoxynius abronius* (M)	PC/SC	$LC_{50\ 10\ days}$ /Acute		2810	{3}	Sediment TOC: 3%

1. M: Marine, F: Freshwater.

Pyrene Toxicity References

{1} Landrum, P.F., W.S. Dupuis and J. Kukkonen. 1994. Toxicokinetics and toxicity of sediment-associated pyrene and phenanthrene in *Diporeia* spp.: Examination of equilibrium-partitioning theory and residue-based effects for assessing hazard. Environmental Toxicology and Chemistry, 13(11): 1769-1780.

{2} Kukkonen, J. and P.F. Landrum. 1994. Toxicokinetics and toxicity of sediment-associated pyrene to *Lumbriculus variegatus* (Oligochaeta). Environmental Toxicology and Chemistry, 13(9): 1457-1468.

{3} Swartz, R.C., S.P. Ferraro, J.O. Lamberson, F.A. Cole, R.J. Ozretich, B.L. Boese, D.W. Schults, M. Behrenfield and G.T. Ankley. 1997. Photoactivation and toxicity of mixtures of polycyclic aromatic hydrocarbon compounds in marine sediment. Environmental Toxicology and Chemistry, 16(10): 2151-2157.

4.10.6. Sediment Physiochemical Factors Mediating Bio-availability and Toxicity of Non-ionic Contaminants

The PAHs entering the marine environment originates from both natural processes and as a result of human activities. As mentioned earlier the sources of PAHs are either petrogenic PAHs originating from fossil organic matter, pyrogenic PAHs from combustion of organic matter or biogenic PAHs from anoxic degradation of certain organic compounds. Once formed PAHs are sTable compounds and are slowly modified by chemical or biological processes over time. The most important routes for degrading involves molecular oxygen by photochemical or biochemical transformation by oxidising. The high affinity of PAHs to particulate organic carbon tends to sorb them to surfaces and co-settling with sedimenting particles. When the sediment layers becomes anoxic as new layers piles up, the degradation process slows down as the oxygen pool in the sediment is depleted due to microbial activity.

At steady state in the sediment there will be equilibrium between free PAH in the interstitial water and PAH associated with sediment surfaces. Due to the low solubility of PAHs in water, and corresponding high affinity to organic carbon, this equilibrium will be shifted from the water-phase to the organic carbon in the sediment phase. Any organisms living in this system will be a part of this system and will over time accumulate PAHs from the environment until the accumulation is balanced with the mechanisms for biotransformation and excretion in the organism.

There are two major sources of organic particles in the sediment. Larger particles originate from degrading of plant material (particulate organic carbon, POC) and minor particles are formed by aggregates from humic or fulvic acids. The minor particles are analytically defined together with dissolved organic carbon, DOC, as they will disintegrate when filtered or centrifuged and can not clearly be separated from truly dissolved organic carbon in the sample. Ingestion of colloidal particles is not likely to be a significant route for uptake among higher organisms as the particles are too small and delicate for ingestion. However this might be a significant route for unicellular and smaller multicellular organisms feeding on organic colloids, and may contribute as an important route for feeding the food webs with PAHs due to their high potential for both bioaccumulation and biomagnification.

The low solubility of PAHs in water and corresponding high affinity to organic carbon makes ingestion of particles the major route for exposure of sediment dwelling animals as many of them feeds on organic particles. Due to the low solubility of PAHs in water the uptake over gills or other surfaces of the body from the interstitial (pore-) water will be of minor importance under natural conditions with organic carbon present in either particulate or aggregated form. The controlled addition of DOC i experiments with both fish (bluegills sunfish, *Lepomis macrochirus*, McCarty and Jimenez, 1985) and amphipods (*Pontoporeia hoyii*, Landrum *et al*., 1985) have demonstrated that increased DOC will decrease the bioavailable fraction of nonionic contaminants. For the PAHs this decrease will be substantial for the more hydrophobe PAHs like benzo[*a*]pyrene but insignificant for the more hydrophile PAHs like fluoranthrene (McCarty and Jimenez, 1985).

Data reviewed by US-EPA as a basis for establishing Sediment Quality Criteria for non-ionic organic contaminants (US-EPA, 1993f) indicated a correlation between observed biological responses and pore water concentration in toxicity studies. In a system at equilibrium the chemical activity of a contaminant expressed as the non-sorbed (bioavailable) fraction, can be calculated by a component-specific partitioning coefficient between the different phases in the sediment. The bioavailability of a contaminant will be the key to its potential for causing a toxic effect, and for organisms living in the sediment the most prominent route for uptake will be chemical sorbed to particulate organic carbon. By normalising the observed biological effects to organic carbon in the sediment the effects can be made independent of other sediment properties, and facilitate comparison between different sediment types with different physical characteristics as long as the content of organic carbon is known.

4.11. Conclusions/Summary from the literature review

According to the EU-TGD (EC, 2003) PNEC for the sediment compartment should be calculated for substances that have potential for either directly depositing on the seafloor or sorbing to sedimenting particles. The different approaches for calculation of $PNEC_{sediment}$ according to the EU-TGD are outlined in Chapter 2 in this report, and include use of an assessment factors and/or the equilibrium method.

4.11.1. Metals

The literature review of marine sediment ecotoxicology did reveal relevant data for use in calculation of $PNEC_{sediment}$ by applying assessment factors for all evaluated metals. However, there is a lack of ecotoxicological endpoints from chronic long-term studies in data from the reviewed literature. Further, there is a general lack of any information on toxicity of metals to some major benthic phyla such as cnidaria (hydroids), echinoderms and molluscs (bivalves and gastropods), and there is a substantial imbalance between the phyla naturally represented in marine sediments and the phyla covered by available guidelines for testing of sediments shown in Table 4.1. All the data for sensitive species were acute data (lethality) from short-term studies which implies that an assessment factor of 1000 should be used with the exception for mercury where only one acute response were identified and an assessment factor of 10000 should be applied. Application of these assessment factors for calculation of $PNEC_{sediment}$ for the evaluated metals will yield values in the range of, or below the natural concentrations on the continental shelf. (See Table 5.12 in Chapter 5 for calculated values for $PNEC_{sediment}$ for the metals).

The results from testing whole sediments should be carefully evaluated since several factors can contribute to variability in the test results. Of major importance to the availability of metals in sediment are the influence of iron (as hydrous oxides), total organic carbon, and sulphide concentration in the sediment (Tessier and Cambell, 1987; Di Toro *et al.*, 1990; Ankley et al, 1996). The physical or chemical species of a metal in the sediment has a marked effect on its availability and toxicity to marine organisms, and understanding of metal speciation is necessary for understanding the impacts from metals.

Several studies (Swartz *et al.*, 1985, Carlson *et al.*, 1991, DiToro *et al.*, 1992, Green *et al.*, 1993, Casas and Creselius, 1994, Berry *et al.*, 1996 and Lee and Lee, 2005) over the past two decades have shown a correlation between the sediment interstitial (pore) water concentration of different metals (nickel, lead, zinc, copper and cadmium) and toxicity to different marine and freshwater benthic organisms (amphipods) indicating that the acute toxicity was controlled by the concentration in the interstitial water rather the total bulk concentration in the sediment. Likewise, in a study of Hansen and others (1996) a comparison between the bulk metals concentration in field collected sediments and the acute response of amphipods and polychaetes, no causal relation between total bulk metal concentration and acute response (mortality) was found (see Figure 4.1).

Normalising metals concentrations to i.e. co-extracted acid volatile sulphide (AVS) concentrations in the sediment (expressed as SEM/AVS ratio) instead of bulk concentrations, yields a better agreement between the observed mortality and the "bioavailable" concentration of metal ions in the sediments (Figure 4.2). However, under oxidising conditions and in areas with low productivity AVS has little to none effect on controlling the bioavailable fraction of the metals. Under these conditions, the metals tend to adsorb strongly to surface organic coatings on solid iron oxide and clay particles thus limiting bioavailability. Iron oxides and organic carbon are important binding phases for reactive metal species in the sediments and therefore, in addition to AVS, limits the reactive pool that is bioavaliable to benthic organisms. Grain size has also been demonstrated to be of importance for toxicity of metals (Correia and Costa, 2000).

The SEM/AVS-approach can be used in support to other "toxicity threshold criteria" (PNECs) used in the risk evaluation of the marine benthic environment. However, as pointed out the variability of the

AVS, both in time and with shifting sediment physical and chemical characteristics of the environment, care has to be taken during planning, sampling, analysis and interpretation of the analytical data. This method has only been tested using acute lethality as the endpoint. Therefore, its applicability to predicting chronic effects is uncertain at present. As a consequence, its immediate application to the development of PNEC or sediment quality objectives (SQOs) is limited to acute toxicity predictions. Therefore, SEM/AVS-approach will most likely add strength and support to the chosen approach for calculation of PNEC.

It is recommended that regional AVS, SEM and interstitial water concentration data from the NCS should be provided as a test-case to evaluate if the approach should be included in the regular surveys as supportive data for interpreting the chemical data from metal analysis and corresponding calculated $\text{PNEC}_{\text{marine sediment}}$ in field areas where metals may be of concern. As demonstrated in both laboratory experiments with spiked sediments as well as field-collected sediments, the SEM/AVS-approach has proved its potential for explaining the acute effects observed of selected metals. According to US-EPA (2000a,b) normalising the SEM/AVS to organic carbon in the sediment could further strengthen the approach.

4.11.2. PAHs and Diesel Fuel

The literature review of marine sediment ecotoxicity did reveal relevant data for use in calculation of $\text{PNEC}_{\text{marine sediment}}$ by applying assessment factors for the evaluated PAHs and the diesel fuel, but data were available only for a minor number of PAHs. Like the metals, ecotoxicological endpoints from chronic long-term studies in the reviewed literature were scarce. Further, the majority of datapoints are from only one phyla (crustacea:amphipoda/insecta) leaving a general lack of information on toxicity to major benthic phyla such as annelids (oligo- and polychaetes), cnidaria (hydroids and sea anemones), echinoderms and molluscs (bivalves and gastropods). All the data for sensitive species were acute data (lethality) from short-term studies, which implies that an assessment factor of 1000 should be used for calculation of $\text{PNEC}_{\text{marine sediment}}$, and the resulting values will be in the range of, or below the natural concentrations of the evaluated PAHs on the continental shelf. (See Table 5.11 in Chapter 5 for calculated values for $\text{PNEC}_{\text{marine sediment}}$ for the evaluated PAHs).

In absence of sufficient amount of relevant ecotoxicological data for sediment-dwelling organisms the EU-TGD (EC, 2003) is open for a provisionally calculation of $\text{PNEC}_{\text{marine sediment}}$ by use of the equilibrium partitioning method. Since the assessment factor approach is not recommended to be applied to the ecotoxicological data obtained in the literature review for calculation of $\text{PNEC}_{\text{marine sediment}}$, the equilibrium partitioning approach has been evaluated. The determination of the $\text{PNEC}_{\text{marine sediment}}$ as input to the risk calculation of the toxicity parameter of the EIF drilling dicharges is dealt with in Chapter 5 in this report.

The results from ecotoxicological testing of whole sediments should be carefully evaluated since physiochemical factors of the sediment will contribute to variability in the test results in addition to the inherit variations encountered when working with biological systems. Several physical aspects were evaluated by US-EPA as a basis for establishing Sediment Quality Criteria for non-ionic organic contaminants. Their conclusion, based on available literature data at that time, was that concentrations of PAHs and PCBs were relatively independent of particle size classes in the sediment, and organic carbon was the predominant controlling factor in determining the partitioning of a contaminant between the different size classes in a sediment sample. This normalisation was found to be valid at least down to 0,2-0,3% organic carbon. (US-EPA, 1993f) The distribution of the PAHs between the different abiotic compartments in the sediment has a marked effect on their bioavailability, and understanding of these mechanisms is necessary for interpreting the observed results.

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5. THE APPROACHES FOR CALCULATION OF ENVIRONMENTAL RISK FOR DRILLING WASTE DISCHARGES – INPUT TO DETERMINATION OF PECs AND PNECs

The approaches selected to calculate the risk contribution from toxicity to the marine environment from drilling waste discharges are described in the following Chapter, addressing both risk in the water column and the sediment compartment. This risk calculation will serve as the basis for calculation of the contribution from toxicity, as one of the main stressors, to the EIF for drilling discharges. The strategy for the EIF drilling discharge development has been to follow the principles of environmental risk calculation described by the EU Technical Guidance Document (TGD) (EC, 1996, 2003). When deviation from the risk principles described by the TGD was found to be appropriate or necessary, the alternative approach selected was fully described and justified.

The relative risk of chemicals in drilling discharges is estimated by the PEC/PNEC ratio. In this report, the Predicted Environmental Concentration (PEC) is defined as the concentration of the bioavailable fraction of a chemical in water or sediment. The Predicted No Effect Concentration (PNEC) is defined as the safe concentration (no observed effect concentration) of the bioavailable fraction of a chemical in water or sediment. First, the partition (distribution) coefficients required for calculation of PEC of organic substances (naturally occurring substances and added drilling fluid chemicals) and metals (in added weighing agents) for both the water column and the sediment compartment are described. Additionally, the calculation rules recommended for determination of PEC in the water column are presented. Thereafter, the approaches to prediction of PNEC of these substances for the two marine compartments are described. Recommendations on PNEC and Kp values to be applied in the calculation of environmental risk for substances in drilling waste discharges are also presented.

5.1. Calculation of Predicted Effect Concentration (PEC)

5.1.1. PEC for Metals in water

Most of the metals associated with drilling waste discharges to the ocean are present in solid, sparingly soluble forms, mostly associated with drilling mud barite or ilmenite. Discharge of drilling muds to the sea during exploration and production drilling results in release to the ocean of substantial amounts of barite used as weighting agent. Barite (barium sulphate) is a natural mineral used as a weighting agent in water-based (WBM), oil-based (OBM) and synthetic-based (SBM) drilling muds. The solid metals are not considered bioavailable or toxic to marine organisms. However, a small fraction of the metals may desorb, partition, or dissolve from the drilling waste particles and enter the ambient water in dissolved, bioavailable forms, both in the water column and in the sediments. Dissolved neutral or ionic species of metals, as well as some metal-organic complexes and colloids, are considered the most bioavailable forms of most metals (Neff, 2002a).

An important input parameter to the estimation of the concentration of PEC of metals from discharge of drilling wastes in the receiving recipient is the solid/water partition coefficient (Kp) for metals between weighing agent particles and metals dissolved in the water phase. There is limited information on metal partitioning for weighting agents such as ilmenite, hematite etc. Therefore, one of the objectives of this task was to establish reliable barite-water distribution coefficients ($Kp_{barite-water}$) for metals both for the water column and the sediments, that as a first approach also could be applied for other weighting agents.This task was carried out by review of the scientific literature.

The naturally-occurring metals in drilling wastes that will be included in the toxicity EIF for drilling discharges are cadmium, chromium, copper, lead, mercury, and zinc (Chapter 3.1). Barium, the most abundant metal in most drilling muds, is included with the PLONOR compounds as barite ($BaSO_4$).

Kp values for metals

Most of the metals in drilling mud/cuttings, are present primarily in drilling mud barite. Although barite itself has a low solubility in seawater (81 µg/l), most of the metals in drilling mud barite are present in even more insoluble phases. They are associated with suphide mineral inclusions in the solid barite, particularly sphalerite (zinc sulphide) (Battelle Northwest Division, 2006).

Mobilisation of metals from barite into more biologically accessible forms (dissolved ions or ion complexes) is dependent on dissolution of solid metal sulphide inclusions in the nearly insoluble barite. Dissolution of metals is controlled in part by accessibility of the metals to the water phase at the solid/water interface (metals in the interior of insoluble particles may not be accessible) and by the solubility product (K_{sp}) of the metal in association with the counter-ions (usually anions) in the ambient water. Since most of the metals in barite appear to be associated with sulphides, the solubility products of the metal suphides are the deteriminants of dissolution rates. The K_{sp} is the product of the molar concentrations of the cation and anion in solution in equilibrium with the solid metal salt.

Sea water contains a high concentration of inorganic sulphates, which can be reduced to sulphide under reducing conditions (low Eh). Thus, metal dissolution from barite should be dependent on the oxidation/reduction potenital (redox potential) of the dissolution medium (water column and sediment pore water). Concentration of free sulphate decreases and concentration of free sulphide increases in sediment pore water with depth and declining redox potential (Eh). Thus, solubility of barite increases and solubility of metal sulfides decreases with depth in sediments.

These solid metals can be released from the solid phase by dissolution into the ambient water, which is an equilibration process between the solid metal salt and the cationic and anionic species of the salt in solution, but not by simple adsorption/desorption partitioning.

The dissolution of each metal of interest in seawater is controlled by the solubility of its most sTable, least soluble salt, which, for all the metals of interest, except barium and chromium, is the sulphide. Chromium does not form sTable sulfides. The most sTable form of chromium in marine sediments appears to be chromic hydroxide ($Cr(OH)_3$). The solubility products (log K_{sp}) of the most sTable forms of the metals of interest in seawater and sediments are summarized in Table 5.1. Log K_{sp} for several metals are summarized in Table 5.1. Solubility products for nearly insoluble metal salts are difficult to estimate accurately, so published values for a particular metal may vary by up to about one order of magnitude (compare Tables 4.17 and 5.1). Therefore, estimates of dissolved metals concentrations in seawater and sediment pore water, based on solubility product may vary by this amount.

Table 5.1 Solubility products (K_{sp}) of the dominant forms of metals in drilling discharges. Data from *bibliochm.uri.edu/CHM112/Tables/Ksp Table.htm.* K_{sp} is the product of the molar concentrations of the ions of a chemical compound in a saturated solution in equilibrium with the solid chemical compound.

Metal Compound	K_{sp}	Metal Compound	K_{sp}
$BaSO_4$	1.1×10^{-10}	HgS	2×10^{-53}
CdS	9.0×10^{-28}	NiS	3×10^{-19}
$Cr(OH)_3$	6.3×10^{-31}	PbS	3×10^{-28}
CuS	6×10^{-37}	ZnS	2×10^{-25}

The solubility product is difficult to use to estimate concentrations of dissolved (bioavailable) metals in sea water and sediment porewater because the concentration of the metal in solution is dependent primarily on the concentration of the counter ion in solution, rather than the concentration of the metal in the solid phase. Because of the slow kinetics (reaction rate) of dissolution of most metal sulfides, it is unlikely that metals in solution will reach equilibrium with the solid metal salts in the diluting drilling discharge plume before the solids settle to the sea floor or are diluted to very low concentrations. Therefore, an empirical approach is best suited for predicting the concentration of dissolved (bioavailable) metals in a drilling waste plume in the ambient water column.

Nominal K_p values for the metals of interest were determined empirically by Crecelius and Trefry (Battelle Northwest Division, 2006). One approach to estimation of the bioavailble fraction of metals associated with drilling mud barite is to measure the solid barite-water distribution coefficients ($Kp_{barite\text{-}water}$) for metals under different pH, dissolved oxygen, and salinity conditions. Several partitioning experiments were performed with three grades of drilling mud barite, including a low trace metal barite, a high trace metal barite, and a laboratory blend of barites from several sources (Battelle Northwest Division, 2006). Metals concentrations varied widely in the three barite samples (Table 5.2). Concentrations of cadmium, mercury, and zinc were the most variable. Metals concentrations in drilling mud barites usually are in the range summarized here. Most drilling in the North Sea and Gulf of Mexico currently is with drilling muds containing barite similar to the low trace metal barite (Table 5.2).

Table 5.2 Concentrations of metals in three samples of barite used in solubility studies and a Norwegian barite. Most of the drilling mud barite used in the Gulf of Mexico and North Sea today resembles the low trace metal barite. Data from Battelle Northwest Division (2006). Concentrations are µg/g dw (parts per million dry wt).

Metal	Low Trace Metal (µg/g dw)	High Trace Metal (µg/g dw)	Laboratory Blend (µg/g dw)	NORBAR Norwegian (µg/g dw)
Barium	538 000	524 000	507 000	---
Cadmium	0,35	0,77	7,0	0.05
Chromium	15	6,5	11	40
Copper	98	88	189	86
Mercury	0,44	5,9	6,7	0.05
Lead	318	243	1368	18
Zinc	35	167	1211	21

Barite samples were equilibrated for 1 to 7 days with natural sea water (20 g/L Gulf of Mexico seawater) at a pH of 7.3 or 8.3. Concentrations of metals were measured in the barite samples and in the water at the end of the equilibration period. Kp is the concentration ratio, µg/g metal in barite divided by µg/g metal in solution in water equilibrated with barite. Log Kp values were calculated as log C_{barite}/log C_{water} at the end of the equilibration period.

Barium was extremely insoluble, with log K_p greater than 7 (Table 5.3). The high K_p values for the metals are caused by high concentrations in the solid (barite) phase (e.g., barium), or extremely low dissolved metal concentrations in the seawater phase (e.g., mercury). Low K_p values were observed for metals that are present in the barite at relatively low concentrations or in the natural seawater at relatively high concentrations (e.g., cadmium and zinc, respectively).

Table 5.3 Ranges of particle/seawater partition coefficients (K_p and log K_p) for metals in barite equilibrated for 1 – 7 days with natural sea water (salinity 31 ‰, temperature 20°C, and pH 7.3 and 8.3. Three grades of drilling mud barite were used: low trace metal; high trace metal; and laboratory blend. Data from Battelle Northwest Division, 2006)).

Metal	K_p	Log K_p	Log $Kp_{barite\text{-}water}$ applied in the water column
Barium	15 000 000 – 25 000 000	7,17 – 7,40	Not included
Cadmium	400 – 6000	2,60 – 3,78	2,6
Chromium	13 000 – 22 000	4,11 – 4,34	4,11

Copper	20 000 – 80 000	4,30 – 4,90	4,3
Mercury	300 000 – 1 300 000	5,48 – 6,11	5,48
Lead	20 000 – 30 000	4,30 – 4,48	4,3
Zinc	2000 – 20 000	3,30 – 4,30	3,3

The potentially bioavailable fraction of a metal in the drilling waste plume decreases as log K_p increases. Thus, cadmium and zinc are the most bioavailable metals from barite in the discharge plume, with log K_p ranging from 2.6 to 4.3 (Table 5.3). The log K_p of 2.6 for cadmium means that water in a discharge plume containing suspended particles with a high concentration of barite contaminated with 1 µg/g cadmium, might contain up to 2.5 µg/L dissolved cadmium (about 10 times the concentration of Cd in filtered Gulf of Mexico seawater used by Crecelius and Trefry (Battelle Northwest Division, 2006) in their experiments). The target metals, other than barium, that leached in smallest amounts from the three barites are copper and mercury, the metals with the lowest K_{sp} values for their respective sulfides (Table 5.1). Very little barium dissolved from the solid barite particles into seawater in 1 to 7 days.

The ranges of barite particle-seawater partition coefficients (Kp and log Kp) for metals in barite and the selected Kp values recommended applied for metals in the water column are summarised in Table 5.3.

Barite grain size in these experiments ranged from 1.35 µm to 5.62 µm, so surface area of the barite in contact with seawater was high, indicating that the barite was very insoluble. Barium solubility from barite measured in these experiments ranged from 10 to 40 µg/L, similar to the background concentration in natural seawater.

Trefry et al., (1986) obtained similar results in earlier studies on partitioning of metals from four barite samples into sea water. Similarly, the results showed that cadmium is the least tightly bound metal and that little barium dissolved into the sea water.

At least in theory, the local PEC_{water} for the metals of concern in the near field receiving waters of discharging rigs could be measured directly in filtered samples of water from the drilling discharge plume. This actually is not practical or cost-effective on a large scale.

Instead the concentration of metals in the drilling discharge plume can be estimated by application of equilibrium partitioning theory. The PEC_{water} for metals originating from barite particles in the water column are estimated the DREAM model by Equation 1 (Rye et al., 2006):

Equation 1: Calculation of local PEC_{water} of metal from barite in the marine environment

$$PEC_{seawater} = \frac{C_{discharge} * FRACTION_{metal}}{DILUTION * Kp_{barite\text{-}water}}$$

in which:

PEC_{water} = local concentration in seawater of metal [mg/l]
$C_{discharge}$ = concentration of barite particles in the discharge [mg/l]
DILUTION = dilution in the recipient water predicted by the model (-)
$FRACTION_{metal}$ = fraction of the metal in barite (kg metal/kg barite)
$Kp_{barite\text{-}water}$ = partition coefficient between the metal in barite particle and dissolved metal in the water phase (l/kg)

Input parameters to the Equation 1 include, the estimated concentration of the metal in the bulk discharge, the solid/water partition coefficient ($Kp_{barite\text{-}water}$) for the metal between the barite particle and metal dissolved in the water phase (Table 5.3), the modelled dilution of the waste plume predicted by the model (DREAM) and the fraction of the metal in barite. Therefore, the PEC_{water} for metals will represent the leached fraction (dissolved) originating from the barite particle but does not take into account the phenomenon that metals are adsorbed or absorbed to drilling waste particles or suspended matter present in the water column. It is recommended to apply the lower level of the $Kp_{barite\text{-}water}$ range presented in Table 5-3 as input to the model calculation, representing the highest potential for metal leaching to the water column.

However, the calculations of PEC_{water} for metals described in the TGD approach, is based on premise that a substance is removed from the aqueous medium by adsorption to suspended matter. The PEC_{water} for metals therefore represent the bioavailable dissolved concentration of metal, calculated by application of the suspended matter-water partition coefficient for the metal ($Kp_{susp\text{-}water}$) (Section 2.3.1). Additionally, the regional background concentration ($PEC_{regional}$) of the metal should be taken into account in the local water column (Section 2.3.1).

5.1.2. PEC for Organic Substances in Water

An evaluation of the organic naturally occurring substances (such as aromatic and aliphatic hydrocarbons) and added chemicals (PLONOR and non-PLONOR chemicals) to be included in this toxicity risk model for drilling discharges took place. Inclusion of PLONOR chemicals in the risk calculation is recommended if the chemical is used in large quantities (Section 3.4). The PLONOR chemicals, ethylene glycols, drilling mud weighting agents, carboxymethyl cellulose and xanthan gum, are in this category.

According to the TGD (Section 2), organic substances with a log K_{ow} below 3 probably exert most of their effects in the water column. They desorb relatively rapidly from drilling waste particles. Thus, the total amount of these organic chemicals in the waste discharge can be considered to be bioavailable. Their concentration in the water column can be measured directly in bulk water samples or modelled with a dilution model as soluble (dissolved) chemicals. Therefore, only added drilling fluid chemicals with low octanol/water partition coefficient or organic carbon/water partition coefficient (log K_{ow} or log K_{oc}) less than 3, are included in the risk calculation of the water column.

It is recommended that the local water column PEC for organic substances should be estimated by Equation 2 with a slight modification of Equation 1, applied to metals, assuming that organic substances in the drilling waste are totally dissolved in the water:

Equation 2: Calculation of local $PEC_{seawater}$ of organic substances in the marine environment

$$PEC_{seawater} = \frac{C_{discharge} * \exp(-Biodeg*t)}{DILUTION}$$

in which:

$PEC_{seawater}$ = local concentration in seawater of metal [mg/l]
$C_{discharge}$ = concentration of barite particles in the discharge [mg/l]
DILUTION = dilution in the recipient water predicted by the model (-)
Biodeg = biodegradation factor (days^{-})
t = time (days)

The dilution and the concentration of the substance in the drilling discharge plume in the water column can be modelled with the DREAM model by applying three-dimensional and time variable ocean current field data and wind data for the release area (Rye et al., 2006). Also, the effects of biodegradation of the dissolved chemicals on concentrations in the water column are included in Equation 2.

The same approach should be used to estimate the PEC_{water} for naturally occurring substances (aromatic and aliphatic hydrocarbons) in oil that might be present in a drilling waste discharge. Since polycyclic aromatic hydrocarbons (PAHs) and most aliphatic hydrocarbons have log K_{ow} greater than 3 (Appendix 5-2), they are assumed to associate to cuttings and mud particles and sink with them to the sea floor, their contribution to dissolved (bioavailable) concentrations in the water column is limited. Polycyclic aromatic hydrocarbons and aliphatic hydrocarbons are therefore excluded from the EIF calculations in the water column.

However, the EU-TGD recommends that the calculation of the PEC_{water} for organic substances be based on the assumption that the substance is removed from the aqueous medium by adsorption to suspended matter. The PEC_{water} for organic substances (as for metals) should therefore be represented by the bioavailable dissolved concentration in the water phase, calculated by application of the suspended matter-water partition coefficient for the substance ($Kp_{susp\text{-}water}$) (Section 2.3.1). Additionally, the background concentration of the substance is taken into account by application of the regional concentration in the seawater ($PEC_{regional}$).

5.1.3. Input to Calculation of PEC for Metals in Sediment

Drilling muds and cuttings solids settle to and accumulate on bottom sediments following discharge of drilling wastes to the sea. Accumulation of cuttings on the sea floor often results in an increase in the concentration of barium in sediments near the discharge as a result of the large amount of drilling mud barite adsorbed to the cuttings. Concentration of other metals also may be elevated above background concentrations in sediments containing drilling muds and cuttings. However, the increments in metals concentrations in sediments due to drilling muds and cuttings accumulations are likely to be small. The most bioavailable fraction of metals associated with WBM and cuttings on the sea floor is that dissolved in the pore water or loosely complexed with particles or dissolved organic matter (colloids). This bioavailable fraction of metals is thought to be in equilibrium with metals in the solid phase of the bulk sediment. Deuel and Holliday (1998) fractioned the metals in a WBM and concluded that most of the total of all but one metal (lead) was in organic/sulphide complexes and fractions considered inaccessible for uptake by marine organismes (non-bioavailable). Part of the lead in WBM was associated with the Fe/Mn oxide phase of the particles; the Fe/Mn oxides dissolved under anoxic conditions, releasing adsorbed metals.

If the settled solids or underlying sediments contain a high concentration of biodegradable organic matter, sediment bacteria may oxidize the organic matter, reducing oxygen concentration in near-surface layers of sediment, eventually rendering the sediment suboxic (low in oxygen) or anoxic (oxygen-free). Under reducing conditions (low O_2 concentration) in sediments, sulfate reducing bacteria utilise sediment pore water sulphate to oxidise the organic matter, reducing the sulphate to sulphide. Sulphate concentration declines, allowing slow dissolution of barium sulphate. Crecelius and Trefry (Battelle Northwest Division, 2006) showed that, under reducing conditions in Gulf of Mexico sediments containing barite, the concentration of dissolved barium in sediment pore water increased gradually to 2600 to nearly 7000 μg/L compared to a concentration of 45 μg/L in oxidized sediment pore water.

Metals associated with sulphide minerals in the barite are essentially insoluble in anoxic marine sediment pore waters (usually high in dissolved sulphide) (Trefry et al., 1986; Neff 2002a,b).

The concentration of oxygen decreases with depth in sediments due primarily to degradation of organic sediment organic matter by aerobic bacteria and fungi. In oxygen deficient layers of sediment, suflate reducing bacteris use sulphate (abundant in seawater) as an alternate electron acceptor to further degrade the organic matter, and in the process reduce sulphate to sulphide. The solubility of barite increases and that of metal sulfides in the barite decreases as sediment sulphate concentration decreases and sulphide concentration in sediment pore water increases. Thus, the concentration of dissolved (bioavailable) barium increases and the concentration in solution of the other metals associated with barite decreases as oxygen is depleted in the cuttings pile sediments. Although chromium precipitates as the hydroxide $(Cr(OH))_3$ rather than the sulfide, little dissolves in anoxic sediment layers despite the small reduction in pH of anoxic sediment pore water.

The surface layer is the most biologically active layer of the sediment because the oxygen concentration is higher there than in deeper layers. Sediment pH varies little with changes in oxygen concentration, so pH has little effect on the solubility of barite or the accessibility of metals in the barite, because of the low solubility of barite in acid. However, the pH of the gut fluids of benthic invertebrates may be low enough to enhance dissolution of small amount of metals adsorbed to sediment iron/manganese oxyhydroxides or associated with drilling mud barite. Therefore, it is recommended that values for Kp applied to sediments should be estimated from data on sediment-water partitioning at lower pH values and/or following longer equilibration times compared to Kp values derived for the water column.

The solubility of metals from barite in acid buffer solutions (from which estimates of K_p for barium and metals in barite can be made) were estimated by Trefry and Trocine in a study of barite solubility (Pacific Northwest Division, 2006). They equilibrated the three barite samples (Table 5.2) with phthalate-buffered fresh water at pH ranging from 2.3 to 6 and measured concentrations of seven metals after different equilibration times in the water and barite fractions (Table 5.4). These data can be used to estimate log K_p for the selected metals between the barite particle and porewater in the sediments.

Table 5.4 Log barite/water partition coefficients (log K_p) for metals in the three barite samples in Table 5.2. Barite samples were incubated in 10:1 or 4:1 dilutions of pH 6 phthalate buffer for 15 minutes to 48 hours. K_p is the concentration ratio, μg/g metal in barite/μg/g metal in solution in water equilibrated with barite. Data from Pacific Northwest Division (2006). The Kp values recommended applied for metals in the sediments is also presented.

Metal	Log Kp Low Trace Metal	Log Kp High Trace Metal	Log Kp Laboratory Blend	Log $Kp_{barite-water}$ applied to the sediments
Barium	4,59	5.09	5,81	Not included
Cadmium	1,46	1,70	1,99	1,46
Chromium	3,85	3,43	3,24	3,24
Copper	2,20	1,64	2,10	1,64
Mercury	4,79	5.77	5,52	4,79
Lead	1,90	2,17	2,98	1,9
Zinc	2,24	1,84	2,08	1,84

The pH of most marine sediments rarely drops below about 6. Fluids in the digestive tract of benthic, sediment ingesting invertebrates usually have a pH of 5 to 6; fish digestive fluids may be somewhat more acidic. Thus, the bioavailability of metals from barite probably would not be increased much by ingestion by benthic marine animals. Therefore, the Kp values obtained at pH of 6 is recommended to be used for calculation of PEC for metals in barite for the sediments.

The Kp data for barite-seawater mixtures in pH 6 buffer and the selected Kp values recommended applied for metals in the sediments are summarized in Table 5.4. The full overview of Kp values obtained for water samples at pH levels below 6 is presented in Appendix 5-1.

For most metals in the three barites, log K_p increased with increasing pH. This indicates that the solubility and potential bioavailability of metals in barite are highest at low pH (lowest log K_p values) and decrease as pH increases (highest log Kp values).

Log Kp is below about 2 for cadmium, copper (except at a pH of 6), and zinc for all three barites at all pH between 2.3 and 6. A log Kp of 2 indicates that the concentration of the metal is 100 times higher in the barite than in the water in equilibrium with the barite. For example, the concentration of cadmium in the pH 6 buffer equilibrated with the laboratory blend barite (containing 7 mg/kg Cd) is 0.07 mg/L (the log Kp is 1.99). These results indicate that cadmium, copper, lead, and zinc are the metals in drilling mud barite with the greatest potential to be bioaccumulated by benthic animals from ingestion of mud/cuttings in seafloor sediments, if the drilling mud barite contains a high concentration of the metal.

However, log K_p for mercury in the two barite samples containing the highest concentrations of mercury was higher at pH 6 than at pH 2.3. The high log K_p values for Hg at all pH probably is due to the extremely low concentration of mercury in the phthalate buffers after equilibration with the different barites. Mercury and the other metals in barite probably are associated with a metal sulfide phase, probably mainly spalerite (zinc sulfide), with smaller amounts of galena (lead sulfide) or pyrite (iron sulfide), in the barite matrix. Dissolution of small amounts of barite, particularly in hypoxic pore water high in sulfide, does not affect the solubility of these metal sulfides. Mercury has the lowest K_p value of the metals examined, because it has a very low solubility product K_{sp} for the sulfide (Table 5.1) and concentrations of mercury in the barite samples were lower than those for the other metals, particularly in the low trace metal barite, typical of the drilling mud barite used offshore in the Gulf of Mexico and North Sea (Tables 5.2).

Another study performed by Terzaghi et al. (1998) with Italian WBM measured the concentration of five metals (arsenic, cadmium, chromium, copper, and lead) in 0.5 M acetic acid extracts (the exchangeable fraction) of seven samples of WBM used in Italian drilling operations in the Mediterranean. The results from this study showed Kp values that were remarkably similar to those produced by Trefry and Trocine (Battelle Northwest Division, 2006). Only chromium has a lower K_p in drilling mud than in barite. This is because chromium often is added to WBM in clay thinners, such as chrome lignosulfonate, which is moderately water-soluble. These data can be used to derive K_p values for the metals in drilling wastes on the sea floor.

Log K_p values from Terzaghi et al. (1998) data indicate that only a small fraction of the metals associated with these typical WBMs is in the exchangeable, readily bioavailable fraction of the drilling muds. Log K_p values range from 1.63 (cadmium in freshwater-lignosulfonate-Soltex mud) to 3.45 (copper in freshwater-gel mud) (Table 5.5). A log K_p of 2 indicates that 1 percent of the metal in the drilling mud is in an exchangeable, readily bioavailable fraction. It is uncertain how much of the metal in the reducible fraction of a drilling mud or barite would actually be bioavailable. Thus, the log K_ps from the Terzaghi et al. (1998) data approximates estimates of the bioavailable fraction of metals from drilling muds. However, if the cuttings contain a large fraction of organic matter, clay or water-sensitive shales, much of the metal desorbing from the mud will rapidly adsorb to the organic mater or clay mineral fraction of the cuttings, decreasing metal bioavailability.

Table 5.5 Metals concentrations in seven samples of Italian WBM, in a 0.5 M acetic acid (HAc) extract of the muds, and resulting K_p and log K_p values. Concentrations are mg/kg in sediment and mg/L in water. From Terzaghi et al. (1998).

Metal & Drilling Mud	Mud (mg/kg	HAc (mg/L)	K_p	Log K_p
Cadmium				
FW-Gel	0.12	0.0009	133	2.12

FW-Gel-Lignosulfonate	0.13	0.001	130	2.11
FW-Lignosulfonate	0.05	0.0009	56	1.74
FW-Lignosulfonate-Soltex	0.03	0.0007	43	1.63
FW-Polymer	1.06	0.0011	964	2.98
SW-Polymer	0.11	0.0021	52	1.72
FW-Mor-Rex	0.02	0.0006	33	1.52
Chromium				
FW-Gel	3.66	0.0039	938	2.97
FW-Gel-Lignosulfonate	1064	10.156	105	2.02
FW-Lignosulfonate	662	6.923	96	1.98
FW-Lignosulfonate-Soltex	325	3.849	84	1.93
FW-Polymer	4.62	0.0372	124	2.09
SW-Polymer	2.99	0.0214	140	2.15
FW-Mor-Rex	4.08	0.0299	136	2.13
Copper				
FW-Gel	3.13	0.0011	2845	3.45
FW-Gel-Lignosulfonate	3.2	0.0362	88	1.95
FW-Lignosulfonate	5.81	0.0906	64	1.81
FW-Lignosulfonate-Soltex	4.89	0.0446	110	2.04
FW-Polymer	3.68	0.0551	67	1.82
SW-Polymer	1.96	0.0479	41	1.61
FW-Mor-Rex	0.87	0.0176	49	1.69
Lead				
FW-Gel	0.21	0.0038	55	1.74
FW-Gel-Lignosulfonate	0.19	0.0015	127	2.10
FW-Lignosulfonate	0.23	0.0025	92	1.96
FW-Lignosulfonate-Soltex	0.43	0.0006	717	2.86
FW-Polymer	0.23	0.0004	575	2.76
SW-Polymer	0.19	0.0019	100	2.00
FW-Mor-Rex	0.42	0.0005	840	2.92

5.1.4. Metals Associated with Other Drilling Mud Ingredients

Although most of the metals in drilling muds are present as impurities in drilling mud barite, drilling muds and associated cuttings also contain metals from other sources. Bentonite clay, used in some WBM, OBM, and SBM as a viscosifier, may contain a variety of metals. Most are associated with the clay matrix and are immobile; some may be adsorbed to the clay particles in exchangeable forms.

Chromium in drilling mud often is derived primarily from chrome- or ferrochrome-lignosulfonates or chromate salts added intentionally to the mud for viscosity control (Neff, 2005). Barite and bentonite clay may also contain traces of chromium (Table 3.2). The chromium in a used drilling mud, even that added as chromate, is in the trivalent chromic valency state. Trivalent chromium salts have low solubilities and limited mobility in the environment. They usually have a low toxicity to plants and animals.

Lead, zinc, and copper also may enter drilling mud in pipe thread compound (pipe dope) or drill collar dope used to lubricate the threads and promote electrical conduction between pipe sections (Ayers et al., 1980). The dopes contain several percent metallic metals; some of the dope gets into the drilling mud, contaminating it. Sulfide may accumulate in drilling muds from the formation being drilled or from bacterial degradation of organic components, particularly carbohydrate gelling agents, in the mud. The usual method for removing sulfide from drilling mud is with inorganic sulfide scavengers. These scavengers react with both H_2S and HS^- to produce insoluble metal sulfide salts. The most frequently used sulfide scavengers in drilling muds are iron oxides, zinc oxide, and basic zinc carbonates (Neff, 2005). These metal salts react with sulfides to form insoluble iron sulfide (FeS_2) and zinc sulfide (ZnS), respectively.

OSPAR (2004) has included ilmenite (iron titanium oxide: $FeTiO_3$) on the PLONOR list (substances used and discharged offshore which are considered to pose little or no risk to the environment) to encourage its use as a replacement for barite in drilling muds discharged to the North Sea, because of concern about possible environmental impacts of metals sometimes found in barite. Ilmenite has a density of 4.5 to 5.0 g/cm^3 and may contain a wide variety of mineral impurities, including zircon, hematite, magnetite, rutile, and spinel. Ilmenite usually contains lower concentrations of metals than barite does. Ilmenite is a denser, harder mineral than barite (Fjogstad et al., 2002). Grain size of ilmenite used in drilling muds has been reduced to a mean of 8.14 µm (compared to a mean of 26.7 µm for barite) to reduce abrasion in the drilling mud system (McCosh and Getliff, 2003).

Like barite, ilmenite from different sources contains variable concentrations of several metals (Table 5.6). Most metals, except chromium, nickel, and zinc are present at much lower concentrations in ilmenite than in barite. The metals in ilmenite probably are present primarily associated with heavy mineral impurities in the ilmenite. The ilmenite, as well as the heavy mineral inclusions in it has a very low aqueous solubility; therefore, it is probable that the metals in ilmenite will have a bioavailability similar to the metals in barite.

Table 5.6 Concentrations of several methals in two samples of drilling mud ilmenite compared to metals concentrations in NCS barite (Table 3.2). Data for Ilmenite No. 1 from McCosh and Getliff (2003) and for Ilmenite No. 2 from Fjogstad et al. (2002).

Metal	NCS Barite	Ilmenite No. 1	Ilmenite No. 2
Arsenic	NV	<0.3	NV
Cadmium	0,7 – 1,7	<0,009	<10
Chromium	9,8 – 14,3	206	0.075% (as Cr_2O_3)
Copper	76,6 – 105	17,9	19
Nickel	1,2 – 2,1	40,8	140
Lead	48,7 – 116	0,79	4
Zinc	42,9 – 139	15,7	150
Mercury	0,31 – 0.69	0,013	0.006

Westerlund et al. (2001, 2002) used a sequential extraction procedure to evaluate the potential bioavailability of metals from barite, ilmenite, natural sediments, and drill cuttings (Table 5.7). A larger fraction of the arsenic, cadmium, and nickel were more exchangeable from ilmenite than from barite. Copper and zinc were more exchangeable from barite than from ilmenite. Similar fractions of chromium and lead were extractable from barite and ilmenite. Because of the high concentration of chromium and nickel in some samples of ilmenite, the amount of these metals released to sediment pore water would be greater from an ilmenite mud than from a barite mud. Most of the other metals examined are present at such low concentrations in ilmenite that it is unlikely that accumulation of an ilmenite mud in sediments would result in a measureable increase in the concentration of these metals in the sediment pore water.

Table 5.7 Fraction of total metals in sediments, barite, ilmenite and cuttings that are in exchangeable, carbonate or Fe/Mn oxide fractions of the solids and, therefore, potentially bioavailable. Data from Westerlund et al., (2001, 2002) as reported by Kjeilen-Eilertsen and Westerland (2004).

Metal	Sediment	Barite	Ilmenite	Cuttings
Arsenic	0,50	0,10	0,80	0,05 – 0,15
Cadmium	0,85	0,70	0,90	0,20 – 0,30
Chromium	0,40	0,30	0,30	0,20 – 0,50
Copper	0,20	0,50	0,10	0,05 – 0,10
Nickel	0,40	0,30	0,80	0,40
Lead	0,40	0,20	0,30	0,20 – 0,30
Zinc	0,50	0,70	0,30	0,20 – 0,30

5.1.5. Evaluation of Partitioning of Metals from Drilling Muds and Cuttings

The limited available data on partitioning and bioavailability of metals from drilling muds and cuttings accumulations on the sea floor generally confirm that drilling mud and cuttings metals have a low accessibility and bioavailability to benthid marine organisms. As discussed above (Section 5.1.3), Deuel and Holliday (1998) performed sequential fractionation on a WBM and concluded that most of all metals, except lead, were associated primarily with insoluble and non-bioavailable sulfide fractions in the mud. Some of the lead was associated with the Fe/Mn oxide fraction from which metals are exchangeable under mild reducing conditions.

Terzaghi et al. (1998) extracted seven WBMs with 0.5 M acetic acid and estimated log K_p for different metals (Table 5.5). Log K_p estimated in this way were comparable to those for barite. Only chromium had a lower log K_p from drilling mud than from barite. This is attributable to the large amounts of chrome-containing deflocculants sometimes added to WBM. Actual bioavailability of the metals from drilling muds may be lower than predicted if the muds or cuttings contain large amounts of organic matter or the sediments become anoxic in the cuttings pile.

Westerlund et al. (2001, 2002) also did sequential extractions of drilling muds and cuttings to evaluate the potential mobility and bioavailability of metals (Table 5.7). In most cased the exchangeable (potentially bioavailable) fraction of the metals was smaller for drill cuttings than for either barite or ilmenite. A larger fraction of chromium was exchangeable from some cuttings than from barite and ilmenite. These studies show that the PECs proposed for metals in water and sediments in this report are reasonable, sufficiently conservative values for drilling fluid discharges to the North Sea.

5.2. Calculation of Predicted No Effect Concentration (PNEC)

One of the objectives of this task force was to consider the methods available for use in developing environmental quality criteria (PNEC values) for water column and sediments, and to reach consensus on the methods most appropriate for this purpose. The strategy for determination of the PNEC for the marine environment has been to follow the principles of TGD (EC, 1996, 2003). However, deviation from the risk principles described by the TGD was occasionally found appropriate, that required alternative approaches to be evaluated. In the following section, the PNEC values are presented that were developed for organic substances, metals and drilling fluid chemicals associated with the drilling waste for the water column and the sediment.

5.2.1. PNEC for Organic Substances in Water

The PNEC values traditionally are determined on the basis of available toxicity data from single species laboratory tests or, in a few cases, established from model ecosystem tests, taking into account adequate assessment factors (EC, 1996, 2003). Use of both freshwater and marine data is recommended in TGD for PNEC derivation. If sufficient data from long-term tests are available, statistical extrapolation methods may be used to derive a PNEC.

The PNEC should be derived from the most sensitive endpoint, regardless of the medium, determined from the available toxicity data and divided by an assessment factor. The PNEC is calculated by dividing the lowest LC/EC50 or NOEC value by an appropriate assessment factor in accordance with the EU-TGD (Table 2.2, Section 2.4.1; EC, 2003).

During the development of EIF produced water, a set of PNEC values was established for selected produced water constituents (Johnsen et al., 2000, Frost, 2002). The PNEC values were determined by applying the assessment factors as described for the freshwater environment (EC, 1996). At that time sufficient data from long-term tests were not available for all groups of components representing the composition of produced water, and therefore statistical extrapolation approach was decided not to be used to derive PNEC values.

In 2003 the freshwater EU-TGD was revised and a risk assessment approach for application in the marine environment was included (EC, 2003). In principle, higher assessment factors should be applied for the marine environment than for the freshwater environment, in accordance to the revised TGD (EC, 2003). The higher assessment factor reflects the greater uncertainty in the extrapolation due to the greater species distribution of the marine environment. In general, marine assessment factors are a factor 10 higher when based on the set of freshwater data; algae, crustacean and fish species. To reduce the assessment factors, chronic toxicity endpoint values are required for additional species from marine taxonomic groups in addition to data for freshwater or marine algae, crustacean and fish species, in order to reduce the uncertainty in the extrapolation due to the higher diversity of marine phyla.

The produced water PNEC values have not been yet updated, incorporating the new assessment factors. However, a project in the Norwegian Oil Industry Association (OLF) currently is updating the produced water PNEC-values in accordance to the revised TGD (EC, 2003). This work will be completed within 2007 and the use of the statistical extrapolation approach, Species Sensitivity Distributions (SSD), will be evaluated for the naturally occurring produced water constituents.

The set of PNEC values currently being used in EIF produced water calculations, are based on toxicity data on at least three selected trophic levels (algae, crustaceans and fish). The assessment factors will decrease in magnitude if long-term chronic studies are available, and the lowest assessment factor obtained is 10, provided long-term chronic toxicity data are available for all three trophic levels (EC, 1996; Frost, 2002).

Natural substances

According to the TGD (Section 2), organic substances with a log K_{ow} below 3 probably exert most of their effects in the water column. They desorb relatively rapidly from drilling waste particles. Thus, the total amount of these organic substances in the waste discharge can be considered to be bioavailable. Their concentration in the water column can be measured directly in bulk water samples or modeled with a dilution model as soluble (dissolved) chemicals. Therefore, only substances with low octanol/water partition coefficient or organic carbon/water partition coefficient (log K_{ow} or log K_{oc}) less than 3, are included in the risk calculation of the water column.

Naturally occurring substances, such as polycyclic aromatic hydrocarbons (PAHs) and most aliphatic hydrocarbons, have log K_{ow} greater than 3 (Appendix Chapter 5, Table 8.2), and are assumed to associate to cuttings and mud particles and sink sink with them to the sea floor. Their contribution to dissolved (bioavailable) concentrations in the water column is limited. Aromatic hydrocarbons and aliphatic hydrocarbons are therefore excluded from the EIF drilling dicharges in the water column.

Drilling fluid chemicals (non-PLONOR and PLONOR)

Calculation of toxicity threshold values (PNECs) for drilling fluid chemicals applied to risk assessment in the water column are based on a similar approach to that being applied for added chemicals for EIF produced water. However, a few adjustments are introduced to the method for calculation of PNECs.

The conclusion from the evaluation of including PLONOR chemicals (Chapter 3.4) in the risk calculation was that all PLONOR chemicals/substances used in high quantities (drilling mud weighting agents, ethylene glycols etc.) should be considered for inclusion of the EIF calculation. As an example, PNECs for suspended particulate matter from weighting agents (e.g. barite, bentonite and attapulgite) added as weighting agents or viscosifiers in WBM are developed in another Task (Task 2) of the ERMS project (Smit et al., 2006a), with focus on physical disturbances on marine organisms. The PNECs for the barite, bentonite and attapulgite were derived by using the Species Sensitivity Distributions in accordance with the EU-TGD approach. Since aquatic toxicity data and biodegradation tests are not required for PLONOR substances according to OSPAR (2000), toxicity data for PNEC derivation have to be obtained by reviewing the literature and/or by performance of additional laboratory toxicity tests on individual substances. Dependent on the number of ecotoxicological data and type of data available, the PNEC should be derived by using assessment factors or the SSD approach following the principles of TGD (Chapter 2.4.1). The assessment factor applied can be lowered provided the substance is released to the environment batch-wise (intermittent release, Chapter 2.5), rather than continuously.

Drilling waste discharges will influence two environmental compartments; water column and sediment over different time frames. During and shortly after discharge, exposure is present in the water column. The time duration of releases from the rig is generally short, especially considering exploration drilling discharges (on order of days). The time duration of the various dicharges may vary. As an example discharge of cementing chemicals is in batch discharges of short duration (within one hour), and discharge of drilling fluid chemicals (e.g. weight agents like barite) and chemicals for testing of the blowout preventer (BOP) are of longer duration (a few days if effective drilling time period is considered). The potential water column impacts are in most cases referred to as acute, with a temporary impact in the water column, while the sediment effects are considered more of chronic nature (order of months and years). One exception might be potential impacts from suspended particulate matter (e.g. barite particles), that may be present at critical concentations over a relatively large area for several days. This phenomenon should be evaluated from case to case basis dependent of the release scenario.

For intermittent releases, the TGD recommends to lower the assessment factor by a factor of 10, because long-term exposure is not expected. Intermittent release is defined as “intermittent when recurring infrequently, i.e. less than once per month and for no more than 24 hours” (EC, 2003). However, the use of this approach needs to be justified and judged on case-by-case basis.

For most PLONOR and non-PLONOR substances used in drilling operations only acute toxicity data are available. Provided that discharge of the substance is considered intermittent the PNEC for EIF calculation of the water column can be derived by use of an assessment factor of 100 applied to the lowest L(E)C50 value of at least three short-term tests from three trophic levels (algae, crustacean and fish). This extrapolation should be carried out with care. Some substances may be taken up rapidly by aquatic organisms. This can lead to delayed effects even after exposure has ceased. This will generally be taken into account by the lowered assessment factor, but there may be occasions when a higher or lower factor would be appropriate. For substances with a potential to bioaccumulate, the lower assessment factor may not always be sufficient to provide adequate protection. For substances with a known non-specific mode of action, interspecies variations may be low. In such cases, a lower factor may be appropriate. In no case should a factor lower than 10 be applied to a short-term L(E)C50 value.

Only chemicals characterised as water soluble, represented with low octanol/water partition coefficient or organic carbon/water partition coefficient (log Kow or log Koc< 3) are included in the risk calculation of the water column. Chemical substances that are highly hydrophobic or insoluble with log K_{ow} or log K_{oc} greater than 3 (hydrophobic) are assumed to accumulate in the sediment on the sea floor (associated to settled cutting/mud particles) and therefore impacts in the water column from these substances are not considered (in accordance to TGD) (Rye et al., 2006).

Therefore, for most drilling operation releases related to exploration drilling it is recommended to lower the assessment factor for determination of the PNEC. An assessment factor of 100 should be applied to the lowest acute toxicity data for water column species, preferably on the individual sustances of the chemical or for the preparation (mixture). However, there might be cases during drilling operations implying release (and exposure) of longer duration and this approach cannot be justified, and a higher assessment factor is required (1000). Consequently, the determination of assessment factor applied for calculation of PNEC for individual chemical substances discharged during drilling operations needs to be judged for the various discharge scenarios/options (cementing, completion, BOP testing etc.) and on case-by-case.

Metals

Weighting agents (e.g. barite, ilmenite) and clay are the main source of heavy metals in drilling discharges to the marine environment on the NCS; metals are present mostly as trace impurities in the natural minerals. In principle, a similar approach to that described for deriving PNEC values for natural organic substances, should also be applied for the metals. However, the experience from the PNEC values currently being used for metals in the EIF calculation of produced water, is that the PNEC for some metals (e.g., Cu) were lower or in the same range as the natural background concentration in seawater on the Norwegian continental shelf (Table 5.8).

If sufficient data from long-term tests are available, the statistical extrapolation approach, Species Sensitivity Distribution (SSD), described by TGD for the marine compartment, is recommended applied for determination of PNEC values. A project was intiated by OLF this year in order to derive PNEC values for metals based on the SSD approach. The project will be finalised by end of 2006.

Table 5.8 Toxicity threshold values, expressed as PNEC, of selected metals applied in the environmental risk calculation (EIF) of produced water discharges (Frost, 2002).

Component	**Assessment factor**	**PNEC$_{\text{produced water}}$ (µg/l)**	**North Sea background concentrations (µg/l)** [g]
Zinc	50	0,46[a]	0,3 -1,4 [g]
Copper	50	0,02 [b]	0,02 -0,5 [g]
Nickel	50	1,22 [c]	NA
Cadmium	50	0,028 [d]	0,004 - 0,023 [g]
Lead	50	0,182 [e]	0,02 – 0,081 [g]
Mercury	100	0,008 [f]	0,001 – 0,003 [g]

a) Dinnel et al., 1989
b) Bambang et al., 1995
c) Gentile et al., 1982
d) Emson & Crane, 1994
e) Steele & Thursby, 1983
f) Gentile et al., 1982
g) Norwegian continental shelf (OLF report, 1998).

Until the new set of PNEC values is available for metals following the TGD guidance and requirements, it is recommended to apply the toxicity threshold values applied in The Netherlands, used for derivation of the, “Integrated Environmental Quality Objectives”, prepared by the Dutch National Institute of Public Health and the Environment (Crommentuijn et al., 1997). So-called Maximum Permissible Concentrations (MPC$_{\text{water}}$), is the concentration above which the risk for the ecosystem is considered unacceptable (VROM, 1989), were derived for eighteen metals taking into account existing national background concentrations following the so-called “added risk approach”. MPCs were derived for water, sediment, soil and air. The MPCc served as a basis for the Dutch government to set generic Environmental Quality Standards (EQS) in The Netherlands. EQS in turn are used by the Dutch government to assess the environmental quality and for other environmental policy purposes (Crommentuijn et al., 1997).

The MPC$_{\text{water}}$ is calculated from the Maximum Permissible Addition (MPA$_{\text{water}}$) derived from laboratory toxicity data on organisms that are representative of the Dutch coastal environment. This

MPA_{water} is used as the concentration of a metal in a specific compartment that may originate from anthropogenic sources and be considered acceptable when added to the background concentration (Cb_{water}). Background concentration is regarded as the concentration that is present in rural sites due to natural causes only. The background concentration consists of two fractions: the active or the bioavailable fraction that may exert an effect and the inactive fraction that is not bioavailable to exert an effect. The MCP_{water} is defined as the sum of the MPA_{water} and the background concentration (Cb_{water}):

Equation 1 Calculation MPC_{water} – Dutch RIVM (Crommentuijn et al., 1997):

$$MPC_{water} = MPA_{water} + Cb_{water}$$

in which:
MPC_{water}= *Maximum Permissible Concentration in the surface water (µg/l)*
MPA_{water} = *Maximum Permissible Additionin the surface water (µg/l)*
Cb_{water} = *background concentration in the surface water (µg/l)*

Traditionally, MPC_{water} values are calculated using either fixed assessment factors by application of the modified EPA-method (Van de Meent et al., 1990; OECD, 1992) or a statistical extrapolation technique (Aldenberg & Slob, 1993). However, special attention has been paid to the evaluation and selection of the toxicity data used in these extrapolation methods. For instance, data on species that are not considered representative for the Dutch environment have not been included. The statistical extrapolation technique is applied if chronic toxicity data (NOECs) for species of at least four different taxonomic groups are available, while the modified EPA method is used if less chronic data or only acute data are available.

The aim is to set MPC_{water} at a level that protects all species in an ecosystem. However, in order to be able to use extrapolation methods, a 95% protection level is chosen as a sort of cut-off value in this work. The concentration corresponding with a 95% protection level is called the MPC_{water}. Statistical extrapolation methods are based on the assumption that the sensitivities of species in an ecosystem, expressed as NOEC or L(E)C50 values, can be described by a statistical frequency distribution. This frequency distribution can be estimated using NOEC or L(E)C50 values of species of different taxonomic groups as input. The method of Aldenberg and Slob (1993) was used if NOEC values for four or more different taxonomic groups were available. The statistically extrapolation method assumes that the NOEC values used for estimating the distribution fit the log-logistic distribution. The modified EPA-method was used if less than 4 NOECs from different taxonomic groups were available. For the metals of concern, the number of data (NOECs) available is considered sufficient to apply statistical extrapolation.

For setting integrated environmental quality standards in The Netherlands, an additional factor was applied to the MPA value to take into account combination toxicity and uncertainties in risk assessment (VROM, 1989). The so-called Negligible Concentration (NC_{water}) was derived by taking the background concentration (Cb_{water}) plus the Negligible Addition (NA_{water}): $NC_{water}=Cb_{water}+NA_{water}$, where $NA_{water}=MPA_{water}/100$. The aim, from a policy point of view, is that the environmental concentration of each metal is at or below its NC in the long run (as a target value), and that the concentration does not exceed the MPC_{water} on a short-term basis, the latter to protect the ecosystem.

The $MPAs_{water}$ ($MPCs_{water}$) for water are based on the combined data sets of for freshwater and marine species to obtain more reliable MPA_{water} values. Therefore, the MPAs for freshwater, marine water and groundwater are the same. It must be noted that salinity may influence metal availability and hence affecting the toxicity. Complexation of metals with chlorides or carbonates, differences in uptake and therefore differences in sensitivity may be expected between freshwater and marine species (Hall and Anderson, 1995). For all metals considered, for which it was possible to statistically test differences in sensitivity, no differences were found (Crommentuijn et al., 1997). However, further research should be carried out prior to including salinity dependent MPCs$_{\underline{water}}$.

Table 5.9 Maximum Permission Addition (MPA$_{\underline{water}}$), background concentration in the Netherlands (Cb$_{marine\ water}$), Maximum Permissible Concentration (MPC$_{\underline{water}}$) and Negligible Concentration (NC$_{\underline{water}}$) for metals for marine surface waters.

Metal	**MPA$_{\underline{water}}$ (µg/l) (PNEC$_{\underline{water}}$)** $^{a)}$	**Cb**$_{marine\ water}$ $^{b)}$ **(µg/l)**	**MPC** $_{water}$ **(µg/l)**	**NC**$_{water}$ **(µg/l)**
Cadmium	**0,34**	0,025	0,37	0,028
Copper	**1,1**	0,25	1,4	0,26
Lead	**11**	0,02	11	0,13
Inorganic mercury	**0,23**	0,0025	0,23	0,0048
Methyl-mercury	**0,01**	0,0025	0,013	0,0026
Nickel	**1,8**	NA	NA	NA
Zinc	**6,6**	0,35	7	0,42

a) MPA$_{\underline{water}}$ based on statistical extrapolation of combined set of toxicity data (NOEC) from both freshwater and marine species.
b) Background concentrations is expressed as dissolved concentrations of metals in the North Sea presented by Van Eck et al., (1985) and proposed by Van den Hoop (1995) to be used as the background concentration for the marine environment.

As a temporary approach, Norwegian adapted MPC$_{\underline{water}}$ values based on dissolved background concentrations of metals from Norwegian marine surface waters should be applied. However, the data on background concentrations of metals in the north-eastern part of the North Sea and the Norwegian Sea are limited and need to be reviewed with regard to quality. If appropriate, region specific background concentration should be addressed. Therefore, the MPA$_{\underline{water}}$ values of the metals derived by Crommentuij et al., (1997, 2000) presented in Table 5.9 should be applied as PNEC$_{\underline{\ water}}$ values for the selected metals of the water column without taking site-specific background concentrations into account.

The present approach is not ideal and reliable since MPA$_{\underline{water}}$ values were derived from data on species that were representative for the Dutch environment only, excluding data on other species from distant areas. The statistical extrapolation approach (SSD), in accordance to TGD guideline for the marine environment, is being examined in the ongoing OLF project and will be the selected approach provided that sufficient chronic aquatic toxicity data are available for metals.

5.2.2 PNEC approaches in the Sediments

In general, the same strategy applied for calculation of PNEC based on aquatic toxicity data also should be applied to sediment data, in accordance to the TGD (EC, 2003). If results from whole-sediment tests with benthic organisms are available, the PNEC sediment should be derived using assessment factors. Only long-term tests studying sub-lethal endpoints are considered applicable to marine risk assessment because of the long-term exposure of benthic organisms to sediment-bound substances that occur under field conditions.

A number of test methods are available, mostly tests that measure acute toxicity. A limited number of test methods measure long-term sub-lethal endpoints. Only whole sediment tests with infaunal and epibenthic organisms are considered for use. No fully international accepted, standardised test methods for testing the whole sediment chronic toxicity are currently available for use in a risk assessment of the marine sediment compartment. OECD has prepared review paper including marine sediment test methods (OECD, 1998). Most of the chronic tests have been developed for amphipods (*Corophium sp*) and polychaetes (*Arenicola marina*) (Chapter 4, Table 4.1).

PNEC for the sediment compartment should be calculated for substances that have potential for either directly depositing on the seafloor or sorbing to sedimenting particles. Organic substances with log K_{oc} or log $K_{ow} \geq 3$

are considered to accumulate in sediments and are therefore included in the risk assessment of the sediment compartment.

Assessment factor approach

Natural organic substances (PAHs)

The literature review of marine sediment ecotoxicity did reveal relevant data for use in calculation of $PNEC_{marine\ sediment}$ by applying assessment factors for the evaluated individual PAHs and the diesel fuel, but data were available only for a minor number of PAHs. The ecotoxicological endpoints from chronic long-term studies in the reviewed literature were scarce. Further, the majority of datapoints were from only one phyla (crustacea:amphipoda/insecta) leaving a general lack of information on toxicity to major benthic phyla such as annelids (oligo- and polychaetes), cnidaria (hydroids and sea anemones), echinoderms and molluscs (bivalves and gastropods). All the data for sensitive species were acute data (lethality) from short-term studies, which implies that an assessment factor of 1000 should be used for calculation of $PNEC_{sediment}$. As seen from Table 5.10 all the calculated $PNEC_{sediment}$ values are below the reported mean natural background concentrations from the Norwegain Continental Shelf (NCS). The use of assessment factors for calculation of $PNEC_{sediment}$ based on the ecotoxicological endpoints from the scientific literature are not applicable under realistic conditions and therefore not considered valid.

Table 5.10 Calculation of $PNEC_{sediment}$ values for PAHs based on the data from the literature review using assessment factors according to the EU-TGD (EC, 2003). Effect data related to bulk concentration of the PAH were used for calculating PNEC-values for marine sediments.

Compound	**Assessment factor**	**Calculated $PNEC_{sediment}$ µg/g dw**	**NCS-background µg/g dw [1]**
Acenaphthene	1000	0,0433	0,208
Fluoranthene	1000	0,0023	5,117
Phenanthrene	1000	0,01	3,452
Pyrene	1000	0,147	3,851

1. Mean background sediment concentrations of metals for the Norwegian Continental Shelf (NCS) based on all reference and regional stations (Bjørgesæter, 2006).

In absence of sufficient amount of relevant ecotoxicological data for sediment-dwelling organisms the EU-TGD (EC, 2003) is open for a provisionally calculation of $PNEC_{sediment}$ by use of the equilibrium partitioning method. Since the assessment factor approach is not recommended to be applied to the ecotoxicological data obtained in the literature review for calculation of $PNEC_{sediment}$, the equilibrium partitioning approach has been evaluated and is dealt with later in the present Chapter in this report.

Drilling fluid chemicals (e.g. non-PLONOR and PLONOR chemicals)

Only acute toxicity data are available for most non-PLONOR substances used in drilling operations. The PNEC can be derived from a standardised acute toxicity test system for offshore chemicals (OSPAR, 2000/5) with one sediment reworker (*Corophium volutator or Abra alba).* Since aquatic toxicity data and biodegradation tests are not required for PLONOR substances, toxicity data for PNEC derivation have to be obtained from the literature review and/or by performance of additional laboratory toxicity tests on individual substances. If only one acute sediment test is available (freshwater or marine) an assessment factor of 10000 should be applied. In addition the $PNEC_{sediment}$ should be calculated from $PNEC_{water}$ using the equilibrium partitioning method (EqP method). The lowest PNEC from both approaches should be used in the risk calculation of the sediment.

Metals

The literature review of the marine sediment toxicity studies did reveal relevant data for use in determination of PNEC$_{sediment}$ for all evaluated metals. However, there is a lack of ecotoxicological endpoints from chronic long-term studies in data from the reviewed literature. Further, there is a general lack of any information on toxicity of metals on some major benthic phyla such as cnidaria (hydroids), echinoderms and molluscs (bivalves and gastropods), and there is a substantial imbalance between the phyla naturally represented in marine sediments and the phyla covered by available guidelines for testing av sediments shown in Table 4-1.

As outlined in Chapter 2 and Table 2.4 in this report, different assessment factors must be applied for calculation of PNECs depending on the nature and quality of the data.The scarcity, and especially the lack of ecotoxicological endpoints from chronic long-term studies in data from the reviewed literature, demands the use of the high assessment factors for developing PNEC$_{sediment}$ for metals. All the data for sensitive species were acute data (lethality) from short-term studies which implies that an assessment factor of 1000 should be used with the exception for mercury where only one acute response were identified, and an assessment factor of 10000 should be applied. The calculated PNEC$_{sediment}$-values from the most sensitive species based on the lowest values for the acute ecotoxicological endpoints for each metal are listed in Table 5.11. As seen from Table 5.11 all the calculated PNEC$_{sediment}$ values are either within or below the range of the reported natural background concentrations from the NCS. The use of assessment factors for calculation of PNEC$_{sediment}$ based on the ecotoxicological endpoints from the literature are not applicable under realistic conditions and therefore not considered valid.

Table 5.11 Calculation of PNEC$_{sediment}$ values based on the data from the literature review using assessment factors according to the EU-TGD (EC, 2003). Only acute effect data related to bulk concentration of the metal were used for calculating PNEC-values for marine sediments.

Metal	**Assessment factor**	**Calculated PNEC$_{sediment}$ (mg/kg dw)**	**NCS-background (mg/kg dw) [1]**	**World Sediments (mg/kg dw) [2]**
Cadmium	1000	0,00126	0,003 - 0,13	0,1 - 0,6
Copper	1000	0,0068	0,3 - 17,2	7 - 33
Chromium	1000	0,147	2,58 - 39,2	36 - 110
Lead	1000	0,029	1,92 - 46,5	10 - 33
Mercury	10000	0,00152	0,003 - 0,10	0,03 – 0,14
Zinc	1000	0,0319	0,42 - 83,7	27 - 88

1. Ranges of NCS (Norwegian Continental Shelf) background concentrations based on samples from about 150 reference stations (extraction with nitric acid). Data from Bjørgesæter (2006).
2. Data from Neff (2005).

Furthermore, the results from these tests (bulk metal concentration) should be carefully evaluated since several factors can contribute to variability in the test results. Of major importance to the availability of metals in sediment are the influence with respect to concentrations of iron (as hydrous oxides), total organic carbon content and sulphide in the sediment (Tessier and Cambell, 1987; Di Toro et al., 1990; Ankley et al, 1996). The physical or chemical species of a metal in the sediment has a marked effect on its availability and toxicity to marine organisms, and understanding of metal speciation is necessary for understanding the impacts from metals.

A number of studies have made comparison between the bulk metal concentration in field collected sediments and the acute response of amphipods and polychaetes for the target metals. These studies have demonstrated that there is no relationship between the total bulk metal concentration in the sediments and the acute response (whole sediment tests) (Hansen et al., 1996). However, several studies have demonstrated over the past two decades that acute toxicity is controlled by the concentration in the interstitial water rather the total bulk concentration in the sediment (Swartz et al., 1985, Carlson et al. 1991, DiToro et al. 1992, Green et al. 1993, Casas and Creselius 1994, Berry et al. 1996, Lee and Lee, 2005), thus indicating that the interstitial water concentrations represent the bioavailable fraction of the metal.

Equilibrium Partitioning Method (EqP method)

In absence of any ecotoxicological data for sediment-dwelling organisms the EU-TGD (EC, 2003) allows a provisional calculation of $PNEC_{sediment}$ by use of the equilibrium partitioning method. Since the assessment factor approach could not be applied to the ecotoxicological data obtained in the literature review for calculation of $PNEC_{sediment}$, the equilibrium partitioning approach was evaluated.
Additionally, when only acute toxicity data with benthic organisms are available the equilibrium partitioning method also should be applied for determination $PNEC_{sediment}$ values as a screening approach, according to TGD. The lowest PNEC derived from use of assessment factor or the equilibrium method should be used for the risk calculation. In accordance with the TGD, a PEC/PNEC ratio exceeding 1 indicates that long-term testing with sediment organisms (spiked sediment) should be considered.

The equilibrium partitioning method derives sediment quality criteria (SQC) or PNECs from water quality criteria by predicting interstitial water concentrations for the protection of benthic organisms. This method assumes that:

- The uptake and hence bioavailability, bioaccumulation and toxicity are closely related to the pore water concentration;
- Equilibrium exists between the concentration of the substance sorbed to the solid phase (sediments) and the concentration in solution in pore water/interstitial water; related by a single partition coefficient;
- The sensitivity distribution for a substance to aquatic and benthic organisms is equal.

The advantage of the EqP method is that the theoretical basis is well established and has been tested for non-ionic organic substances and metals.

Natural organic substances and drilling fluid chemicals
For non-ionic organic substances the sediment quality criteria (SQC) or $PNEC_{sediment}$ is recommended derived by the following formula (US EPA, 1997, US EPA, 2003a):

Equation 2 Calculation of SQC ($PNEC_{sediment}$) for organics - EqP approach (US-EPA, 1997):

$$\mathbf{SQC\ (PNEC_{sediment}) = Kp_{sediment} * WQC\ (PNEC_{produced\ water})}$$

in which:
SQC = Sediment Quality Criteria (mg/kg) or $PNEC_{sediment}$
$Kp_{sediment}$ *= partition coefficient between sediment and water (l/kg)*
WQC = Water Quality Criteria (mg/l)

This Equation is recommended applied for derivation of $PNEC_{sediment}$ for added drilling fluid chemicals (e.g. non-PLONOR and some PLONOR chemicals) with log K_{ow} or K_{oc} values > 3 and for naturally occurring substances (PAHs, aliphatic hyrdrocarbons). The EqM-method was originally proposed to develop sediment quality criteria for organic substances by Pavlou and Weston (1984), and was further described by DiToro et al., (1991), OECD (1992) and Van der Koy et al., (1991). In the current US-EPA approach (2003a,b) derivation of sediment quality criteria (SQC) or the so-called ESB (Equilibrium Partitioning Sediment Benchmarks), the WQC (water toxicity threshold) is expressed by the "Final Chronic Value" (FCV) for the individual PAHs or the PAH mixtures multiplied by the Koc of for the particular PAH (US-EPA, 2003b) (Chapter 8.3, Appendix 5-2). The ESB concentration is expressed as µg chemical/g sediment organic carbon (µg /g_{oc}). The PNEC approach (EC, 1996) applied to produced water constituents is recommended to represent the acceptable effects concentration of a substance in the interstitial/porewater in the present approach (Johnsen et al., 2000; Frost, 2002).

The Kp is the partitioning coefficient between sediments (l/kg) and water, and WQC ($PNEC_{-water}$) is the effects-based water quality criteria. Organic carbon appears to be the dominant sorption phase for non-ionic organic substances in naturally occurring sediments and thus controls the bioavailability in sediments (Di Toro et al., 1991). Derivation of Kp values for non-ionic organic substances is suggested expressed as shown in Equation 3:

Equation 3: Calculation of $Kp_{sediment\text{-}water}$ – TGD (EC, 2003)

$$Kp_{sediment\text{-}water} = f_{oc} * K_{oc}$$

in which:

Kp = partition coefficient between sediment and water (m3/m3)

f_{oc} =weight fraction of organic carbon-water (kg/kg)

K_{oc} = partition coefficient organic carbon-water [l/kg]

This Equation is in accordance to TGD (Chapter 2.3.3, Equation 3). K_{oc} is not usually measured directly. However, K_{oc} is closely related to the octanol-water partion coefficient (K_{ow}) which has been measured for many compounds, and is recommended used if no K_{oc} value is available. K_{oc} should be derived from K_{ow} by following Equation (Di Toro et al., 1991) for non-ionic organic substances as shown in Equation 4:

Equation 4: Calculation of K_{oc} – TGD (EC, 2003)

$$\log K_{oc} = 0{,}00028 + 0{,}983 * \log K_{ow}$$

in which:

K_{oc} = partition coefficient organic carbon-water [l/kg]

K_{ow} = octanol-water partioning coefficient [l/kg]

In Table 5.12 an overview of the input data for calculation of SQC and $PNEC_{sediment}$ for aromatic and aliphatic hydrocarbons by applying the equilibrium partitioning method (Equation 2) is presented. The $PNEC_{water}$ values for naphthalenes, 2-3 ring PAHs, 4+ ring PAHs and aliphatic hydrocarbons currently applied in the EIF produced water are recommended to be used for aromatic/aliphatic hydrocarbons representing potential oil residues associated with drilling discharges. Values for log K_{ow} and log K_{oc}/K_{oc} are based on average values for individual substances represented within the various groups of

PAHs where available data have been found (US-EPA, 2003) (Appendix 5-2). Both $\text{PNEC}_{\text{sediment}}$ based on dry weight (µg/g oc) and the $\text{PNEC}_{\text{sediment}}$ based on average total organic carbon content in sediments on the NCS (1%) (Pers. Comm. Bjørgesæter, 2006) were determined for the different groups of aromatic and aliphatic hydrocarbons.

Table 5.12 Log Kow, log Koc, Koc, $\text{PNEC}_{\text{water}}$ and $\text{PNEC}_{\text{sediment}}$ (µg/g oc) and $\text{PNEC}_{\text{sediment}}$ based on 1 % organic carbon (TOC) in the sediment (µg/g dry weight) for aromatic and aliphatic hydrocarbons.

PAHs	Log K_{ow}	Log K_{oc}	K_{oc}	$\text{PNEC}_{\text{water}}$ (mg/l)*	$\text{PNEC}_{\text{sediment}}$ (µg/g oc)	$\text{PNEC}_{\text{sediment}}$ (µg/g dry wt) 1% TOC
C0-C3 naphthalenes	4,064	3,9953	9891,22	0,021	205,5	2,05
2-3 ring PAHs	4,9555	4,8717	74416	0,00015	11,2	0,11
4+ ring PAHs	5,9998	5,8981	790861	0,00005	39,5	0,40
Aliphatic hydrocarbons	6**	5,8981	790861	0,040	31950,8	319,5

* Toxicity threshold values, expressed as PNEC, of aromatic and aliphatic hydrocarbons applied in the environmental risk calculation (EIF) of produced water discharges (Johnsen et al., 2000, Frost, 2002).

** Log Kow data for aliphatic hydrocarbons are represented by the average log K_{ow} for C12-C14 hydrocarbons.

The exposure scenario of discharges related to drilling operations (from rig) is different from the exposure scenario refered to by the TGD. All chemical substances with log K_{ow} or K_{oc} values > 3 are assumed to deposit on the sea bed after release through processes such as agglomeration (forming new and larger particles) and/or attachment to cuttings/mud particles. These processes may cause that the chemicals sink to the sea floor immediately rather than stay suspended in the the water column before settling on the seabed. This means that K_p related to drilling discharges is expressed as the partitioning between the deposited chemical substance and the porewater in the sediment compartment, and deviates from the TGD where K_p expresses the partitioning of the organic substances between the suspended particles and water. The concentration in freshly deposited sediment is taken as the PEC for sediment by the TGD; therefore, the properties of suspended matter are used (Equation 5). Therefore, the EqP approach applied to non-ionic organics applied by US-EPA (1997) (Equation 2) is recommended to be used for calculation of $\text{PNEC}_{\text{sediment}}$ for for non-ionic organic substances, including both naturally occurring substances such as aromatic and aliphatic hydrocarbons, and added drilling fluid chemicals with log K_{ow} or K_{oc}-values > 3. For added chemical substances with a log K_{ow} >5, an additional assessment factor of 10 is added to the EqP approach used, to account for ingestion of sediment according to TGD (EC, 2003).

Equation 5: Calculation of $\text{PNEC}_{\text{marine sediment}}$ - EqP approach (TGD - EC, 2003):

$$\text{PNEC}_{\text{sediment}} = [Kp_{\text{susp-water}}/\text{RHO}_{\text{susp}}] * \text{PNEC}_{\text{water}} * 1000$$

in which:

$\text{PNEC}_{\text{water}}$ = Predicted No Effect Concentration in seawater [mg/l]

$\text{RHO}_{\text{susp bulk}}$ = density of suspended matter [kg/m^3]

$Kp_{\text{susp-water}}$ = partition coefficient suspended matter water [m^3/m^3]

$\text{PNEC}_{\text{sediment}}$ = Predicted No Effect Concentration in marine sediment [mg/kg]

TGD states that is not necessary to apply the equilibrium partitioning method to $\text{PEC}_{\text{marine sediment}}$ from application of an exposure model when such a model will have used the same K_p value as that used to predict $\text{PNEC}_{\text{sediment}}$. (TGD, Equation 8, Section 2.4.2). The reason is that the resulting PEC/PNEC ratio of the sediment will have the same risk value as for the water compartment. In this case no quantitative risk characterisation for marine sediment should be performed. Since the Kp value for a certain substance applied for calculation of PEC and PNEC for the water column and sediment will be different, the PEC/PNEC ratio for these compartments will give different results.

The equilibrium partitioning method approach can be applied provided that the $PEC_{marine\ sediment}$ can be determined on the basis of a measured concentration of the substance in the seawater, that is independent of the value of the K_{oc}/K_p. (TGD, Equation 2, Section 2.3.2). The current approach is not based on measured concentrations in the seawater. However, the predictions will regularly be validated through performance of monitoring surveillance/studies.

Metals

The EqM-method was originally proposed to develop sediment quality criteria for organic substances, normalising the concentrations in the solid phase to the organic carbon content. The method was further modified for metals and metalloids by use of empirically derived sediment/water partition coefficients. For metals, two approaches utilising partitioning models have been proposed to relate biological effects to interstitial water and sediment concentration (deriviation of sediment quality criteria):

- The Dutch approach determining $MPC_{\underline{sediment}}$ based upon empirically derived $Kp_{sediment}$ values together with water quality criteria (MPA) added to the background concentration in the sediment ($Cb_{sediment}$) (Crommentuijn et al., 1997, Crommentuijn et al., 2000);

- The US SEM/AVS approach, a partitioning model that relates interstitial water concentration and sediment toxicity to the molar ratio of the Simultaneously Extracted Metal (SEM) to acid Volatile Sulphide Concentration (AVS) (US-EP, 1994a, b).

The similar recommendation as for non-ionic organic chemicals is made regarding the development of $PNEC_{sediment}$ or SQC for metals, except that Kp should be based upon measured (empirical) values (partitioning between sediment -water) and not estimated from $f_{\underline{oc}}$ and $K_{\underline{oc}}$, as for non-ionic organics (US-EPA, 2003). However, it was recommended that background concentrations must be taken into account in SQC for metals which occur naturally in the environment, so the Dutch developed the "added risk approach", which forms the basis of the recommendations to the EC (Fraunhaufer Instititute, 2002). The Dutch EqP approach applied by Crommentuijn et al. (1997, 2000) is recommended for determination of the $MPC_{\underline{sediment}}$ or $PNEC_{sediment}$ for metals and is outlined in Equation 6 and 7, subsequently:

Equation 6: Calculation $MPC_{sediment}$ for metals - EqP approach (Dutch RIVM - Crommentuijn et al., 1997, 2000):

$$\mathbf{MPC_{sediment} = Kp_{sediment} * MPA_{water} + Cb_{sediment}}$$

In which:
$MPC_{sediment}$ = Maximum Permissible Concentration in marine sediment [mg/kg]
$Kp_{sediment}$ = partition coefficient sediment and water [m^3/m^3]
$MPC_{\underline{water}}$ = Maximum Permissible Concentration in the surface water
$Cb_{sediment}$ = background concentration in the sediment (mg/kg)

where $Kp_{sediment}$ is the partitioning coefficient between sediment particles (l/kg) and pore water in the sediment compartment and MPA_{water} is the effects-based water quality criteria.

Equation 7: Calculation of $PNEC_{sediment}$ for metals - EqP approach (Crommentuijn et al., 1997, 2000):

$$PNEC_{sediment} = Kp_{sed.\ barite\text{-}seawater} * PNEC_{water} + Cb_{sediment}$$

In which:
$PNEC_{sediment}$ = *Predicted No Effect Concentration in marine sediment [mg/kg]*
$Kp_{sed.\ barite\text{-}seawater}$ = *partition coefficient barite particles and water [m^3/m^3]*
$PNEC_{water}$ = *Predicted No Effect Concentration in seawater [mg/l]*
$Cb_{sediment}$ = *background concentration in the sediment (mg/kg)*

The Kp related to drilling discharges is expressed as the partitioning between the deposited particles and the porewater in the sediment compartment and deviates from TGD in that $Kp_{susp\text{-}water}$ expresses the partitioning between the suspended particles and water (Equation 5), and is also different from the Dutch approach that is based upon the relationship of the substance between the concentration in the solid phase in the sediment (distributions processes in the Dutch environment) and the pore water (Yland, 1996).

In Table 5.13 an overview of the input data and the calculated PNEC values recommended applied for metals for the sediment compartment is presented. The $PNEC_{sediment}$ ($MPC_{\_sediment}$) is calculated using Equation 7, applying the Dutch approach of EqM-method described by Crommentuijn et al. (1997, 2000). The $PNEC_{\_sediment}$ values are based upon experimentally derived $Kp_{\mathbf{barite\text{-}seawater}}$ values for the sediment together with water quality criteria ($PNEC_{water}$ or MPA_{water}) added to the background concentration of metals in the sediment. In Table 5.13 the mean background concentations measured in the sediments on the Norwegian Continental Shelf (NCF) ($Cb_{sediment}$) were applied. Preferably, it is recommended that region specific background concentration values for metals should be used, if available (from NCS, US/Canada or other parts of the world).

However, the current approach for calculation of $PEC_{sediment}$ (and $PNEC_{sediment}$) for metals in EIF drilling discharges is based on measured partition coefficients for metals between the barite particle and porewater in the sediment, $Kp_{sed.\ barite\text{-}water}$, derived from the scientific literature (Table 5.4), simulating conditions in the sediment compartment (and not the partitioning between supended matter considered as freshly deposited sediment and seawater described in the TGD). However, the PEC_{water} for metals is calculated from measured barite-seawater partitioning coefficients ($Kp_{susp.\ barite\text{-}water}$) for barite particles suspended in the water column (Table 5.3). The Kp value for a certain metal applied for calculation of PEC and PNEC for the water column and sediment will therefore be different, the PEC/PNEC ratio for the two compartments will give different results.

The present approach applying log Kp for metals between the barite particle and porewater in the sediment ($Kp_{sed.\ barite\text{-}water}$) instead of using Kp for partition between sediment and porewater, is a conservative approach for calculation of sediment quality criteria (SQC or $PNEC_{\mathbf{sediment}}$). It is thereby assumed that the distribution of the metal between the barite particle and the porewater is similar to partitioning between the sediment and the porewater, which is not the case. The $Kp_{sediment\text{-}water}$ values applied for derivation of SQC for the Dutch sector are considerably higher than the partition coefficients for metals between the barite particle and porewater applied to the sediment ($Kp_{sed.\ barite\text{-}water}$), that result into lower SCQ ($PNEC_{\mathbf{sed}}$ values) for the latter. The Dutch Kp values are based on measured values on the Dutch sector based on monitoring data in marine surface water and sediment at different locations in the North Sea and Wadden Sea during 1995 (Yland, 1996) represented with high levels of organic carbon content (10%). Due to lack of reliable $Kp_{\text{sediment-water}}$ values for the NCS it is recommended to use the $Kp_{\text{sed. barite-water}}$ values as basis for determination of $PNEC_{\text{sediment}}$ for the NCS, shown in Table 5.13.

The $Kp_{\text{sed. barite-water}}$ value derived for chromium and mercury was not found reliable (Chapter 5.1). It is therefore recommended that region specific field-derived values (F-TEL), addressed in Chapter 7, should be used as PNEC values for Cr and Hg until more reliable Kp values are available.

Table 5.13 Mean background concentrations of metals in sediment at the NCS, $Kp_{\text{(barite-water) sediment}}$ values, PNEC values derived from literature data by use of the Equilibrium Partitioning approach.

Metals	$PNEC_{\text{water}}$* (MPA_{water}) (ug/l)	Log $K_{p\ \text{(barite-water) sediment}}$ (L/kg)	$K_{p\ \text{(barite-water) sediment}}$	$PNEC_{\text{sediment}}$ (MPA_{sed}) (mg/kg)	Cb_{sed}** (mg/kg)	$PNEC_{\text{sediment}}$ (MPC_{sed}) (mg/kg)
Cadmium	0,34	1,46	28,8	**0,009792**	0,037	**0,05**
Chromium	8,5	3,24	1738	**14,773**	14,6	**29,37**
Copper	1,1	1,64	43,7	**0,04807**	4,1	**4,15**
Lead	11	1,9	79,4	**0,8734**	10,7	**11,57**
Mercury (inorganic)	0,23	4,79	61660	**14,1818**	0,021***	**14,20**
Zinc	6,6	1,84	69,2	**0,4567**	20,7	**21,16**

* $PNEC_{\text{water}}$ or MPA_{water} is based on statistical extrapolation of aquatic data applied in the Netherlands (RIVM, Crommentijn et al., 1997).

** Mean background sediment concentrations of metals for the Norwegian Continental Shelf (NCS) based on all reference and regional stations (Bjørgesæter, 2006).

*** Based on total concentration (inorganic + organic) of Hg in the sediment.

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6. INTERNATIONAL PRACTICES FOR REGULATION AND TESTING OF OFFSHORE DISCHARGES OF DRILLING WASTES CHEMICALS

Requirements for toxicity testing of drilling mud and drilling mud ingredients differ in different regions of the world. For instance the United States requires testing on whole muds, while Russia and the North Sea countries require testing of the individual drilling mud components. All chemicals used offshore by OSPAR countries are subjected to HOCNF (Harmonised Offshore Chemical Notification Format).

The major solid wastes generated during exploratory and development drilling of oil and gas wells are spent drilling muds/fluids and drill cuttings. There are three major types of drilling fluids:

- **Water based drilling muds (WBM)**: formulated mixtures of natural clays, organic polymers, weighting agents and other ingredients suspended in water;
- **Oil based drilling muds (OBM)**: drilling fluids in which the continuous phase is a refined petroleum product, in which water, weighting agents, emulsifiers, and other additives are dispersed;
- **Synthetic based drilling muds (SBM)**: drilling muds in which the continuous phase is a synthetic organic chemical, in which water, weighting agents, salts, emulsifiers, and other additives are dispersed.

Drilling muds usually are cleaned to remove cuttings and recycled during drilling. Drill cuttings may be reinjected into a suitable subsea geologic formation, sent to shore for upland disposal, or discharged to the ocean if local environmental regulations permit it. OBM and SBM are not discharged to the ocean, but are returned to shore for reformulation/regeneration and reuse or for disposal. WBM may be discharged if they meet regulatory requirements.

6.1 Current Practices in the United States

6.1.1. Regulation of Ocean Discharge of Drilling Wastes

Discharges to the ocean of drilling muds and cuttings are regulated in the United States by the Federal Water Pollution Control Act (commonly known as the Clean Water Act). The Environmental Protection Agency (EPA) or a state environmental agency designated by EPA administers provisions of this act that apply to oil and gas activities in State and Federal waters.

There are three options for disposal of wastes generated offshore during exploration, development, and production of oil and gas resources:

1. Discharge to the ocean
2. Underground injection
3. Haul to shore for upland disposal or recycling.

EPA has the responsibility under the Clean Water Act to regulate discharges to the ocean. Upland disposal is under the jurisdiction of EPA and State environmental agencies. The US Dept. of the Interior, Minerals Management Service (MMS) oversees injection of drilling wastes into offshore geologic formations.

Sections 402 and 403 of the Clean Water Act require that National Pollutant Discharge Elimination System (NPDES) permits for discharges to the territorial seas, the contiguous zone, and the ocean be issued in compliance with EPA's regulations for preventing unreasonable degradation of the receiving waters (USEPA, 1993, 1996). Before a permit can be issued, the discharge must be evaluated in relation to EPA's published criteria for determination of unreasonable degradation. EPA develops effluent limitations guidelines (ELG) and new source performance standards (NSPS) that are intended to protect the receiving water environment from unreasonable degradation. Discharges of wastes from offshore platforms to the ocean must comply with ELG and NSPS in NPDES permits.

EPA develops these ELG and NSPS based on the degree of control that can be achieved using various levels of pollution control technology. In establishing ELG, EPA must consider the technologies that are already successfully in use, costs and economic impacts of implementation of the control technologies, and non-water quality environmental impacts of the discharge or alternative treatment technologies or disposal options.

Most discharges of wastes to Federal waters from offshore platforms are covered by general NPDES permits issued by the responsible EPA regions or State environmental agencies authorized by EPA. General permits cover all offshore platform discharges within a designated area, such as the western Gulf of Mexico. EPA also can issue a special NPDES permit for a single facility if it determines that geological, environmental, or cultural conditions or requirements at the site warrant specific, usually more stringent, permit conditions.

The current ELG for discharges of WBMs, SBMs, and OBMs and associated cuttings are summarized in Table 6-1. WBMs and associated cuttings are no longer permitted for discharge to U.S. State waters (within 4.8 km from shore). Discharge of WBMs and associated cuttings is permitted in Federal waters if they meet permit requirements (Table 6-1). Discharge of WBMs or cuttings containing refined, mineral, or formation (crude) oil is forbidden. Discharge of OBMs and associated cuttings has never been permitted in U.S. State or Federal waters.

SBM are not permitted for discharge to US State or Federal waters. Because of their high cost, they are recovered and recycled for use in drilling additional wells. However, drill cuttings generated during drilling with SBM are permitted for discharge to Federal, but not to State waters of the Gulf of Mexico and Cook Inlet, AK, if they meet certain requirements (Table 6.1). The new General Permit (CAG280000) for Federal waters off southern California, which became effective on 1 December, 2004, prohibits discharge of both SBM and SBM cuttings off California. As with WBM, formation oil and diesel fuel oil must be absent from the SBM cuttings as indicated by a static sheen test.

Table 6.1 Current Effluent Limitation Guidelines (ELG) for discharges of drilling muds and cuttings to State and Federal waters of the United States from offshore oil and gas exploration and development platforms.

Waste Source and Receptor Body	**Pollutant Parameter**	**Effluent Limitation**
WBM and cuttings - Discharge to State waters[a]	All	No discharge
WBM and cuttings - Discharge to Federal waters[c]	Suspended particulate phase toxicity	Minimum 96-h LC_{50}[b] of suspended particulate phase of 3% by volume to the mysid *Mysidoposis bahia*
	Free oil	No discharge
	Diesel fuel oil	No discharge
	Mercury	Maximum 1 mg/kg dw in stock barite
	Cadmium	Maximum 3 mg/kg dw in stock barite
OBM and cuttings - Discharge to State or Federal Waters	All	No discharge
SBM - Discharge to State or Federal waters	All	No discharge
Drill cuttings associated with SBM - Discharge to State waters	All	No discharge

Drill cuttings associated with SBM - Discharge to Federal waters (Gulf of Mexico, Cook Inlet, AK)	Base fluid retained on cuttings	≤ 6.9% olefin (weighted average) or ≤ 9.4% ester (weighted average)
	Sediment toxicity	Stock base fluid and discharged cuttings can be no more toxic to marine amphipods than a C_{16}-C_{18} IO base fluid and IO-contaminated cuttings
	Formation oil	No discharge
	Diesel fuel oil	No discharge
	Mercury	≤ 1 mg/kg dw in stock barite
	Cadmium	≤ 3 mg/kg dw in stock barite
	Polycyclic aromatic hydrocarbons	≤ 10 mg/kg based on phenanthrene/wt of stock base fluid
	Biodegradation rate	Biodegradation rate in 120-day anaerobic test shall be no slower than that of a C_{16}-C_{18} IO base fluid
Drill cuttings associated with SBM - Discharge to Federal waters of S. California	All	No discharge

[a] State waters are defined as the territorial sea between the shore and 3 miles offshore; [b] LC50 is the median lethal concentration; [c] Federal waters are offshore waters > 3 miles from shore.

WBMs and cuttings destined for disposal in U.S. territorial waters must pass an aquatic toxicity test. The toxicity of the suspended particulate phase of the water-based mud or cuttings is tested with the mysid *Americamysis bahia* (a shrimp-like crustacean) in a 96-hour test. The suspended particulate phase must have a 96-h LC50 greater than 30,000 mg/L (ppm). Muds with a lower LC50 (greater toxicity) are not permitted for discharge. Because the mud or cuttings will have been discharged before the test results are available, exceedences of the toxicity limitation are reported to EPA and future discharges of the same or similar muds are prohibited. The suspended particulate phase is prepared by thoroughly mixing one part drilling mud or muddy cuttings with nine parts seawater, allowing the solids to settle out for a set period of time, and then decanting the aqueous phase (the suspended particulate phase) for use in the test. This testing is intended to protect water- column organisms from adverse effects of water-based mud and cuttings discharges to the ocean. There currently is not a requirement for sediment toxicity tests to evaluate the effects of WBM and cuttings solids on sediment-dwelling organisms.

However, SBM base chemicals and SBM cuttings must pass a solid-phase toxicity test. The base synthetic chemical used in a SBM and SBM cuttings must be less toxic to sediment-dwelling amphipods than a standard C_{16}-C_{18} internal olefin (IO) or mud cuttings generated with an IO SBM. EPA recommends but does not require that operators use a solid phase toxicity test with the benthic amphipod *Leptocheirus plumulosus* performed according to a standard EPA protocol (USEPA, 2001a).

During development of ELG, eight generic WBM, representative of the types of drilling fluids used offshore in US waters, were identified and characterized chemically and toxicologically (Ayers et al., 1983). The mysid (*Americamysis [Mysidopsis] bahia*), a small shrimp-like crustacean, was identified as one of the most sensitive species to drilling fluids and a suspended particulate phase preparation was recommended as the best simulation of the type of drilling fluid dispersion encountered by water column organisms (Neff et al., 1980). Bioassays performed by the USEPA (1985a,b) with the suspended particulate phase of 8 generic muds and mysids gave 96-h LC_{50}s ranging from 3,300 mg/L to >100,000 mg/L mud added (Duke et al., 1984) (Table 6-2), similar to results obtained by Ayers et al. (1983). A KCl-polymer mud had the lowest LC_{50} (was most toxic), still within the low-toxicity range. The results of these tests were used by EPA to set an acute toxicity (LC_{50}) limit for water based drilling muds of 3,000 ppm drilling mud added (30,000 ppm suspended particulate phase) in the current ELG.

Table 6.2. Acute toxicity of the suspended particulate phase (SPP) of 8 generic drilling muds to mysids. 96-hour LC_{50} Concentrations are mg/L mud added. From Duke et al., (1984).

Water Based Drilling Mud Type	96-Hour LC_{50}
KCl Polymer Mud	3,300
Seawater Lignosulfonate Mud	62,100
Lime Mud	20,300
Non-Dispersed Mud	>100,000
Seawater Spud Mud	>100,000
Seawater/Freshwater Gel Mud	>100,000
Lightly Treated Lignosulfonate Mud	68,200
Freshwater Lignosulfonate Mud	30,000

All US offshore operators are required by the NPDES permit to perform suspended particulate phase bioassays on used WBM and cuttings each month during drilling and at the end of the well. Data collected by EPA between 1986 and 1989 showed that 99.9 percent of 10,397 Gulf of Mexico drilling mud bioassays yielded a 96-h LC_{50} in excess of the 30,000 ppm suspended particulate phase limit (SAIC, 1992). Thus, the vast majority of water based drilling muds used offshore in U.S. waters are not toxic to marine organisms.

SBM cuttings also must pass a biodegradation test. The biodegradation rate of the SBM cuttings must be no less than that of cuttings containing C_{16}-C_{18} internal olefin SBM in a 120-day anaerobic biodegradation test.

There also are limits on the concentrations of mercury, cadmium, and PAH in the muds and cuttings. No discharge of free oil is permitted.

General and special permits may contain additional requirements for drilling mud and cuttings discharges. All permits contain specific requirements for:

- Monitoring frequency for compliance with different effluent guidelines;
- Analytical methods for chemicals in drilling fluids and cuttings and toxicity test methods;
- Reporting and record keeping. Results of monitoring activities are submitted periodically to EPA in a Discharge Monitoring Report (DMR); and
- Technical and operational requirements.

In writing a new permit, each EPA region may add special requirements specific to the outer continental shelf region under their jurisdiction. For example, permits for the Gulf of Mexico include the following requirements:

- No discharge of drilling wastes within 1000 m of (Region 4: eastern Gulf) or into (Region 6: central and western Gulf) an Area of Biological Concern;
- Used oils from the platform may not be added to drilling muds to be discharged from the platform;
- The rate of drilling mud and cuttings discharge from a single platform may not exceed 1000 bbl/hr (159 m^3/hr); and
- The operator must maintain and report an inventory of all chemical additives to drilling fluids destined for ocean disposal.

Special requirements for California (Region 9) include:

- Maximum permissible volume of drilling mud and cuttings discharge is set for each offshore platform and ranges from 50,000 bbl/year (7,950 m^3/y) to 240,000 bbl/year (38,200 m^3/y).
- Used oils from the platform may not be added to drilling muds to be discharged from the platform.

- The operator must maintain and report an inventory of all chemical additives to drilling muds destined for ocean disposal.
- Toxicity test limit for drilling fluids can be met by using one of eight generic drilling muds with approved additives. Toxicity of additives may have to be determined.
- Discharge of SBM and cuttings is not permitted.

Permits for Cook Inlet, Alaska and the Beaufort Sea (Region 10) include the following requirements:

- Rate of drilling fluid and cuttings discharge is set on a case-by case basis, based on water depth and ranges from 0 to 1000 bbl/hr (159 m^3/hr).
- Drilling wastes from no more than five wells can be discharged at one location.
- The operator must prepare and submit a mud plan outlining the types of drilling muds and additives to be used.
- The operator must maintain an inventory of all the drilling mud additives actually used.
- Restrictions are placed on setbacks from sensitive environments and in ice-covered areas.
- The operator must perform an environmental monitoring program to evaluate the impacts of drilling discharges on the marine environment.
- Additional monitoring is required for concentrations of barium, cadmium, chromium, copper, mercury, and lead in drilling muds.

6.2. Current Practices in the OSPAR countries

6.2.1. Regulation of Ocean Discharge of Drilling Wastes

All chemicals used offshore by OSPAR countries (Oslo-Paris Convention for the protection of the Marine Environment of the North-East Atlantic) are subjected to HOCNF (Harmonised Offshore Chemical Notification Format). According to the HOCNF (OSPAR, 2000), marine ecotoxicological test data (as well as other data) should be available unless the substance is on the PLONOR list. The requirements and test procedures are described in the follwing documents: “The Norwegian offshore HSE regulations; Activities Regulations §56 a” and “OSPAR Guidelines for Toxicity Testing of Substances and Preparations Used and Discharged Offshore (Reference number: 2002-3)”.

Discharges of OBM and SBM are strictly regulated within the OSPAR area. Discharge of diesel based drilling fluids was prohibited in 1984, while discharges of OBM as contamination on cuttings have been prohibited in the area since 1996. The use of SBM in the North Sea has been minor after 2001, due to the OSPAR Decision 2000/3 *on the Use of Organic-Phase Drilling Fluids (OPF) and the Discharge of OPF-Contaminated Cuttings,* in which the requirements for discharges of SBM as contamination on cuttings were tightened. Paragraph 3.1.6 in OSPAR Decision 2000/3 states “the discharge into the sea of cuttings contaminated with synthetic fluids shall only be authorised in exceptional circumstance”. “In reaching a decision on any authorisation, Contracting Parties shall apply to the management of OPF-contaminated cuttings:

a. the principles of the Harmonised Mandatory Control System for the Use and Reduction of the Discharge of Offshore Chemicals as set out in the applicable OSPAR Decision;

b. Best Available Technologies (BAT) and Best Environmental Practice (BEP) as set out in Appendix 1 of the OSPAR Convention;

c. the waste management hierarchy set out in Appendix 1 to this Decision.”

OSPAR Decision 200/3 states further that:

3.1.3 The discharge of whole OPF to the maritime area is prohibited. The mixing of OPF with cuttings for the purpose of disposal is not accepTable.

3.1.4 The discharge into the sea of cuttings contaminated with OPF at a concentration greater than 1% by weight on dry cuttings is prohibited.

3.1.5 The use of OPF in the upper part of the well is prohibited. Exemptions may be granted by the national competent authority for geological or safety reasons.

3.1.6 The discharge into the sea of cuttings contaminated with synthetic fluids shall only be authorised in exceptional circumstances. Such authorisations shall be based on the application of BAT/BEP as set out in Appendix 1 of this Decision.

In other words, discharges of OPFs are prohibited, but competent authorities can, under specific conditions, give a limited discharge permit for SBM.

The OSPAR Decisions and Recommentdations are to be implemented and followed up by each Contracting Party. Although the principles of the Harmonised Mandatory Control System (OSPAR 2000/2) are followed, the implementation and requirements to meet the goals differ from one Contracting party to another.

The following descriptions of the regulations regarding ecological testing of chemicals and drilling waste are in compliance with the OSPAR regulations, but because the information is from the The Norwegian offshore HSE regulations, there might be deviations from other national requirements.

Based on the intrinsic properties of each substance (described in the HOCNF), the substance will be evaluated for substitution (the OSPAR pre-screening scheme; OSPAR Recommendation 2000/4). In Norway chemicals are categorised by a colour code depending of their intrinsic properties (the activity regulations § 56b). Black and red components are hazardous (components of special concern), while yellow and green components are not hazardous, but might cause harm to the environment depending on amounts, time and place of the discharge. Substances in black and red categories will be prioritised for substitution due to their intrinsic properties, while substances in the yellow and green categories shall be evaluated for substitution, if less toxic alternatives are available. For example, barite should be considered for replacement with ilmenite as a weighting agent because some grades of mineral barite contain high concentrations of some metals. Such an evaluation shall be carried out every third year.

The Norwegian pollution control authority classifies the different substances proposed for use and discharge offshore as indicated in Table 6.3. Because of this pollution control strategy, the mass of additives in the black and red categories (most hazardous) has declined by more than ten-fold between 1997 and 2004 (OLF, 2004). There were smaller decreases in the masses of yellow and green chemicals discharged.

Table 6.3 SFT's categorisation and colour code for chemicals used and discharged offshore. The mass (tonnes) of chemical additives in each class discharged offshore is included.

SFT Categorization	SFT Colour Code	Ocean Discharge (tonnes)
Chemicals prioritized for substitution (White Paper No 25 (2002-2003 (Table 8.1))	Black	1997: 228 2004: 2
Hormone disrupting substances	Black	
Biodegradation < 20% and log Pow ≥ 5	Black	
Biodegradation < 20% and toxicity EC50 or LC50 ≤ 10 mg/l	Black	
Two out of three categories: biodegradation < 60%, log Pow ≥ 3, EC50 or LC50 ≤ 10 mg/l	Red	1997: 3933 2004: 299
Inorganic and EC50 or LC50 ≤ 1 mg/l	Red	
Biodegradation < 20%	Red	

Chemicals on OSPAR's tainting list	Red	
Other chemicals	Yellow	1997: 39,684 2004: 10,599
Chemicals on the PLONOR list (little or no environmental risk)	Green	1997: 114,778 2004: 91,044

The substances in the green and yellow categories will be evaluated as part of the risk assessment. Substances in black and red categories will not be evaluated, because they should not be used. However, if required for technical or safety reasons, substances in the black and red category will be included in the risk assessment. Operators are not allowed to use the risk assessment as an argument for offshore use and discharge of chemicals containing black and red substances.

6.2.2. OSPAR Guidelines for Toxicity Testing of Substances and Preparations Used and Discharged Offshore

The operator shall ensure that chemicals that are used or discharged have been tested with regard to eco-toxicological properties. In the North Sea countries, testing of the individual drilling mud components is required. Ecotoxicological testing of substances shall be performed by laboratories that are approved in accordance with OECD's principles for good laboratory practice (GLP). Ecotoxicological documentation in the form of OSPAR HOCNF shall exist for all chemicals used in the petroleum industry on the Norwegian Continental Shelf. This requirement does not apply to lubricants which are used in small amounts and chemicals in closed systems which are used in small amounts. The requirement does not apply to laboratory chemicals, dispersants and beach-cleaning agents to combat oil spills, and to new chemicals during the period of field testing. Only part 1 and 3 of the HOCNF must be completed for substances on the OSPAR List of Substances/Preparations Used and Discharged Offshore which are Considered to Pose Little or No Risk to the Environment.

Chemicals shall be tested for the following ecotoxicological properties:

1. *Biodegradability*

Chemicals that consist of several substances shall be tested for the individual organic substance's biodegradability. The substances shall preferably be tested in accordance with the seawater test OECD 306 "Biodegradability in Seawater". If this test is not applicable for the test substance, one of the following seawater tests shall be performed:

- Marine CO_2 Evolution test (mod. Sturm), modified OECD 301B
- Marine BODIS test (for insoluble substances), modified ISO/TC 147/SC 5 N141
- Marine CO_2 Headspace test, modified ISO/TC 147/SC 5/WG 4 N182

For substances known to be toxic to microorganisms (e.g. biocides), SFT must be contacted if alternative tests are planned to be used.

For substances with moderate biodegradability (equivalent to BOD_{28} from 20 to 60%), the properties of the degradation products also shall be evaluated.

When evaluating the properties of the degradation products for substances with moderate degradation (BOD28 between 20 and 60%), the results from testing of inherent biodegradability may be used together with other available information regarding the substances. The evaluations should be documented.

2. *Bioaccumulation*

Chemicals that consist of several substances shall be tested for the individual organic substance's bioaccumulation potential. This requirement applies to substances with a molecular weight below 1500 g/mol. The substances shall be tested according to OECD 117 "Partition Coefficient (n-octanol/water), High Performance Liquid Chromatography (HPLC) Method”. If OECD 117 gives no result, the substance shall be tested in accordance with OECD 107 “Partition Coefficient (n-octanol/water): Shake Flask Method”. For substances where standardised tests are not applicable, as for surfactants, an evaluation of the bioaccumulation potential shall be performed. Such evaluations shall be documented and preferably be performed by an independent party.

The potential for bioaccumulation presented as partition coefficient octanol/water, Log K_{ow}, may be given as a weighted average, cf. method described in ”Additional guideline for filling in HOCNF for the Norwegian sector of the Continental Shelf “ drawn up by SKIM (see below). Bioconsentration factor (CBF) may be used to argue that a substance does not bioaccumulate even if OECD 117 or 107 shows that Log $K_{ow} >3$. Scientific evaluations of the potential for bioaccumulation and estimated values for Log K_{ow} should be made clear as a comment in the HOCNF.

3. *Acute toxicity*

According to the HOCNF, marine ecotoxicological test data (as well as other data) should be available unless the substance is on the PLONOR list. These ecotoxicological test data include tests with a micro-alga (*Skeletonema costatum*), crustacean (*Acartia tonsa*), and fish (*Scophthalmus maximus* (juveniles)). For substances that are known to adsorb to particles or be deposited in sediments, an additional sediment reworker test with the benthic amphipod, *Corophium* spp, is required.

Inorganic and organic chemicals shall be tested for acute toxicity. The requirement does not apply to substances/preparations on OSPAR’s PLONOR list.
The following toxicity tests are required:

- *Skeletonema costatum,* ISO/DIS 10253:1995
- *Acartia tonsa,* ISO 14669:1999
- *Scophtalamus maximus*; Part B in the OSPAR Protocols on Methods for the testing of Chemicals Used in the Offshore Industry, 1995. Sheepshead minnow is accepted as an alternative species.
- *Corophium volutator*; Part A in the OSPAR Protocols on Methods for the Testing of Chemicals Used in the Offshore Industry, 1995. Required if the chemicals absorb to particles ($K_{oc}>1000$) and/or sink and end up in the sediments (e.g. surfactants)

Organic substances that are not very prone to degrade (BOD < 20% over 28 days) and new chemicals being used after 1 January 2004 shall be tested for acute toxicity at substance level.

All chemicals shall be tested for toxicity at substance level after 1 January 2007.
The fish test shall be performed on all new/modified chemicals from 1 January 2002. The requirement does not apply if the chemical is:

- inorganic and with a toxicity to the other test organisms of EC_{50} or $LC_{50} \leq 1$ mg/l
- organic and with a toxicity to the other test organisms of EC_{50} or $LC_{50} \leq 10$ mg/l.

If results from alternative toxicity testing are used, documentation may be presented to SFT for SFT to evaluate.

Norwegian Accreditation (NA) is the Norwegian agency for the accreditation of technical issues, including GLP as mentioned in the first paragraph of the Section. A summary of different types of chemicals which require ecotoxicological documentation in the form of a HOCNF, is shown in the Table below. The operator should do an independent (in-house) environmental evaluation of those chemicals which do not require a HOCNF. To fill in the HOCNF, the OSPAR Guidelines for Completing the Harmonized Offshore Chemical Notification Format should be used. Guidance for the completing of HOCNF is given in "Supplementary guidance for the completing of harmonised offshore notification format (HOCNF) for Norwegian sector”.

No.	Type of Chemical	HOCNF requirement	Comment
1	Chemicals which only consist of substances on the PLONOR list	Yes, except part 2	Exceptions for requirements for testing
2	All chemicals intended for use in offshore drilling, well maintenance operations, and production	Yes	Applies also to exploration drilling
3	Chemicals in water based, synthetic and oil based drilling fluids	Yes	Base fluid included
4	Chemicals which are used in utility systems, pipelines and water injection	Yes	This includes chemicals which will stay in the well and chemicals which will follow the exported oil, even if these chemicals will not be discharged offshore
5	Chemicals in closed systems, including BOP fluid and hydraulic fluids	No Yes	When small amounts are being used When large amounts are being used, HOCNF is required
6	Lubricants	No Yes	When small amounts are being used When large amounts are being used, HOCNF is required
7	Pipe dope	Yes	For testing of bioaccumulation and biodegradation of metals in pipe dope; the grease part may be handled as one substance. All of substances in the grease shall be listed in the HOCNF
8	Water and gas tracers	Yes	The requirement to have a HOCNF applies to water tracers only
9	Deck washing agents	Yes	
10	Chemicals for emergency preparedness (contingency chemicals)	Yes	The Operator shall evaluate the chemicals for emergency preparedness (contingency chemicals) which they plan to use, and have a list which cover these. There is no requirement to send the list and the corresponding HOCNFs to SFT. Please also see the Activity regulation § 58 regarding chemicals for emergency preparedness.
11	New chemicals to be field tested	No	The operator should do an evaluation of the toxicity of the product, and the biodegradation and potential for bio-accumulation of each substance in the product. The evaluation shall be documented and may be based on test data or literature data. If the chemical is taken into use, a HOCNF shall be available within 6 months.
12	Dispersants and beach cleaning agents to combat oil spills	No	For testing and documentation regarding dispersants and beach cleaning agents the requirements in the regulations of 1 June 2004 No. 931 Chapter 19 regarding the composition and use of dispersants and beach cleaning agents to combat oil spills apply.
13	Laboratory chemicals	No	
14	Chemicals in fire water systems	No	

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7. Validation of the toxicity threshold values derived from literature data versus field data

Task 5 in the ERMS project was initiated for the purpose of validation of the toxicity threshold values derived from the literature review. Two different approaches, the species sensitivity distribution (SSD) approach and the moving window modelling (MWM) approach, have been carried out to establish field derived threshold effect levels (F-TEL) based on existing sediment data from the NCS.

The data used is collected from the Norwegian oil associations’ Miljøovervåkingsdatabase (MOD) containing complete datasets from environmental monitoring in the vicinity of petroleum installations on the NCS since 1990. The database covers selected heavy metals and hydrocarbons, grain size and more than 2000 benthic species from depths ranging from 63 to 1500 meters.

Additionally, the field derived threshold effect levels (F-TEL) based upon the species sensitivity distribution and the moving window modelling approach, have been compared with TELs derived from the US and Canadian Sediment Quality Guidelines (SQG).

7.1. Species Sensitivity Distribution (SSD) approach

For establishment of the Field-Based SSD (F-SSD) for a specific component in the presence of other substances in the sediment, scatter plots of abundance and contaminant concentration for all species in the MOD were constructed to investigate sensitivity and estimate effect concentrations (EC50s). Only the sensitive species (species that decline in abundance when the contaminant concentration increase) are used to derive SSDs, but all species that are not regarded as rare, as defined by Bjørgesæter (2006), are used for calculation of the 95% protection level. The rare species were removed to be able to establish reliable scatter plots.

The F-SSDs are constructed by plotting the EC50 values (defined as the contaminant concentration in sediment corresponding to a 50% reduction in relative abundance of the species in question). The F-PNEC i.e. the level below which harmful ecological effects are not expected to be observed were determined from the F-SSDs. The fit between the data points and the SSD curve is often poor in the upper and lower part of the SSD plots. Bjørgesæter (2006) demonstrates a better fit in the critical lower area (around the 5%) by using the bootstrap method.

7.2. Moving Window Modelling (MWM)

The same data as used for the calculation of F-SSD were used for establishment of the Field Threshold Values (FTV) (B. Grung et al. 2005).

The MWM approach uses multivariate data analysis on samples near the background concentrations to identify samples where only one of the investigated chemical stressors causes the effect on a group of sensitive species (specific to the particular chemical stressor). Results from these analyses are used to establish FTV values for single components. The FTV is defined as the highest observed level of the investigated chemical stressor found in the field data without any observed effect on the macro fauna and where the other measured components levels were on background levels.

The the MWM approach shows that grain size is very important for the threshold effect levels for metals, PAH and NDP in sediments (B. Grung et al. 2005). The inverse relation between grain size and bioavailability of metals is supported by other studies (see chapter 4.8.2; H.C. Trannum et al., 2004).

7.3. Comparison

Generally, there was good correlation between the PNEC values derived from the equilibrium partitioning (EqP) method and the F-TELs derived from field data on the NCS (Table 7.1 and Appendix 8.4.2 – MEMO Comparing results from the approaches). On the other hand TELs from the US and Canadian Sediment Quality Guidelines (SQG) are generally higher for all the selected components. This might be due to the fact that the US and Canadian SQGs were derived from coastal and laboratory species, so both the fauna and the environmental conditions are different. Interactions between the investigated component, adsorption (and less bioavailability) and other components present in the field can also lead to lower TELs compared to laboratory data were only one component is present. The various TELs based upon US and Canadian SQGs are further addressed in Chapter 7.4.

Even though there was a general good correlation between the values calculated from the EqP approach and the field derived data, this was not the case for Cr and Hg. For these two components the EqP approach was less conservative than the field derived data. Sticking to the conservative approach, the F-PNEC's for these two metals will be used until we have gained more information from case studies and ongoing projects. The high K_p value for mercury (see Chapter 5) is caused by the extremely low solubility of HgS in drilling mud barite under both oxidizing and reducing conditions. Historically, much of the chromium in WBM and cuttings was from chrome lignosulfonates and inorganic chromates added to drilling muds for viscosity control and, therefore, was more mobile forms than predicted by K_p derived from the solubility behaviour of solid $Cr(OH)_3$ (Tables 5-1 and 5-5). Chrome lignosulfonates and chromate are no longer used for most WBM, and the chromium present in mud and cuttings associated with the solid phase and its behaviour is modelled adequately by equilibrium partitioning.

Table 7.1 Background concentrations of metals in sediment, PNEC values derived from literature data and field derived PNEC values given in mg/kg

Metals	World sediments*	NCS sediments**	PNEC sediments EqP▪	F-TEL◊	FTV◊◊	ER-L [b]	TEL [d]
Ba	1 – 2000	4.6 – 554 (mean 131)	-	2286	848		
Cd	0,1 – 0,6	0,003 – 0,130 (mean 0,037)	0,047	0,062	0,030	1,2	0,68
Cr	36 – 110	2,58 – 39,2 (mean 14,6)	29,37	10,08	10,47	81	52,3
Cu	7 – 33	0,3 – 17,2 (mean 4,10)	4,148	6,46	3,23	34	18,7
Hg (inorganic)		0,003 – 0,100 (mean 0,021)***	14,18	0,104***	0,020***	0,15	
Hg (methyl)							0,13▪
Pb	10 – 33	1,92 – 46,5 (mean 10,7)	11,57	14,65	9,93	46,7	30,2
Zn	27 – 88	0,42 – 83,7 (mean 20,7)	21,16	30,97	19,15	150	124

* World background concentrations

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

*** Based on total concentration of Hg

▪ Calculated from mean bakground consentrations from NCS

◊ Data from A. Bjørgesæter 2006

◊◊ Data from B. Grung et all 2006

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

M is the median concentration (50th percentile) of the database of compiled studies that were screened for samples and labeled “toxic” by the original investigators. Concentrations above the ER-M are defined as the “probable effects range”. Concentrations between the ER-L and ER-M are considered to be within the defined “possible effects range.”

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

- Methyl mercury

7.4. Sediment Quality Guidelines Proposed for North America

Several approaches have been used in the United States and Canada for developing sediment quality guidelines. The National Oceanic and Atmospheric Administration (NOAA) developed preliminary sediment quality guidelines to aid in interpreting analytical chemistry data for sediments collected from coastal waters of the US as part of the National Status and Trends Program with respect to potential adverse effects in sediment-dwelling organisms (Long and Morgan, 1990). SQGs were intended to aid in ranking sediments that warranted further detailed study for evidence of ecological harm and to rank chemicals in sediments with respect to their potential to cause harm to sediment-dwelling organisms.

NOAA collected data from published and unpublished scientific reports that contained information on concentrations of chemicals and toxic responses in aquatic organisms of freshwater and marine sediments collected from throughout North America. SQGs were derived initially from a database compiled from laboratory and field studies performed in both saltwater and freshwater (Long and Morgan, 1990). Subsequently, a larger database compiled from many studies performed by numerous investigators and relying on several different measures of sediment toxicity for just saltwater sediments and organisms was used to revise and update the SQGs (Long et al., 1995).

Data from each study were arranged in order of ascending chemical concentrations. Study endpoints in which adverse effects were reported were identified. The 10th and 50th percentile (median) of the effects database were identified from the ascending data Tables for each chemical. The 10th percentile values were termed the Effects-Range-Low (ERL), indicative of concentrations below which adverse effects rarely occur. The 50th percentile values were called the Effects-Range-Median (ERM) values, representative of concentrations above which effects are expected.

Effects-based sediment quality values, derived by several different laboratory or sediment assessment methods were used to derive SQGs. Because SQGs were derived from data from several different sediment toxicity assessment methods, the guidelines are considered consensus values. Data from the following types of assessment were used.

7.4.1. Sediment-Water Equilibrium Partitioning (EP) Approach

This approach estimates the concentration of individual chemicals in bulk sediment below which the chemical in the dissolved (bioavailable) phase in sediment pore water does not exceed the USEPA chronic water quality criterion for the chemical (Di Toro et al., 1991). The approach assumes that the chemical becomes distributed at equilibrium between the adsorbed and dissolved phases in sediments in accordance with its relative affinity for the two phases. Most nonpolar organic chemicals of concern adsorb most strongly to dissolved and particulate organic matter in sediments. For these compounds, the equilibrium relationship is between sediment organic carbon and sediment pore water, described by the sediment organic carbon/water partition coefficient (K_{oc}). Equilibrium for most metal cations and polar organic compounds is between exchangeable sites on the surface of fine sediment particles, particularly clays and iron and manganese oxide coatings on clays, described by the particle/water partition coefficient (K_p).

7.4.2. Spiked Sediment Bioassay (SSB) Approach

In this approach, benthic organisms are exposed to clean natural or "synthetic" sediments that have been spiked in the laboratory with different concentrations of one or more chemicals (Swartz et al., 1988). A dose/response relationship is recorded, based on either lethality or sublethal effects. Results usually are reported as median lethal concentration (LC_{50}) or median effects concentration (EC_{50}). These toxicity endpoints are considered acute and may be modified by an application factor or acute/chronic ratio to estimate chronic toxicity. Contaminated sediments also can be used for the laboratory bioassays. Tests with contaminated sediments have the advantage that the chemicals of interest probably are in the same physical forms in sediment that they were in the field (if physical/chemical conditions in the sediments are not changed). They have the disadvantage that the chemicals causing or contributing to sediment toxicity are not known with certainty.

7.4.3. Screening Level Concentrations (SLC) Approach

Field-collected sediment chemistry and benthic ecology data are used in this approach (Neff et al., 1986). The SLC is the estimated highest concentration of a target nonpolar organic chemical at which approximately 95 percent of the benthic fauna occur. The cumulative frequency distribution of all stations at which a particular species of benthic invertebrate is present is plotted against the organic carbon-normalized concentration of the organic chemical in the sediment. The concentration of the contaminant at the highest 90th percentile station is estimated by interpolation and recorded as the species screening level concentration (SSLC). SSLCs for a large number of benthic organisms are plotted as a frequency distribution.The concentration above which 95 percent of the SSLCs are found is the SLC for the chemical.

7.4.4. Apparent Effects Threshold (AET) Approach

The AET approach also relies on field data on the co-occurrence of concentrations of the chemical of interest and specific species of benthic fauna. The AET concentration is the lowest concentration of the target chemical in sediments that is correlated statistically with different adverse biological effects (e.g., decreased abundance, or impaired growth or reproduction of the species of interest), a concentration which adverse effects are always expected (PTI Environmental Services, 1988). Unlike the FTV, the AET does not identify a concentration of a sediment contaminant below which effects are not expected to occur. Because the AET approach attributes all observed biological effects to the chemical of interest and most of the field samples used in the analysis contain many contaminants, the AET provides a very conservative estimate of the toxicity of chemicals in sediments.

7.4.5. Bioeffects/Contaminant Co-occurrence Analysis (COA) Approach

This method, like the SLC and AET approaches, relies of field-collected data on chemicals and biota in sediments. COA involves calculation of the central tendency (i.e., means, standard deviations, maxima, minima) of chemical concentrations in field-collected sediments associated with matching samples determined to have high, intermediate, and low indications of biological effects (DeWitt et al., 1988). Effects usually are based on laboratory sediment toxicity tests. Test results are ranked as highly toxic, intermediate toxicity, and low toxicity, and chemical concentrations in sediments in the different ranks are compared to concentrations in field sediments.

A similar approach was used to develop SQGs for Canada (MacDonald et al., 1992). A database of freshwater and marine sediment chemistry and toxicity data were compiled. Published SQG values were included in the databased if they passed screening criteria. The resulting TEL (threshold effects level) or TEC (threshold effects concentration) corresponds to the ERL, and the PEL (probable effects level) or probable effects concentration (PEC) corresponds to the ERM. Concentrations in sediment below the TEL are not expected to be harmful to benthic organisms; concentrations above the PEL are likely to be harmful to benthic organisms.

The current US (ERL/ERM) and Canadian (TEC/PEC) SQGs for the naturally-occurring metals and organics (PAH) in marine sediments are summarized in Table 7.1. An example of data analysis for derivation of ERL and ERM values for naphthalene is given in appendix 8.4.1. In most cases, Canadian TEL/PEL values are lower than US ERL/ERM values, but the differences are not large. These values can be used for comparison with and validation of the PNEC values for the drilling waste toxicity model for sediments as described in Section 5.2.2 of this report.

Table 7.1. Summary of US effects range low (ERL) and effects range median (ERM) concentrations and Canadian threshold effect levels (TEL) and probable effects level (PEL) for the naturally-occurring chemicals of concern in this drilling waste toxicity modeling. All concentrations are mg chemical/kg dry wt sediment.

Chemical	**US Sediment Quality Guidelines**		**Canadian Sediment Quality Guidelines**	
	ERL	ERM	TEC	PEC
Cadmium	1200	9600	700	4200
Chromium	81,000	370,000	52,300	160,000
Copper	34,000	270,000	18,700	108,000
Lead	46,700	218,000	30,200	112,000
Mercury	150	710	130	700
Zinc	150,000	410,000	124,000	271,000
Naphthalene	160	2100	34.6	391
2-Methylnaphthalene	70	670	20.2	201
Acenaphthene	16	500	6.71	88.9
Acenaphthylene	44	640	5.87	128
Fluorene	19	540	21.2	144
Anthracene	85.3	1100	46.9	245
Phenanthrene	240	1500	86.7	544
Fluoranthene	600	5100	113	1494
Pyrene	665	2600	153	1398
Benz(a)anthracene	261	1600	74.8	693
Chrysene	384	2800	108	846
Benzo(a)pyrene	430	1600	88.8	763
Dibenz(a,h)anthracene	63.4	260	6.22	135
Total Low MW PAH	552	3160	NV	NV
Total High MW PAH	1700	9600	NV	NV
Total PAH	4022	44,792	NV	NV

7.5. References

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8. Appendices

8.1. *Appendix - Chapter 2*

Test Methods - Biodegradation

Standard simualation test methods for biodegradation for various marine compartments:

- *Aquatic (pelagic) compartment:* ISO/DIS method 14592-1 “Evaluation of the aerobic biodegradability of organic compounds at low concentrations – Part I” and new OECD guideline “Simulation test – Aerobic transformation in surface water”
- *Turbid aquatic/sediment dispersed compartment:* ISO/DIS method 14592-2 “Evaluation of the aerobic biodegradability of organic compounds at low concentrations – Part 2” and OECD 308 “Aerobic and anaerobic transformation in aquatic sediment systems” (aerobic test).
- *Anerobic sediment compartment:* OECD 308 “Aerobic and anaerobic transformation in aquatic sediment systems” (strictly anaerobic test)

Most fine-grained marine sediments are anaerobic below the upper 5-10 mm. The assessment of the biodegradation in marine sediments should ideally be based on results from investigations simulating these conditions. If not available, other approaches may be used.

Marine screening tests may be:
Ready Biodegradability Tests: OECD 306 “Biodegradability in Seawater” test (OECD, 1992e) comprises two methods:,

1. Shake Flask Method
2. Closed Bottle Method.

These tests are seawater variants of the Modified OECD Screening Test (EU Annex V C.4-B and OECD 301E, 1992f) and Closed Bottle Test (EU Annex V C.4-E and OECD 301D, 1992f), respectively, the main difference being the use of a marine inoculum.

Three additional screening tests (ready biodegradability tests) are:

1. “Marine CO2 Evolution Test”, the “Marine
2. “Marine BODIS Test”
3. “Marine CO2 Headspace Test”

- An approach similar to the one used for freshwater sediments could be used, i.e., use a scenario consisting of a 30 mm thick sediment layer of which the upper 3 mm are considered aerobic and the remaining part anaerobic. If separate degradation rates are available for aerobic and anaerobic sediment, these could be used for estimating the half-life. If only data on aerobic degradation in sediment is available, no degradation in the anaerobic compartment should be assumed and consequently, a 10 times longer half-life than the half-life in aerobic sediment should be used

- Anaerobic screening tests may be performed using a sediment inoculum (Horowitz et al.,1982; Madsen et al., 1995), and the observed biodegradability may then be used as an indication of the potential biodegradability of the substance in anaerobic sediment.
  Degradation rates should be derived by expert judgement

- If no degradation data from studies with sediment or soil are available, the use of data ondegradation in water could be considered. The degradation potential in the upper aerobic sediment layer is generally assumed to be similar to the degradation potential in the overlying water. However, the possible very low bioavailability in the sediment of highly hydrophobic and/or poorly water-soluble substances should be taken into consideration as is done also for freshwater sediments.

8.2. Appendix - Chapter 4: Toxcity review

Appendix 4.1 Bulk metal effect concentration data for cadmium. References to the cited literature are listed at the end of the table.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	Effect endpoint/ type	Effect conc. (µg/g dw)	Ref.	Comments
CdCl$_2$	Experimental Method: 1), Protocol: 1), 2), 3)	Bulk metal analysis: 1)	*Arenicola marina* (Annelida:Polychaeta) Marine infaunal. East Atlantic boreal.	NOEC $_{\text{Mortality 10 days}}$ /Acute	Between 9 and 25	[4]	1), Effect concentration estimated from figure 2, p. 227 in the paper.
CdCl$_2$	Experimental Method: 1), Protocol: 1), 2), 3)	Bulk metal analysis: 1)	*Arenicola marina* (Annelida:Polychaeta) Marine infaunal. East Atlantic boreal.	NOEC $_{\text{Zero emergence 10 days}}$ /Acute	< 25	[4]	1), Effect concentration estimated from figure 3, p. 229 in the paper.
CdCl$_2$	Experimental Method: 1), Protocol: 1), 2), 3)	Bulk metal analysis: 1)	*Arenicola marina* (Annelida:Polychaeta) Marine infaunal. East Atlantic boreal.	NOEC $_{\text{Number of casts 10 days}}$ /Acute	< 9	[4]	1), Effect concentration estimated from figure 4, p. 231 in the paper.
CdCl$_2$	Experimental Method: 1), Protocol: 1), 2), 3)	Bulk metal analysis: 1)	*Arenicola marina* (Annelida:Polychaeta) Marine infaunal. East Atlantic boreal.	NOEC $_{\text{size of casts 10 days}}$ /Acute	< 9	[4]	1), Effect concentration estimated from figure 5, p. 232 in the paper.
CdCl$_2$	Experimental Method: 2), Protocol: 4)	Bulk metal analysis: 2)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	LC$_{50\ \text{10 days}}$ /Acute	6,9	[6]	2)
CdCl$_2$	Experimental Method: 2), Protocol: 4)	Bulk metal analysis: 2)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	LC$_{50\ \text{4 days}}$ /Acute	25,9	[6]	2), Water-only test preformed in the study LC$_{50\ \text{96 hours}}$: 1,61 mg/l.
CdCl$_2$	Experimental Method: 2), Protocol: 4)	Bulk metal analysis: 2)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	EC$_{50\ \text{1hr. Reburial}}$ /Acute	6,5	[6]	2), Effect endpoint: reburial activity in clean sediment within 1 hour after 10 days exposure to Cd in sediment.
CdCl$_2$	Experimental Method: 2), Protocol: 4)	Bulk metal analysis: 2)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	EC$_{50\ \text{1hr. Reburial}}$ /Acute	20,8	[6]	2), Effect endpoint: reburial activity in clean sediment within 1 hour after 4 days exposure to Cd in sediment.
CdCl$_2$	Experimental method: 3), Protocol: 5)	Bulk metal analysis: 3)	*Ruditapes philippinarum* (Mollusca: Bivalvia) Marine infaunal. Atlantic and Pacific tropical to temperate.	LC$_{50\ \text{48 hour}}$ /Acute	4,52	[8]	3)
CdCl$_2$	Experimental method: 3), Protocol: 5)	Bulk metal analysis: 3)	*Ruditapes philippinarum* (Mollusca: Bivalvia) Marine infaunal. Atlantic and Pacific tropical to temperate.	LC$_{50\ \text{48 hour}}$ /Acute	1,26	[8]	3)
Cd-salt (quality not stated)	Experimental method: 4), Protocol: 6)	Bulk metal analysis: 4)	*Cylindrotheca closterium* (Algae:Bacillariophyceae) Marine epi-bentic. Boreal to temperate.	EC$_{50\ \text{72hour}}$ /Acute	79	[11]	4)
CdCl$_2$	Experimental Method: 2), Protocol: 4)	Bulk metal analysis: 5)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	LC$_{50\ \text{10 days}}$ /Acute	9,8	[12]	5)

Appendix 4.1 Bulk metal effect concentration data for cadmium continued.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	Effect endpoint/ type	Effect conc. (µg/g dw)	Ref.	Comments
CdCl$_2$	Experimental Method: 2), Protocol: 4)	Bulk metal analysis: 5)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	EC50 $_{\text{10 days emergence}}$ /Acute	9,72	[12]	5), Effect endpoint: animals emerged from the sediment after 10 days exposure to Cd in sediment.
CdCl$_2$	Experimental Method: 2), Protocol: 4)	Bulk metal analysis: 5)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	EC$_{\text{50 1hr. Reburial}}$ /Acute	9,07	[12]	5), Effect endpoint: Reburial activity in clean sediment within 1 hour after 10 days exposure to Cd in sediment.
CdCl$_2$	Experimental Method: 5), Protocol: 1), 2), 4)	Bulk metal analysis: 6)	*Corophium volutator* (Crustacea:Amphipoda) Marine infaunal. Atlantic boreal.	LC$_{\text{50 10 days}}$ /Acute	14,42	[4]	6)
CdCl$_2$	Experimental Method: 5), Protocol: 1), 2), 4)	Bulk metal analysis: 6)	*Corophium volutator* (Crustacea:Amphipoda) Marine infaunal. Atlantic boreal.	EC$_{\text{50 1hr. Reburial}}$ /Acute	9,3	[4]	6), Effect endpoint: reburial activity in clean sediment within 1 hour after 10 days exposure to cadmium-spiked sediment.
CdCl$_2$	Experimental Method: 6), Protocol: 3)	Bulk metal analysis: 7)	*Arenicola marina* (Annelida:Polychaeta) Marine infaunal. East Atlantic boreal.	LC$_{\text{50 10 days}}$ /Acute	35	[4]	1)
Cd-salt (quality not stated)	Experimental Method: 7) Protocol: 4)	Bulk metal analysis: 8)	*Amphiascus tenuiremis* (Crustacea: Copepoda) Marine Meio-bentic. Atlantic boreal to temperate.	LC$_{\text{50 96 hour}}$ /Acute	37,9	[13]	7)
Cd-salt (quality not stated)	Experimental Method: 7) Protocol: 4)	Bulk metal analysis: 8)	*Amphiascus tenuiremis* (Crustacea: Copepoda) Marine Meio-bentic. Atlantic boreal to temperate.	LC$_{\text{50 96 hour}}$ /Acute	52,5	[13]	7), Supernatant aspired away before sediment was used.
CdCl$_2$	Experimental method: 8), Protocol: 7)	AVS: 9), Bulk metal analysis: 10)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	LC$_{\text{50 10 days}}$ /Acute	2580	[16]	8), Sediment effect concentration - AVS-normalisation (µmol Cd/µmol AVS): 1,54.
CdCl$_2$	Experimental method: 8), Protocol: 7)	AVS: 9), Bulk metal analysis: 10)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	LC$_{\text{50 10 days}}$ /Acute	2850	[16]	8), Sediment effect concentration - AVS-normalisation (µmol Cd/µmol AVS): 1,70.
CdCl$_2$	Experimental method: 8), Protocol: 7)	AVS: 9), Bulk metal analysis: 10)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	LC$_{\text{50 10 days}}$ /Acute	1070	[16]	9), Sediment effect concentration - AVS-normalisation (µmol Cd/µmol AVS): 2,19.
CdCl$_2$	Experimental method: 8), Protocol: 7)	AVS: 9), Bulk metal analysis: 10)	*Rhepoxynius hudsoni* (Crustacea:Amphipoda) Marine infaunal. East Pacific and West Atlantic boreal to temperate.	LC$_{\text{50 10 days}}$ /Acute	290	[16]	10), Sediment effect concentration - AVS-normalisation (µmol Cd/µmol AVS): 1,97.

Appendix 4.1 Bulk metal effect concentration data for cadmium continued.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	Effect endpoint/ type	Effect conc. (µg/g dw)	Ref.	Comments
Cd-salt (quality not stated)	Experimental method: 9), Protocol: 8)	AVS: 9), Bulk metal analysis: 5)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	2608	[17]	11), 12), 13)
Cd-salt (quality not stated)	Experimental method: 9), Protocol: 8)	AVS: 9), Bulk metal analysis: 5)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	1866	[17]	12), 13), 14)
Cd-salt (quality not stated)	Experimental method: 9), Protocol: 8)	AVS: 9), Bulk metal analysis: 5)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	1664	[17]	12), 13), 15)

Experimental Methods:

1): Static exposure performed at a salinity of 32±1ppt with adult animals (aver. wet weight 4,3 gr.) collected from natural populations.
2): Static exposure performed at a salinity of 25 ppt with adult animals collected from natural populations.
3): Static exposure performed at a salinity of 33 ppt with adult animals (3-4 cm shell length) collected from natural populations.
4): Algae grown in static culture in Artificial sea water (American Society for Testing and Materials [9]) enriched with nutrients.
5): Static exposure performed at a salinity of 32±1 ppt with adult animals (4-7mm) collected from natural polulations.
6): Static exposure at a salinity of 32±1 ppt with adult animanls (average wet weight 4,3 g) collected from natural polulations.
7): Static exposure performed at a salinity of 30,7±0,3 ppt with adult animals.
8): Natural populations (sub-adult animal). 31 ppt. Flowing filtered seawater and aeration ensured acceptable dissolved oxygen concentration and cadmium-free overlying water.
9): Flow-trough exposure performed at a salinity of 28-34 ppt with adult animals from natural populations.

Protocol:

1): American Society for Testing and Materials [1].
2): US Environmental Protection Agency and US Army Corps of Engineers [2].
3): Thain et. al. [3].
4): Based on Swartz et. al. [5].
5): Based on Phelps et. al. [7].
6): Based on OECD [10].
7): Based on American Society for Testing and Materials [14].
8): No reference to experimental protocol other than the published paper.

Chemical analysis:

1): Bulk metal analysis on sediment fraction < 500 µm. Sediment digested with conc. HNO_3 and analysed by AAS.
2): Bulk metal analysis by extracting dried sediment with cold 4N HCl and analysis by flame-AAS.
3): Bulk metal analysis on dried sediment digested in hot conc. HNO_3 and HCl (2:1) and analysed by Plasma Emission Spectroscopy with Buffalo River Sediment (SRM2704).
4): Total decomposition method as described Loring and Rantala [15]. Analysis performed by flame AAS.
5): Analytic values reported but no reference to protocol or eqipment.
6): Bulk metal analysis on sediment fraction < 63µm. Sediment digested with conc. HNO_3 and analysed by AAS.
7): Bulk metal nalysis on sediment fraction < 500 µm. Sediment digested with conc. HNO_3 and analysed by AAS.
8): Bulk metal analysis on digested sediment conc. HNO_3 and analysed with AAS.
9): AVS was analyzed by cold-acid purge-and-trap technique.
10): Wet sediment digested with cold conc. HNO_3 followed by peroxide oxidation and analysed by AAS.

Appendix 4.1 Bulk metal effect concentration data for cadmium continued.

Comments:

1): Sediment sieved at 500 μm to remove macrofauna and lager particles prior to spiking. TOC: 1,58 ±0,29 %.

2): Natural sediment sieved at 500 um to remove macrofauna. Total volatile solids (TVS): 1,05% as percentage of weight lost after ignition of dry sediment.

3): Field collected sediment sieved through a 2 mm mesh.

4): Natural sediment washed with 0,1N HNO_3 and rinsed with Ultrapure H_2O (Milli-Q). More than 95% of sediment particles < 63 μm.

5): Natural sediment, mainly clean sand, with 1,2 % total volatile solids on average.

6): Natural sediment sieved at 500 μm to remove macrofauna and 300 um prior to spiking to remove particles in the size 300-500 μm. TOC = 2,1±0,38%.

7): Natural sediment sieved at <63 μm. Organic content = 3,8 %. Total solids (dry weight) = 13 %.

8): Long Island Sound sediment wet-sieved trough a 2 mm mesh stainless stell screen. Sediment AVS averaging 13,9 μmol/gr.

9): 50/50-mixture of Long Island Sound (sed. 8) and Ninigret Pond (sed. 10). Sediment AVS averaging 3,23 μmol/gr.

10): Ninigret Pond sediment wet-sieved wet trough a 2 mm mesh stainless steel screen. Sediment AVS averaging 0,28 μmol/gr.

11): Natural sediment from Long Island Sound wet-siewed trough 2 mm mesh. Total cationic [SEM] in unspiked sediment averaging 3,2 μmol/g and TOC: 0,88%. Sediment made up of 5 % sand, 71 % silt and 24 % clay.

12): Water-only test performed in the study: $LC_{50\ 96\ \mathrm{hours}}$: 0,036 mg/l.

13): LC50-value calculated by non-liear regression based on the number of survivors vs. exposure concentrations in Table 1, p. 2071 in the paper.

14): Natural sediment from Ninigret Pond wet-siewed trough 2 mm mesh and washed several times to remove excess organic material prior to use. Total cationic [SEM] in unspiked sediment averaging 0,081 μmol/g and TOC: 0,15%. Sediment made up of 100% sand.

15): 50/50-mixture of Long Island Sound and Ninigret Pond sediment. Sediment AVS averaging 4,34 μmol/gr.

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Appendix 4.1 Bulk metal effect concentration data for cadmium continued.

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Appendix 4.2 SEM effect concentration data for cadmium. References to the cited literature are listed at the end of this table.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	AVS (µmol/g dw)	Effect endpoint/ type/ Test duration	Effect size	Effect conc. [SEM] (µmol/g dw)	[SEM]/ AVS-ratio	Ref.	Comments
Un-spiked control	Experimental method: 1), Protocol: 1)	AVS: 1) [SEM]: 2)	*Leptocheirus plumulosus* (Crustacea:Amphipoda) Marine tube-dwelling infaunal. West Atlantic boreal to temperate.	6,25	Mortality/Chronic/28 days	5 %	0,0	0,00	[18]	1), Un-spiked control.
Cd	Experimental method: 1), Protocol: 1)	AVS: 1) [SEM]: 2)	*Leptocheirus plumulosus* (Crustacea:Amphipoda) Marine tube-dwelling infaunal. West Atlantic boreal to temperate.	5,09	Mortality/Chronic/28 days	0 %	1,6	0,34	[18]	1)
Cd	Experimental method: 1), Protocol: 1)	AVS: 1) [SEM]: 2)	*Leptocheirus plumulosus* (Crustacea:Amphipoda) Marine tube-dwelling infaunal. West Atlantic boreal to temperate.	5,22	Mortality/Chronic/28 days	5 %	3,2	0,74	[18]	1)
Cd	Experimental method: 1), Protocol: 1)	AVS: 1) [SEM]: 2)	*Leptocheirus plumulosus* (Crustacea:Amphipoda) Marine tube-dwelling infaunal. West Atlantic boreal to temperate.	5,84	Mortality/Chronic/28 days	0 %	6,6	1,55	[18]	1)
Cd	Experimental method: 1), Protocol: 1)	AVS: 1) [SEM]: 2)	*Leptocheirus plumulosus* (Crustacea:Amphipoda) Marine tube-dwelling infaunal. West Atlantic boreal to temperate.	10,28	Mortality/Chronic/28 days	5 %	12,2	1,31	[18]	1)
Cd	Experimental method: 1), Protocol: 1)	AVS: 1) [SEM]: 2)	*Leptocheirus plumulosus* (Crustacea:Amphipoda) Marine tube-dwelling infaunal. West Atlantic boreal to temperate.	8,55	Mortality/Chronic/28 days	100 %	17,4	2,23	[18]	1)
Cd	Experimental method: 1), Protocol: 1)	AVS: 1) [SEM]: 2)	*Leptocheirus plumulosus* (Crustacea:Amphipoda) Marine tube-dwelling infaunal. West Atlantic boreal to temperate.	7,00	Mortality/Chronic/28 days	100 %	22,5	4,82	[18]	1)
Un-spiked cntrol	Experimental method: 1), Protocol: 1)	AVS: 1) [SEM]: 2)	*Leptocheirus plumulosus* (Crustacea:Amphipoda) Marine tube-dwelling infaunal. West Atlantic boreal to temperate.	6,25	Growth/Chronic/28 days	5,24 mm	0,0	0,00	[18]	1), Un-spiked control
C	Experimental method: 1), Protocol: 1)	AVS: 1) [SEM]: 2)	*Leptocheirus plumulosus* (Crustacea:Amphipoda) Marine tube-dwelling infaunal. West Atlantic boreal to temperate.	5,09	Growth/Chronic/28 days	5,73 mm	1,6	0,34	[18]	1)
Cd	Experimental method: 1), Protocol: 1)	AVS: 1) [SEM]: 2)	*Leptocheirus plumulosus* (Crustacea:Amphipoda) Marine tube-dwelling infaunal. West Atlantic boreal to temperate.	5,22	Growth/Chronic/28 days	5,74 mm	3,2	0,74	[18]	1)

Appendix 4.2 SEM effect concentration data for cadmium continued.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	AVS (µmol/g dw)	Effect endpoint/ type/ Test duration	Effect size	Effect conc. [SEM] (µmol/g dw)	[SEM]/ AVS-ratio	Ref.	Comments
Cd	Experimental method: 1), Protocol: 1)	AVS: 1) [SEM]: 2)	*Leptocheirus plumulosus* (Crustacea:Amphipoda) Marine tube-dwelling infaunal. West Atlantic boreal to temperate.	5,84	Growth/Chronic/28 days	5,73 mm	6,6	1,55	[18]	1)
Cd	Experimental method: 1), Protocol: 1)	AVS: 1) [SEM]: 2)	*Leptocheirus plumulosus* (Crustacea:Amphipoda) Marine tube-dwelling infaunal. West Atlantic boreal to temperate.	10,28	Growth/Chronic/28 days	5,87 mm	12,2	1,31	[18]	1)
Un-spiked control	Experimental method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Leptocheirus plumulosus* (Crustacea:Amphipoda) Marine tube-dwelling infaunal. West Atlantic boreal to temperate.	6,25	Fertility/Chronic/28 days	7,47	0,0	0,00	[18]	1), 2) Un-spiked control
Cd	Experimental method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Leptocheirus plumulosus* (Crustacea:Amphipoda) Marine tube-dwelling infaunal. West Atlantic boreal to temperate.	5,09	Fertility/Chronic/28 days	15,71	1,6	0,34	[18]	1)
Cd	Experimental method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Leptocheirus plumulosus* (Crustacea:Amphipoda) Marine tube-dwelling infaunal. West Atlantic boreal to temperate.	5,22	Fertility/Chronic/28 days	12,85	3,2	0,74	[18]	1)
Cd	Experimental method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Leptocheirus plumulosus* (Crustacea:Amphipoda) Marine tube-dwelling infaunal. West Atlantic boreal to temperate.	5,84	Fertility/Chronic/28 days	10,65	6,6	1,55	[18]	1)
Cd	Experimental method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Leptocheirus plumulosus* (Crustacea:Amphipoda) Marine tube-dwelling infaunal. West Atlantic boreal to temperate.	10,28	Fertility/Chronic/28 days	14,71	12,2	1,31	[18]	1)
Un-spiked control	Experimental method: 2), Protocol: 1)	AVS: 1), Bulk metal analysis: 3)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	14,9	Mortality/Acute/10 days	1,7 %	0	0,00	[17]	3), 4), 5) Un-spiked control
Cd-salt (quality not stated)	Experimental method: 2), Protocol: 1)	AVS: 1), Bulk metal analysis: 3)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	14,9	Mortality/Acute/10 days	8,4 %	1,57	0,10	[17]	3), 4), 5)
Cd-salt (quality not stated)	Experimental method: 2), Protocol: 1)	AVS: 1), Bulk metal analysis: 3)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	14,9	Mortality/Acute/10 days	16,7 %	4,85	0,33	[17]	3), 4), 5)

Appendix 4.2 SEM effect concentration data for cadmium continued.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	AVS (µmol/g dw)	Effect endpoint/ type/ Test duration	Effect size	Effect conc. [SEM] (µmol/g dw)	[SEM]/ AVS-ratio	Ref.	Comments
Cd-salt (quality not stated)	Experimental method: 2), Protocol: 1)	AVS: 1), Bulk metal analysis: 3)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	14,9	Mortality/Acute/10 days	10 %	16,7	1,12	[17]	3), 4), 5)
Cd-salt (quality not stated)	Experimental method: 2), Protocol: 1)	AVS: 1), Bulk metal analysis: 3)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	14,9	Mortality/Acute/10 days	100 %	51,7	3,50	[17]	3), 4), 5)
Cd-salt (quality not stated)	Experimental method: 2), Protocol: 1)	AVS: 1), Bulk metal analysis: 3)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	14,9	Mortality/Acute/10 days	88,4 %	177	11,90	[17]	3), 4), 5)
Un-spiked control	Experimental method: 2), Protocol: 1)	AVS: 1), Bulk metal analysis: 3)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	1,31	Mortality/Acute/10 days	5 %	0	0,00	[17]	4), 5), 6) Un-spiked control
Cd-salt (quality not stated)	Experimental method: 2), Protocol: 1)	AVS: 1), Bulk metal analysis: 3)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	1,31	Mortality/Acute/10 days	12,5 %	0,15	0,12	[17]	4), 5), 6)
Cd-salt (quality not stated)	Experimental method: 2), Protocol: 1)	AVS: 1), Bulk metal analysis: 3)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	1,31	Mortality/Acute/10 days	12,5 %	0,64	0,50	[17]	4), 5), 6)
Cd-salt (quality not stated)	Experimental method: 2), Protocol: 1)	AVS: 1), Bulk metal analysis: 3)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	1,31	Mortality/Acute/10 days	40 %	2,57	1,95	[17]	4), 5), 6)
Cd-salt (quality not stated)	Experimental method: 2), Protocol: 1)	AVS: 1), Bulk metal analysis: 3)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	1,31	Mortality/Acute/10 days	95 %	5,9	4,34	[17]	4), 5), 6)
Cd-salt (quality not stated)	Experimental method: 2), Protocol: 1)	AVS: 1), Bulk metal analysis: 3)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	1,31	Mortality/Acute/10 days	100 %	24,3	18,50	[17]	4), 5), 6)
Un-spiked control	Experimental method: 2), Protocol: 1)	AVS: 1), Bulk metal analysis: 3)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	4,34	Mortality/Acute/10 days	16,7 %	0	0,00	[17]	4), 5), 7) Un-spiked control

Appendix 4.2 SEM effect concentration data for cadmium continued.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	AVS (µmol/g dw)	Effect endpoint/ type/ Test duration	Effect size	Effect conc. [SEM] (µmol/g dw)	[SEM]/ AVS-ratio	Ref.	Comments
Cd-salt (quality not stated)	Experimental method: 2), Protocol: 1)	AVS: 1), Bulk metal analysis: 3)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	4,34	Mortality/Acute/10 days	11,7 %	0,3	0,10	[17]	4), 5), 7)
Cd-salt (quality not stated)	Experimental method: 2), Protocol: 1)	AVS: 1), Bulk metal analysis: 3)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	4,34	Mortality/Acute/10 days	23,4 %	1,75	0,40	[17]	4), 5), 7)
Cd-salt (quality not stated)	Experimental method: 2), Protocol: 1)	AVS: 1), Bulk metal analysis: 3)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	4,34	Mortality/Acute/10 days	46,7 %	9,64	2,22	[17]	4), 5), 7)
Cd-salt (quality not stated)	Experimental method: 2), Protocol: 1)	AVS: 1), Bulk metal analysis: 3)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	4,34	Mortality/Acute/10 days	100 %	20,7	4,80	[17]	4), 5), 7)
Cd-salt (quality not stated)	Experimental method: 2), Protocol: 1)	AVS: 1), Bulk metal analysis: 3)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	4,34	Mortality/Acute/10 days	85 %	48,4	11,20	[17]	4), 5), 7)

Experimental Methods:
1): Static-renewal exposure at a salinity of 20 ppt.
2): Flow-trough exposure performed at a salinity of 28-34 ppt with adult animals from natural populations.

Protocols:
1): No reference to Experimental Protocol other than the published paper.

Chemical Analysis:
1): AVS was analyzed by cold-acid purge-and-trap technique.
2): [SEM] was analysed in the filtrate of the acid-sediment slurry and analysed by ICP-AES or GF-AAS with Zeeman backgound correction.
3): Analytic values reported but no reference to protocol or equipment. See comment no. 5).

Comments:
1): Average AVS and SEM values for each cadmium/AVS treatment were derived by averaging concentrations in core sections across sediment depth and time, using dry weight of each core section as a weighting factor.
2): Fertility as average number of offspring pr. surviving female.
3): Natural sediment from Long Island Sound wet-sieved trough 2 mm mesh. Total cationic [SEM] in unspiked sediment averaging 3,2 µmol/g and TOC: 0,88%. Sediment made up of 5 % sand, 71 % silt and 24 % clay.
4): Water-only test performed in the study: $LC_{50\ 10\ days}$: 0,036 mg/l.
5): Listed effect concentration from analysis of bulk sediment concentration, but acc. to Berry ***et al.*** [17] for cadmium this concentrations equals [SEM] as the cadmiumsulfide is fully extractable under conditions used for [SEM]-extraction.
6): Natural sediment from Ninigret Pond wet-sieved trough 2 mm mesh and washed several times to remove excess organic material prior to use. Total cationic [SEM] in unspiked sediment averaging 0,081 µmol/g and TOC: 0,15%. Sediment made up of 100% sand.
7): 50/50-mixture of Long Island Sound and Ninigret Pond sediment. Sediment AVS averaging 4,34 µmol/gr.

Appendix 4.2 SEM effect concentration data for cadmium continued.

References:

[17] Berry, W.J., J.D. Hansen, J.D. Mahony, D.L. Robson, D.M. Di Toro, B.P. Shipley, B. Rogers, J.M. Corbin and W.S. Bootman. 1996. Predicting the toxicity of metal-spiked laboratory sediments using acid-volatile sulphide and interstitial water normalizations. Environ. Toxicol. Chem., 15: 2067-2079.

[18] DeWitt, T.H., R.C. Swartz, D.J. Hansen, D. McGovern and W.J. Berry. 1996. Bioavailiability and chronic toxicity of cadmium in sediment to the estuarine amphipod *Leptocheirus plumulosus*. Environ. Toxicol. Chem., 15: 2095-2101.

Appendix 4.3 Bulk metal effect concentration data for chromium. References to the cited literature are listed at the end of this table.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	Effect endpoint/ type	Effect conc. (µg/g dw)	Ref.	Comments
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 1). Protocol: 1).	Bulk metal analysis: 1).	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	1227	[2]	1), 2), 3)
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 1). Protocol: 1).	Bulk metal analysis: 1).	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	147	[2]	2), 3), 4)

Experimental Methods:

1): Flow-trough exposure performed at a salinity of 31±1 ppt with adult animals collected from natural populations.

Protocols:

1): Based on Berry et. al. [1].

Chemical Analysis:

1): Bulk metal analysis by total decomposition in concentrated nitric, hydrofluoric, and hydrochloric acids, following U.S. Environmental Protection Agency Method 3052 (http://www.epa.gov/epaoswer/hazwaste/ test/pdfs/3052.pdf) and chromium determined in the digestates by ICP-AES.

Comments:

1): Natural sediment from Long Island Sound wet-sieved trough 2 mm mesh. TOC: 1,6±0,4% and AVS: 6,6±1,2 µmol/gram dw.

2): Effect-concentration value calculated by non-linear regression based on the number of survivors vs. exposure concentrations in Table 3, p. 2986 in the paper.

3): Water-only test performed in the study: $LC_{50\ 10\ days}$: 1,98 mg/l Cr(VI).

4): Natural sediment from Ninigret Pond wet-sieved trough 2 mm mesh and washed several times to remove excess organic material prior to use. TOC: 0,13±0,26% and AVS: 1,1±0,5µmol/gram dw.

References:

[1] Berry, W.J., D.J. Hansen, J.D. Mahony, D.L. Robson, D.M. DiToro, B.P. Shipley, B. Rogers, J.M. Corbin and W.S. Boothman. 1996. Predicting the toxicity of metal-spiked laboratory sediments using acid-volatile sulfide and interstitial water normalizations. Environ. Toxicol. Chem., 15: 2067–2079.

[2] Berry, W.J., W.S. Boothman, J.R. Serbst and P.A. Edwards. 2004. Predicting the toxicity of chromium in sediments. Environ. Toxicol. Chem., 23: 2981-2992.

Appendix 4.4 SEM effect concentration data for chromium. References to the cited literature are listed at the end of this table.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	AVS (µmol/g dw)	Effect endpoint/ type/ Test duration	Effect size	Effect conc - Bulk (µmol/g - µg/g dw)	Effect conc. - [SEM] (µmol/g dw)	Ref.	Comments
Unspiked control	Experimental Method: 1). Protocol: 1).	Bulk metal analysis: 1), AVS: 2), [SEM]: 3).	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	19,2	Mortality/Acute/10 days	10,0 %	1,3 - 66	0,2 Cr total/ 0,0 Cr(VI)	[2]	1), 2) Unspiked control
Cr(III) as $CrCl_3$ x $6H_2O$	Experimental Method: 1). Protocol: 1).	Bulk metal analysis: 1), AVS: 2), [SEM]: 3).	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	5,3	Mortality/Acute/10 days	5,0 %	399 - 20771	329 Cr total/ 0,0 Cr(VI)	[2]	1), 2)
Unspiked control	Experimental Method: 1). Protocol: 1).	Bulk metal analysis: 1), AVS: 2), [SEM]: 3).	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	5,9	Mortality/Acute/10 days	7,5 %	0,2 - 10	0,2 Cr total/ 0,0 Cr(VI)	[2]	1), 2) Unspiked control
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 1). Protocol: 1).	Bulk metal analysis: 1), AVS: 2), [SEM]: 3).	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	6,1	Mortality/Acute/10 days	7,5 %	1,29 - 152	1,2 Cr total/ 0,0 Cr(VI)	[2]	1), 2)
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 1). Protocol: 1).	Bulk metal analysis: 1), AVS: 2), [SEM]: 3).	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	5,5	Mortality/Acute/10 days	2,5 %	4,87 - 253	2,8 Cr total/ 0,0 Cr(VI)	[2]	1), 2)
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 1). Protocol: 1).	Bulk metal analysis: 1), AVS: 2), [SEM]: 3).	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	4,5	Mortality/Acute/10 days	0 %	8,94 - 465	6,0 Cr total/ 0,0 Cr(VI)	[2]	1), 2)
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 1). Protocol: 1).	Bulk metal analysis: 1), AVS: 2), [SEM]: 3).	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	1,5	Mortality/Acute/10 days	7,5 %	13,82 - 719	13,7 Cr total/ 0,0 Cr(VI)	[2]	1), 2)
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 1). Protocol: 1).	Bulk metal analysis: 1), AVS: 2), [SEM]: 3).	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	0,6	Mortality/Acute/10 days	67,5 %	25,79 - 1341	28,2 Cr total/ 0,4 Cr(VI)	[2]	1), 2)
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 1). Protocol: 1).	Bulk metal analysis: 1), AVS: 2), [SEM]: 3).	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	0,05	Mortality/Acute/10 days	100 %	52,69 - 2740	53,0 Cr total/ 8,1 Cr(VI)	[2]	1), 2)
Unspiked control	Experimental Method: 1). Protocol: 1).	Bulk metal analysis: 1), AVS: 2), [SEM]: 3).	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	1,4	Mortality/Acute/10 days	0 %	0,0 – 0,2	0,2 Cr/ total 0,0 Cr(VI)	[2]	2), 3) Unspiked control.

Appendix 4.4 SEM effect concentration data for chromium continued.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	AVS (µmol/g dw)	Effect endpoint/ type/ Test duration	Effect size	Effect conc - Bulk (µmol/g - µg/g dw)	Effect conc. - [SEM] (µmol/g dw)	Ref.	Comments
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 1). Protocol: 1).	Bulk metal analysis: 1), AVS: 2), [SEM]: 3).	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	1,3	Mortality/Acute/10 days	0 %	0,12 - 6	0,2 Cr/ total 0,0 Cr(VI)	[2]	2), 3)
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 1). Protocol: 1).	Bulk metal analysis: 1), AVS: 2), [SEM]: 3).	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	1,3	Mortality/Acute/10 days	0 %	0,46 - 24	0,5 Cr total/ 0,0 Cr(VI)	[2]	2), 3)
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 1). Protocol: 1).	Bulk metal analysis: 1), AVS: 2), [SEM]: 3).	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	0,9	Mortality/Acute/10 days	5 %	1,29 - 67	1,3 Cr total/ 0,0 Cr(VI)	[2]	2), 3)
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 1). Protocol: 1).	Bulk metal analysis: 1), AVS: 2), [SEM]: 3).	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	0,6	Mortality/Acute/10 days	2,5 %	2,12 - 110	2,1 Cr total/ 0,0 Cr(VI)	[2]	2), 3)
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 1). Protocol: 1).	Bulk metal analysis: 1), AVS: 2), [SEM]: 3).	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	0,01	Mortality/Acute/10 days	72,5 %	3,37 - 175	3,7 Cr total/ 1,0 Cr(VI)	[2]	2), 3)
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 1). Protocol: 1).	Bulk metal analysis: 1), AVS: 2), [SEM]: 3).	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	0	Mortality/Acute/10 days	97,50 %	4,21 - 219	6,5 Cr total/ 4,1 Cr(VI)	[2]	2), 3)

Experimental Methods:

1): Flow-trough exposure performed at a salinity of 31±1 ppt with adult animals collected from natural populations. Test animals not fed during exposure.

Protocols:

1): Based on Berry *et al.* [1].

Chemical Analysis:

1): Bulk metal analysis by total decomposition in concentrated nitric, hydrofluoric, and hydrochloric acids, following U.S. Environmental Protection Agency Method 3052. (http://www.epa.gov/epaoswer/hazwaste/ test/pdfs/3052.pdf) and chromium determined in the digestates by ICP-AES.

2): AVS analyzed by purge-and-trap with sulfide-specific electrode detection.

3): [SEM] analyzed by inductively coupled plasma atomic emission (ICP-AES) spectrometry and GFAA.

Comments:

1): Natural sediment from Long Island Sound wet-sieved trough 2 mm mesh. TOC: 1,6±0,4% and AVS: 6,6±1,2 µmol/gram dw.

2): Water-only test performed in the study: $LC_{50\ 10\ days}$: 1,98 mg/l Cr(VI).

3): Natural sediment from Ninigret Pond wet-sieved trough 2 mm mesh and washed several times to remove excess organic material prior to use. TOC: 0,13±0,26% and AVS: 1,1±0,5µmol/gram dw.

Appendix 4.4 SEM effect concentration data for chromium continued.

References:

[1] Berry, W.J., D.J. Hansen, J.D. Mahony, D.L. Robson, D.M. DiToro, B.P. Shipley, B. Rogers, J.M. Corbin and W.S. Boothman. 1996. Predicting the toxicity of metal-spiked laboratory sediments using acid-volatile sulfide and interstitial water normalizations. Environ. Toxicol. Chem., 15: 2067-2079.

[2] Berry, W.J., W.S. Boothman, J.R. Serbst and P.A. Edwards. 2004. Predicting the toxicity of chromium in sediments. Environ. Toxicol. Chem., 23: 2981-2992.

Appendix 4.5 Water only exposure effect concentration data for chromium. References to the cited literature are listed at the end of this table.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	Effect endpoint/ type	Effect conc. (mg/l)	Ref.	Comments
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 1). Protocol: 1).	Metal analysis: 1).	*Neanthes arenaceodentata* (Annelida:Polychaeta) Marine infaunal. Worldwide temperate to tropical.	$LC_{50\ 96\ hours}$ /Acute	2,22	[3]	
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 1). Protocol: 1).	Metal analysis: 1).	*Neanthes arenaceodentata* (Annelida:Polychaeta) Marine infaunal. Worldwide temperate to tropical.	$LC_{50\ 7\ days}$ /Acute	1,89	[3]	
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 1). Protocol: 1).	Metal analysis: 1).	*Neanthes arenaceodentata* (Annelida:Polychaeta) Marine infaunal. Worldwide temperate to tropical.	$LC_{50\ 7\ days}$ /Acute	1,15	[3]	
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 2). Protocol: 1).	Metal analysis: 1).	*Neanthes arenaceodentata* (Annelida:Polychaeta) Marine infaunal. Worldwide temperate to tropical.	$LC_{50\ 96\ hours}$ /Acute	3,23	[3]	
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 2). Protocol: 1).	Metal analysis: 1).	*Neanthes arenaceodentata* (Annelida:Polychaeta) Marine infaunal. Worldwide temperate to tropical.	$LC_{50\ 7\ days}$ /Acute	1,48	[3]	
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 1). Protocol: 1).	Metal analysis: 1).	*Neanthes arenaceodentata* (Annelida:Polychaeta) Marine infaunal. Worldwide temperate to tropical.	$LC_{50\ 96\ hours}$ /Acute	3,45	[3]	
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 1). Protocol: 1).	Metal analysis: 1).	*Neanthes arenaceodentata* (Annelida:Polychaeta) Marine infaunal. Worldwide temperate to tropical.	$LC_{50\ 7\ days}$ /Acute	1,78	[3]	
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 1). Protocol: 1).	Metal analysis: 1).	*Neanthes arenaceodentata* (Annelida:Polychaeta) Marine infaunal. Worldwide temperate to tropical.	$LC_{50\ 7\ days}$ /Acute	1,77	[3]	1)
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 1). Protocol: 1).	Metal analysis: 1).	*Neanthes arenaceodentata* (Annelida:Polychaeta) Marine infaunal. Worldwide temperate to tropical.	$LC_{50\ 96\ hours}$ /Acute	3,63	[3]	2)
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 1). Protocol: 1).	Metal analysis: 1).	*Neanthes arenaceodentata* (Annelida:Polychaeta) Marine infaunal. Worldwide temperate to tropical.	$LC_{50\ 7\ days}$ /Acute	1,7	[3]	2)
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 1). Protocol: 1).	Metal analysis: 1).	*Neanthes arenaceodentata* (Annelida:Polychaeta) Marine infaunal. Worldwide temperate to tropical.	$LC_{50\ 7\ days}$ /Acute	1,67	[3]	3)
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 3). Protocol: 2).	Metal analysis: 1).	*Neanthes arenaceodentata* (Annelida:Polychaeta) Marine infaunal. Worldwide temperate to tropical.	$EC_{50\ Reduction\ in\ brood\ size}$ /Chronic	0,025	[3]	4)
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 4). Protocol: 3).	Metal analysis: 2).	*Allorchestes compressa* (Crustacea:Amphipoda) Marine Epi-bentic. Austral-asian to New Zealand.	$LC_{50\ 96\ hours}$ /Acute	5,56	[6]	Broodstock of test animals initially originating from Middle Spit, Australia.

Appendix 4.5 Water only exposure effect concentration data for chromium continued.

Comp.	**Experimental Methods/ Protocol**	**Chemical Analysis**	**Species/ Taxon/ Habitat/ Distribution**	**Effect endpoint/ type**	**Effect conc. (mg/l)**	**Ref.**	**Comments**
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 4). Protocol: 3).	Metal analysis: 2).	*Allorchestes compressa* (Crustacea:Amphipoda) Marine Epi-bentic. Austral-asian to New Zealand.	$LC_{50\ 96\ hours}$ /Acute	6,34	[6]	Broodstock of test animals initially originating from Somers, Australia.
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 5). Protocol: 1).	Metal analysis: 3).	*Callinectes sapidus* (Crustacea: Decapoda Brachyura) Epi-bentic. Western Atlantic boreal to tropic.	$LC_{50\ 24\ hours}$ /Acute	171	[7]	5)
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 5). Protocol: 1).	Metal analysis: 3).	*Callinectes sapidus* (Crustacea: Decapoda Brachyura) Epi-bentic. Western Atlantic boreal to tropic.	$LC_{50\ 48\ hours}$ /Acute	130	[7]	5)
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 5). Protocol: 1).	Metal analysis: 3).	*Callinectes sapidus* (Crustacea: Decapoda Brachyura) Epi-bentic. Western Atlantic boreal to tropic.	$LC_{50\ 72\ hours}$ /Acute	114	[7]	5)
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 5). Protocol: 1).	Metal analysis: 3).	*Callinectes sapidus* (Crustacea: Decapoda Brachyura) Epi-bentic. Western Atlantic boreal to tropic.	$LC_{50\ 96\ hours}$ /Acute	98	[7]	5)
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 6). Protocol: 1).	Metal analysis: 3).	*Rangia cuneata* (Mollusca:Bivalvia) Marine (estuarine) infaunal. Atlantic east coast boreal to tropic.	$LC_{50\ 48\ hours}$ /Acute	86	[8]	6)
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 6). Protocol: 1).	Metal analysis: 3).	*Rangia cuneata* (Mollusca:Bivalvia) Marine (estuarine) infaunal. Atlantic east coast boreal to tropic.	$LC_{50\ 72\ hours}$ /Acute	73	[8]	6)
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 6). Protocol: 1).	Metal analysis: 3).	*Rangia cuneata* (Mollusca:Bivalvia) Marine (estuarine) infaunal. Atlantic east coast boreal to tropic.	$LC_{50\ 96\ hours}$ /Acute	35	[8]	6)
Cr(VI) as CrO_3	Experimental Method: 7). Protocol: 1).	Metal analysis: 3).	*Neanthes arenaceodentata* (Annelida:Polychaeta) Marine infaunal. Worldwide temperate to tropical.	$LC_{50\ 28\ days}$ /Chronic	0,7	[9]	
Cr(VI) as CrO_3	Experimental Method: 7). Protocol: 1).	Metal analysis: 3).	*Neanthes arenaceodentata* (Annelida:Polychaeta) Marine infaunal. Worldwide temperate to tropical.	$LC_{50\ 28\ days}$ /Chronic	0,55	[9]	
Cr(VI) as CrO_3	Experimental Method: 7). Protocol: 1).	Metal analysis: 3).	*Neanthes arenaceodentata* (Annelida:Polychaeta) Marine infaunal. Worldwide temperate to tropical.	$LC_{50\ 96\ hours}$ /Acute	5	[9]	
Cr(VI) as CrO_3	Experimental Method: 7). Protocol: 1).	Metal analysis: 3).	*Neanthes arenaceodentata* (Annelida:Polychaeta) Marine infaunal. Worldwide temperate to tropical.	$LC_{50\ 28\ days}$ /Chronic	0,28	[9]	

Appendix 4.5 Water only exposure effect concentration data for chromium continued.

Comp.	**Experimental Methods/ Protocol**	**Chemical Analysis**	**Species/ Taxon/ Habitat/ Distribution**	**Effect endpoint/ type**	**Effect conc. (mg/l)**	**Ref.**	**Comments**
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 8). Protocol: 1).	Metal analysis: 3).	*Capitella capitata* (Annelida:Polychaeta) Marine infaunal. Worldwide boreal to temperate.	$LC_{50\ \text{5 months}}$ /Chronic	0,26	[10]	LC_{50}-value calculated by non-liear regression based on the number of survivors vs. exposure concentrations in Table 1, p. 204 in the paper.
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 9). Protocol: 1).	Metal analysis: 4).	*Tisbe battagliai* (Crustacea:Copepoda) Marine meiobenthic. Atlantic east and west coast boreal to temperate.	$LC_{50\ \text{96 hours}}$ /Acute	5,9	[11]	
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 9). Protocol: 1).	Metal analysis: 4).	*Tisbe battagliai* (Crustacea:Copepoda) Marine meiobenthic. Atlantic east and west coast boreal to temperate.	NOEC $_{\text{8 days Reproduction}}$ /Chronic?	0,32	[11]	
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 9). Protocol: 1).	Metal analysis: 4).	*Tisbe battagliai* (Crustacea:Copepoda) Marine meiobenthic. Atlantic east and west coast boreal to temperate.	LOEC $_{\text{8 days Reproduction}}$ /Chronic?	0,56	[11]	
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 9). Protocol: 1).	Metal analysis: 4).	*Tisbe battagliai* (Crustacea:Copepoda) Marine meiobenthic. Atlantic east and west coast boreal to temperate.	SChV $_{\text{8 days Reproduction}}$ /Chronic?	0,42	[11]	7)
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 10). Protocol: 1).	Metal analysis: 4).	*Tisbe battagliai* (Crustacea:Copepoda) Marine meiobenthic. Atlantic east and west coast boreal to temperate.	$LC_{50\ \text{96 hours}}$ /Acute	1,6	[11]	
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 10). Protocol: 1).	Metal analysis: 4).	*Tisbe battagliai* (Crustacea:Copepoda) Marine meiobenthic. Atlantic east and west coast boreal to temperate.	NOEC $_{\text{8 days Survival}}$ /Chronic	0,32	[11]	
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 10). Protocol: 1).	Metal analysis: 4).	*Tisbe battagliai* (Crustacea:Copepoda) Marine meiobenthic. Atlantic east and west coast boreal to temperate.	LOEC $_{\text{8 days Survival}}$ /Chronic	0,56	[11]	
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 10). Protocol: 1).	Metal analysis: 4).	*Tisbe battagliai* (Crustacea:Copepoda) Marine meiobenthic. Atlantic east and west coast boreal to temperate.	SChV $_{\text{8 days Survival}}$ /Chronic	0,42	[11]	7)
Cr(VI) as $K_2Cr_2O_7$	Experimental Method: 11). Protocol: 4).	Metal analysis: 5).	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. Atlantic west coast boreal to temperate.	$LC_{50\ \text{10 days}}$ /Acute	1,98	[2]	
Cr(VI) as K_2CrO_4	Experimental Method: 12). Protocol: 1).	Metal analysis: 6).	*Nereis virens* (Annelida:Polychaeta) Marine infaunal. Pacific and Atlantic boreal to temperate.	$LC_{50\ \text{24 hours}}$ /Acute	80	[15]	
Cr(VI) as K_2CrO_4	Experimental Method: 12). Protocol: 1).	Metal analysis: 6).	*Nereis virens* (Annelida:Polychaeta) Marine infaunal. Pacific and Atlantic boreal to temperate.	$LC_{50\ \text{96 hours}}$ /Acute	2	[15]	
Cr(VI) as K_2CrO_4	Experimental Method: 12). Protocol: 1).	Metal analysis: 6).	*Nereis virens* (Annelida:Polychaeta) Marine infaunal. Pacific and Atlantic boreal to temperate.	$LC_{50\ \text{168 hours}}$ /Acute	0,7	[15]	

Appendix 4.5 Water only exposure effect concentration data for chromium continued.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	Effect endpoint/ type	Effect conc. (mg/l)	Ref.	Comments
Cr(VI) as K_2CrO_4	Experimental Method: 13). Protocol: 1).	Metal analysis: 6).	*Pagurus longicarpus* (Crustacea:Decapoda Anomura) Marine Epifaunal. Western Atlantic Ocean boreal to temperate.	$LC_{50\ 24\ hours}$ /Acute	31	[15]	
Cr(VI) as K_2CrO_4	Experimental Method: 13). Protocol: 1).	Metal analysis: 6).	*Pagurus longicarpus* (Crustacea:Decapoda Anomura) Marine Epifaunal. Western Atlantic Ocean boreal to temperate.	$LC_{50\ 96\ hours}$ /Acute	10	[15]	
Cr(VI) as K_2CrO_4	Experimental Method: 13). Protocol: 1).	Metal analysis: 6).	*Pagurus longicarpus* (Crustacea:Decapoda Anomura) Marine Epifaunal. Western Atlantic Ocean boreal to temperate.	$LC_{50\ 168\ hours}$ /Acute	2,7	[15]	
Cr(VI) as K_2CrO_4	Experimental Method: 14). Protocol: 1).	Metal analysis: 6).	*Mya arenaria* (Mollusca:Bivalvia) Marine Infaunal. Western and Eastern Atlantic Ocean boreal to temperate.	$LC_{50\ 24\ hours}$ /Acute	225	[15]	
Cr(VI) as K_2CrO_4	Experimental Method: 14). Protocol: 1).	Metal analysis: 6).	*Mya arenaria* (Mollusca:Bivalvia) Marine Infaunal. Western and Eastern Atlantic Ocean boreal to temperate.	$LC_{50\ 96\ hours}$ /Acute	57	[15]	
Cr(VI) as K_2CrO_4	Experimental Method: 14). Protocol: 1).	Metal analysis: 6).	*Mya arenaria* (Mollusca:Bivalvia) Marine Infaunal. Western and Eastern Atlantic Ocean boreal to temperate.	$LC_{50\ 168\ hours}$ /Acute	8	[15]	
Cr(VI) as K_2CrO_4	Experimental Method: 15). Protocol: 1).	Metal analysis: 6).	*Asterias forbesi* (Echinodermata:Asteroidea) Marine Epifaunal. Western Atlantic Ocean boreal to temperate.	$LC_{50\ 24\ hours}$ /Acute	540	[15]	
Cr(VI) as K_2CrO_4	Experimental Method: 15). Protocol: 1).	Metal analysis: 6).	*Asterias forbesi* (Echinodermata:Asteroidea) Marine Epifaunal. Western Atlantic Ocean boreal to temperate.	$LC_{50\ 96\ hours}$ /Acute	32	[15]	
Cr(VI) as K_2CrO_4	Experimental Method: 15). Protocol: 1).	Metal analysis: 6).	*Asterias forbesi* (Echinodermata:Asteroidea) Marine Epifaunal. Western Atlantic Ocean boreal to temperate.	$LC_{50\ 168\ hours}$ /Acute	10	[15]	
Cr(VI) as K_2CrO_4	Experimental Method: 16). Protocol: 1).	Metal analysis: 6).	*Nassarius obsoletus* (Mollusca:Gastropoda) Marine Epifaunal. East Pacific, Western Atlantic Ocean boreal to temperate.	$LC_{50\ 24\ hours}$ /Acute	390	[15]	
Cr(VI) as K_2CrO_4	Experimental Method: 16). Protocol: 1).	Metal analysis: 6).	*Nassarius obsoletus* (Mollusca:Gastropoda) Marine Epifaunal. East Pacific, Western Atlantic Ocean boreal to temperate.	$LC_{50\ 96\ hours}$ /Acute	105	[15]	

Appendix 4.5 Water only exposure effect concentration data for chromium continued.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	Effect endpoint/ type	Effect conc. (mg/l)	Ref.	Comments
Cr(VI) as K_2CrO_4	Experimental Method: 16). Protocol: 1).	Metal analysis: 6).	*Nassarius obsoletus* (Mollusca:Gastropoda) Marine Epifaunal. East Pacific, Western Atlantic Ocean boreal to temperate.	$LC_{50\ 168\ hours}$ /Acute	10	[15]	
Cr(VI) as CrO_3	Experimental Method: 17). Protocol: 1).	Metal analysis: 3).	*Ctenodrilus serratus* (Annelida:Polychaeta) Marine Infaunal. Atlantic temperate to tropic.	$LC_{50\ 96\ hours}$ /Acute	4,4	[16]	LC_{50}-value calculated by non-liear regression based on the number of survivors vs. exposure concentrations in Table 1, p. 25 in the paper.

Experimental Methods:

1): Static exposure in 500ml erlen-meyer flasks with one animal/100ml test solution. Test solutions prepared from natural seawater at a salinity of 33,5 filtered trough 0,45µm Millipore filters. Juvenile animals (10mg wet-weight, 30-40 segment stage) from laboratory culture and fed dried *Enteromorpha crinita* (algae) during exposure.

2): Static exposure in 500ml erlen-meyer flasks with one animal/100ml test solution. Test solutions prepared from natural seawater at a salinity of 33,5 filtered trough 0,45µm Millipore filters. Adult animals (20-30mg wet-weight, 80-90 segment stage) from laboratory culture and fed dried *Enteromorpha crinita* (algae) during exposure.

3): Semi-static in 3,75l (1 gal) glass jars with 3l test solution/worm or pair of worms. Test solutions prepared from natural seawater at a salinity of 33,5 filtered trough Whatman no. 1 filters. Test solution re-newed every 2 or 3 week. Animals from laboratory culture and fed dried *Enteromorpha crinita* (algae) weekly during exposure.

4): Exposure in flow-trough in tanks with 8l exposure solution with spiked natural seawater at a salinity of 33. Adult animals (1-1,5cm body length) from laboratory culture.

5): Static exposure in 10l rectangular polyethylene pans filled partially with 3l exposure solution made from "Instant Ocean" Artificial Seawater diluted to the given salinity (see comments). To avoid cannibalism the test animals were kept individually in compartments made of perforated polystyrene containers with 5 cm radius and 4,5 cm deep. The exposure solution was not renewed during exposure, but aerated. Test performed with juvenile animals (carapace width 1,2-2,2cm) from natural populations. Animals were not fed during exposure. 6): Static exposure in "pans" accommodating 6l of exposure solution and 15 test animals for each concentration. Exposure solutions made from "Instant Ocean" Artificial Seawater diluted to the given salinity (see comments). Test animals collected from natural populations.

7): Static exposure in 500ml erlen-meyer flasks with one animal/100ml test solution. Test solutions prepared from natural seawater (salinity not stated). Juvenile animals (30-40 segment stage) from laboratory culture and fed dried *Enteromorpha crinita* (algae) during exposure.

8): Semi-static in 3,75l (1 gal) glass jars with 2,5l test solution. Test solutions prepared from natural seawater (salinity not stated) and solution was not re-newed during exposure. Test animals from laboratory culture and fed dried *Enteromorpha crinita* (algae) and ground Tetramin (Tetra Werke, Germany) during exposure.

9): Semi-static exposure in polystyrene tissue culture well plates with 5 ml test solution in each well. Test solutions prepared from natural seawater at a salinity of 34,5 - 35,0, and the test solutions were renewed daily. Exposure performed with adult animals from laboratory culture and fed *Isochrysis galbana* (algae) at a concentration of 2,0x105 cells/ml at renewal of exposure solutions.

10): Semi-static exposure in polystyrene tissue culture well plates with 5 ml test solution in each well. Test solutions prepared from natural seawater at a salinity of 34,5 - 35,0, and 50% of the test solution were renewed daily. Exposure performed with juvenile animals from laboratory culture and fed *Isochrysis galbana* (algae) at a concentration of $2,0x10^5$ cells/ml at renewal of exposure solutions.

11): Semi-static exposure in 900ml glass jars that contained 800ml of seawater. Test solutions prepared from natural sand-filtered seawater at a salinity of 25±1, and 75-100% of the test solution were renewed every other day. Exposures performed with adult animals from natural populations and were not fed during exposure.

12): Static exposure in widemouth glass jars with 2l exposure solution. Test solutions prepared from natural sand- and glasswool-filtered seawater at a salinity of 20. Exposure performed with adult animals (average body length 260mm, weight 7,6gr.) from natural populations and were not fed during exposure.

13): Static exposure in widemouth glass jars with 2l exposure solution. Test solutions prepared from natural sand- and glasswool filtered seawater at a salinity of 20. Exposure performed with adult animals (average body length 19,3mm (length of gastropod housing), weight 0,5gr.) from natural populations and were not fed during exposure.

Appendix 4.5 continued.

14): Static exposure in widemouth glass jars with 2l exposure solution. Test solutions prepared from natural sand- and glasswool-filtered seawater at a salinity of 20. Exposure performed with adult animals (average body length 42mm, weight of soft parts 4,6gr.) from natural populations and were not fed during exposure.

15): Static exposure in widemouth glass jars with 2l exposure solution. Test solutions prepared from natural sand- and glasswool filtered seawater at a salinity of 20. Exposures performed with subadult animals (average body length measured from center madreporite to end of longest arm 34mm, weight 11,2gr.) from natural populations and were not fed during exposure.

16): Static exposure in widemouth glass jars with 2l exposure solution. Test solutions prepared from natural sand- and glasswool-filtered seawater at a salinity of 20. Exposure performed with adult animals (average length of shell from apex to tip of siphonal canal 21mm, weight of soft parts 0,4gr.) from natural populations and were not fed during exposure.

17): Static in a 30ml stender dish with 20ml test solution and four test animals each. Test animals obtained from laboratory culture and fed dried *Enteromorpha crinita* (algae) during exposure.

Protocols:

1): No reference to Experimental Protocol other than the published paper.

2): No reference to Experimental Protocol, however see Reish and Richards [4] for culture conditions.

3): No reference to Experimental Protocol, but method is referred to as "described in detail" in Ahsanullah and Palmer [5].

4): Exposure performed according to Berry et. al. [1].

Chemical Analysis:

1): Dissolved metal analyzed at start and end of exposure, however analytical protocol not stated.

2): Dissolved metal analyzed in samples taken twice a day, but no reference to analytical protocol.

3): Not stated.

4): Dissolved metal analysed, but no method or protocol stated. Measured concentrations reported within the range 98-109% of nominal value.

5): Samples analyzed for Cr(IV) were filtered to 0,4µm and acidified with concentrated nitric acid (10% v/v). Cr(IV) was analyzed on GF-AAS after removing Cr(III) by co-precipitation by a modified $Fe(OH)_3$-technique [14].

6): Dissolved metal analyzed by AAS at start of exposure, but values not reported otherwise than "within 5% of calculated values". No reference to analytical protocol.

Comments:

1): Test animals were offspring (F_1) of parents exposed to 0,0125 mg/L of Cr(VI) trough their life cycle (chronic).

2): Test animals were offspring (F_1) of parents exposed to 0,025 mg/L of Cr(VI) trough their life cycle (chronic).

3): Test animals were offspring (F_1) of parents exposed to 0,05 mg/L of Cr(VI) trough their life cycle (chronic).

4): Test animals were offspring (F_1) of parents exposed to 0,025 mg/L of Cr(VI) throughout their life cycle (chronic) in a previous exposure. Second exposure lasted for > 153 days.

5): Salinity 35 ppt. (Artificial seawater ("Instant Ocean") prepared at 70 ppt and diluted with aged tap water to desired salinity).

6): Salinity 22 ppt. (Artificial seawater - "Instant Ocean").

7): Hutchinson et. al. [11]: The geometric mean of the highest NOEC and the lowest LOEC values was determined, termed the sub-chronic value (SChV). The SChV is an estimate of the chronic value (termed the ChV and historically referred to as the maximum acceptable threshold concentration or 'MATC'). The ChV or SChV represents the hypothetical toxic threshold between the NOEC and LOEC for a given biological endpoint [12], [13].

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Appendix 4.6 Bulk metal effect concentration data for copper. References to the cited literature are listed at the end of this table.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/Taxon/Habitat/ Distribution	Effect endpoint/ type	Effect conc. (µg/g dw)	Ref.	Comments
$CuCl_2$	Experimental Method: 1), Protocol: 1) & 2)	Bulk metal analysis: 1), AVS: 2)	*Gammarus locusta* (Crustacea:Amphipoda) Marine bentic. East Atlantic boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	18	[4]	Natural sediment with 0,5% size-fraction < 63µm. TOC = 1%
$CuCl_2$	Experimental Method: 1), Protocol: 1) & 2)	Bulk metal analysis: 1), AVS: 2)	*Gammarus locusta* (Crustacea:Amphipoda) Marine bentic. East Atlantic boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	159	[4]	Natural sediment with 25% size-fraction < 63µm. TOC=2%
$CuCl_2$	Experimental Method: 1), Protocol: 1) & 2)	Bulk metal analysis: 1), AVS: 2)	*Gammarus locusta* (Crustacea:Amphipoda) Marine bentic. East Atlantic boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	Over 402	[4]	Natural sediment with 75% size-fraction < 63µm. TOC=4%. 402 µg/g highest exposure concentration
Cu	Experimental Method: 2), Protocol: 3)	Bulk metal analysis: 3)	*Cylindrotheca closterium* (Algae:Bacillariophyceae) Marine epi-bentic. Boreal to temperate.	$EC_{50\ 72\ hours}$ /Acute	26	[8]	Natural sediment washed with 0.1N HNO_3 and rinsed with Ultrapure H_2O (Milli-Q). More than 95% of sediment particles <63 µm
$CuSO_4x5H_2O$	Experimental Method: 3), Protocol: 4), 5) & 6)	Bulk metal analysis: 4)	*Corophium volutator* (Crustacea:Amphipoda) Marine infaunal. Atlantic Boreal.	$LC_{50\ 10\ days}$ /Acute	36,85	[12]	1)
$CuSO_4x5H_2O$	Experimental Method: 3), Protocol: 4), 5), 6) & 7)	Bulk metal analysis: 4)	*Corophium volutator* (Crustacea:Amphipoda) Marine infaunal. Atlantic Boreal.	$EC_{50\ 1hr.\ Reburial}$ /Acute	31,66	[12]	1), Effect endpoint: The ability of the test animals to rebury within 1 hour after 10 days exposure to copper-spiked sediment
$CuSO_4x5H_2O$	Experimental Method: 4), Protocol: 8)	Bulk metal analysis: 5)	*Arenicola marina* (Annelida:Polychaeta) Marine infaunal. East Atlantic boreal.	$LC_{50\ 10\ days}$ /Acute	20	[12]	2)
$CuSO_4x5H_2O$	Experimental Method: 4), Protocol: 8)	Bulk metal analysis: 5)	*Arenicola marina* (Annelida:Polychaeta) Marine infaunal. East Atlantic boreal.	$NOEC_{Mortality\ 10\ days}$ /Acute	Between 7 and 14	[12]	2), Effect concentration estimated from figure 2, p. 227 in the paper
$CuSO_4x5H_2O$	Experimental Method: 4), Protocol: 8)	Bulk metal analysis: 5)	*Arenicola marina* (Annelida:Polychaeta) Marine infaunal. East Atlantic boreal.	$NOEC_{Zero\ emergence\ 10\ days}$ /Acute	< 14	[12]	2), Effect concentration estimated from figure 3, p. 229 in the paper
$CuSO_4x5H_2O$	Experimental Method: 4), Protocol: 8)	Bulk metal analysis: 5)	*Arenicola marina* (Annelida:Polychaeta) Marine infaunal. East Atlantic boreal.	$NOEC_{Number\ of\ casts\ 10\ days}$ /Acute	< 7	[12]	2), Effect concentration estimated from figure 4, p. 231 in the paper

Appendix 4.6 Bulk metal effect concentration data for copper continued.

Comp.	**Experimental Methods/ Protocol**	**Chemical Analysis**	**Species/Taxon/Habitat/ Distribution**	**Effect endpoint/ type**	**Effect conc. (µg/g dw)**	**Ref.**	**Comments**
$CuSO_4x5H_2O$	Experimental Method: 4), Protocol: 8)	Bulk metal analysis: 5)	*Arenicola marina* (Annelida:Polychaeta) Marine infaunal. East Atlantic boreal.	$NOEC_{\text{Size of casts 10 days}}$ /Acute	Between 7 and 14	[12]	2), Effect concentration estimated from figure 5, p. 232 in the paper
$CuSO_4x5H_2O$	Experimental Method: 5), Protocol: 9)	Bulk metal analysis: 6)	*Paracorophium excavatum* (Crustacea:Amphipoda) Marine infaunal. Indo-Pacific and Australia to New Zealand.	$LC_{50\ \text{10 days}}$ /Acute	43	[17]	Natural sediment sieved at 300 µm to remove macrofauna prior to spiking
$CuCl_2$	Experimental Method: 1), Protocol: 1) & 9)	Bulk metal analysis: 1)	*Gammarus locusta* (Crustacea:Amphipoda) Marine bentic. East Atlantic boreal to temperate.	$LC_{50\ \text{10 days}}$ /Acute	6,8	[18]	3), Size-fraction < 63µm: 0,5%. Total volatile solids (TVS): 0,9% as percentage of weight lost after ignition of dry sediment
$CuCl_2$	Experimental Method: 1), Protocol: 1) & 2)	Bulk metal analysis: 1)	*Gammarus locusta* (Crustacea:Amphipoda) Marine bentic. East Atlantic boreal to temperate.	$LC_{50\ \text{10 days}}$ /Acute	56,7	[18]	3), Size-fraction < 63µm: 25%. Sediment total volatile solids (TVS): 1,9% as percentage of weight lost after ignition of dry sediment
$CuCl_2$	Experimental Method: 1), Protocol: 1) & 2)	Bulk metal analysis: 1)	*Gammarus locusta* (Crustacea:Amphipoda) Marine bentic. East Atlantic boreal to temperate.	$LC_{50\ \text{10 days}}$ /Acute	Over 160	[18]	3), Size-fraction < 63µm: 75%. Sediment total volatile solids (TVS): 7,1% as percentage of weight lost after ignition of dry sediment. 160 µg/g highest exposure concentration
$CuCl_2$	Experimental Method: 6), Protocol: 10)	Bulk metal analysis: 7)	*Corophium volutator* (Crustacea:Amphipoda) Marine infaunal. Atlantic boreal.	$LC_{50\ \text{10 days}}$ /Acute	129	[20]	Natural sediment defaunated by wet-sieving using a 500 µm sieve prior to spiking
$CuCl_2$	Experimental Method: 7), Protocol: 11)	Bulk metal analysis: 8)	*Mulinia lateralis* (Mollusca:Bivalvia) Marine infaunal. West Atlantic boreal to temperate.	$LC_{50\ \text{96 hours}}$ /Acute	44,5	[21]	4), Test animals 35 days old at start of exposure
$CuCl_2$	Experimental Method: 7), Protocol: 11)	Bulk metal analysis: 8)	*Mulinia lateralis* (Mollusca:Bivalvia) Marine infaunal. West Atlantic boreal to temperate.	$LC_{50\ \text{96 hours}}$ /Acute	53,4	[21]	4), Test animals 42 days old at start of exposure
$CuCl_2$	Experimental Method: 7), Protocol: 11)	Bulk metal analysis: 8)	*Mulinia lateralis* (Mollusca:Bivalvia) Marine infaunal. West Atlantic boreal to temperate.	$LC_{50\ \text{96 hours}}$ /Acute	23,5	[21]	4), Test animals 56 days old at start of exposure
$CuCl_2$	Experimental Method: 7), Protocol: 11)	Bulk metal analysis: 8)	*Mulinia lateralis* (Mollusca:Bivalvia) Marine infaunal. West Atlantic boreal to temperate.	$LC_{50\ \text{96 hours}}$ /Acute	19,9	[21]	4), Test animals 49 days old at start of exposure

Appendix 4.6 Bulk metal effect concentration data for copper continued.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/Taxon/Habitat/ Distribution	Effect endpoint/ type	Effect conc. (µg/g dw)	Ref.	Comments
$CuCl_2$	Experimental Method: 7), Protocol: 11)	Bulk metal analysis: 8)	*Mulinia lateralis* (Mollusca:Bivalvia) Marine infaunal. West Atlantic boreal to temperate.	$LC_{50\ 96\ hours}$ /Acute	21,3	[21]	4), Test animals 63 days old at start of exposure
$CuCl_2$	Experimental Method: 7), Protocol: 11)	Bulk metal analysis: 8)	*Mulinia lateralis* (Mollusca:Bivalvia) Marine infaunal. West Atlantic boreal to temperate.	$LC_{50\ 96\ hours}$ /Acute	29,5	[21]	4), Test animals 77 days old at start of exposure
$CuCl_2$	Experimental Method: 7), Protocol: 11)	Bulk metal analysis: 8)	*Mulinia lateralis* (Mollusca:Bivalvia) Marine infaunal. West Atlantic boreal to temperate.	$LC_{50\ 96\ hours}$ /Acute	31,2	[21]	4), Test animals 70 days old at start of exposure
$CuCl_2$	Experimental Method: 7), Protocol: 11)	Bulk metal analysis: 8)	*Mulinia lateralis* (Mollusca:Bivalvia) Marine infaunal. West Atlantic boreal to temperate.	$LC_{50\ 96\ hours}$ /Acute	57,1	[21]	4), Test animals 84 days old at start of exposure
$CuCl_2$	Experimental Method: 7), Protocol: 11)	Bulk metal analysis: 8)	*Mulinia lateralis* (Mollusca:Bivalvia) Marine infaunal. West Atlantic boreal to temperate.	$LC_{50\ 96\ hours}$ /Acute	29	[21]	4), Test animals 91 days old at start of exposure
$CuCl_2$	Experimental Method: 7), Protocol: 11)	Bulk metal analysis: 8)	*Mulinia lateralis* (Mollusca:Bivalvia) Marine infaunal. West Atlantic boreal to temperate.	$LC_{50\ 96\ hours}$ /Acute	48,9	[21]	4), Test animals 98 days old at start of exposure
$CuCl_2$	Experimental Method: 7), Protocol: 11)	Bulk metal analysis: 8)	*Mulinia lateralis* (Mollusca:Bivalvia) Marine infaunal. West Atlantic boreal to temperate.	$LC_{50\ 96\ hours}$ /Acute	38,2	[21]	4), Test animals 112 days old at start of exposure
$CuCl_2$	Experimental Method: 7), Protocol: 11)	Bulk metal analysis: 8)	*Mulinia lateralis* (Mollusca:Bivalvia) Marine infaunal. West Atlantic boreal to temperate.	$LC_{50\ 96\ hours}$ /Acute	14,6	[21]	4), Test animals 105 days old at start of exposure

Experimental Methods:

1): Static exposure performed at a salinity of 33±2 ppt with juvenile animals (2-4mm) from laboratory culture.

2): Algae grown in static culture in Artificial sea water (American Society for Testing and Materials [5]) enriched with nutrients.

3): Static exposure performed at a salinity of 32±1 ppt with adult animals (4-7mm) collected from natural populations.

4): Static exposure performed at a salinity of 32±1 ppt with adult animals (aver. wet weight 4,3gr.) collected from natural populations.

5): Static exposure performed at a salinity of 20 ppt with adult animals (3-4,5 mm) collected from natural populations.

6): Static exposure performed at a salinity of 35 ppt in Tropic Marin Artificial Seawater with adult animals (approx. 5mm) from natural populations.

7): Semistatic exposure with daily renewal of overlying seawater added algae as feed performed at a salinity of 30±2 ppt with juvenile animals from laboratory culture.

Appendix 4.6 Bulk metal effect concentration data for copper continued.

Protocols:

1): Based on American Society for Testing and Materials [1].
2): Based on SETAC [2].
3): Based on OECD [6].
4): Based on American Society for Testing and Materials [9].
5): Based on US Environmental Protection Agency and US Army Corps of Engineers [10].
6): Based on Swartz *et al.* [11].
7): Based on Swartz *et al.* [13].
8): Based on Thain *et al.* [14].
9): Based on Environment Canada [15].
10): Based on American Society for Testing and Materials [19].
11): No reference to Experimental Protocol other than the published paper.

Chemical Analysis:

1): Acid digestion with Aqua Regia and HF. Analysis by AAS. Certified reference material BCSS-1 was used.
2): Evaporation of sulfides as H_2S with 3M HCl, collected in 1M NaOH and analysed by differential pulse cathodic stripping voltammetry (DPCSV) acc. to Henneke *et al.* [3].
3): Bulk metal analysis by total decomposition method as described by Loring and Rantala [7]. Analysis performed by flame AAS.
4): Bulk metal analysis on sediment fraction <63 µm. Sediment digested with conc. HNO_3 and analysed by AAS.
5): Bulk metal analysis on sediment fraction <500 µm. Sediment digested with conc. HNO_3 and analysed by AAS.
6): Bulk metal analysis according to USEPA method 200 [16] with analysis on stable temp Graphite Furnace AAS.
7): Bulk metal analysis: Acid digestion with Analar Grade Nitric Acid (HNO_3) with analysis on Flame-AAS.
8): Bulk metal analysis: Analysis performed by ICP on sediment samples digested in 2N HNO_3. Analysis performed on 3 subsamples of the spiked sediment stock.

Comments:

1): Natural sediment sieved at 500 µm to remove macrofauna and 300 µm prior to spiking to remove particles in the size 300-500 µm. TOC=2,1±0,38%.
2): Natural sediment sieved at 500 µm to remove macrofauna and larger particles prior to spiking. TOC=1,58±0,29%.
3): Natural sediment sieved at 1500 µm to remove macrofauna.
4): Natural sediment washed with deionised water and muffled at 450°C for 6 hours. Major particle size in the range 90-355 µm.

References:

[1] ASTM. 1992. Standard guide for conducting 10-day static sediment toxicity tests with marine and estuarine amphipods. In: Annual Book of ASTM Standards, Water and Environmental Technology, Vol. 11.04, E1367-90. American Society for Testing and Materials (ASTM), Philadelphia.

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[5] ASTM. 1975. Standard Specification for Substitute Ocean Water. Designation D 1141-75.

[6] OECD. 1998. OECD Guideline for Testing of Chemicals: Alga, Growth Inhibition Test, OECD Publications, Organisation for the Economic Cooperation and Development, Paris.

[7] Loring, D.H., and R.T.T. Rantala. 1992. Manual for the geochemical analyses of marine sediments and suspended particulate matter. Earth Sci. Rev., 32: 235-283.

[8] Moreno-Garrido, I., M. Hampel, L.M. Lubián and J. Blasco. 2003. Sediment toxicity tests using benthic marine microalgae *Cylindrotheca closterium* (Ehremberg) Lewin and Reimann (Bacillariophyceae). Ecotox. Environ. Safe., 54: 290-295.

[9] ASTM. 1990. Standard Guide for Conducting 10-day Static Sediment Toxicity Tests with Marine and Estuarine Amphipods, American Society for Testing and Materials, Philadelphia, PA, pp. 1-24.

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Appendix 4.6 Bulk metal effect concentration data for copper continued.

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[14] Thain, J., P. Matthiessen, S. Bifield and W. McMinn, 1994. Assessing sediment quality by bioassay in UK coastal water and estuaries. Proceedings of the Scientific Symposium on the North Sea Quality Status Report, pp. 1-10.

[15] Environment Canada 1992. Biological test method: Acute test for sediment toxicity using marine or estuarine amphipods, Environment Canada Report EPS 1/RM/26. Environment Canada, Hull, Quebec. 106pp.

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Appendix 4.7 SEM effect concentration data for copper. References to the cited literature are listed at the end of this table.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	AVS (µmol/g dw)	Effect endpoint/ type/ Test duration	Effect size (%)	Effect conc. [SEM] (µmol/g dw)	[SEM]/ AVS-ratio	Ref.	Comments
Unspiked control	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	13,3	Mortality/Acute/10 days	12,5	0,27	0,02	[23]	1), 2), Unspiked control.
Cu-salt (quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	12,2	Mortality/Acute/10 days	7,5	1,00	0,10	[23]	1), 2).
Cu-salt (quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	4,44	Mortality/Acute/10 days	17,5	1,57	0,35	[23]	1), 2).
Cu-salt (quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	1,21	Mortality/Acute/10 days	100,0	11,6	9,6	[23]	1), 2).
Cu-salt (quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	1,94	Mortality/Acute/10 days	100,0	47,0	24,3	[23]	1), 2).
Cu-salt (quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	1,67	Mortality/Acute/10 days	100,0	176,0	105,0	[23]	1), 2).
Cu-salt (quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	1,84	Mortality/Acute/10 days	100,0	306,0	166,0	[23]	1), 2).
Unspiked control	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	1,22	Mortality/Acute/10 days	22,5	0,00	0,00	[23]	2), 3), Unspiked control.
Cu-salt (quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	1,42	Mortality/Acute/10 days	5,0	0,05	0,04	[23]	2), 3).
Cu-salt (quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	1,08	Mortality/Acute/10 days	15,0	0,09	0,08	[23]	2), 3).
Cu-salt (quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	0,635	Mortality/Acute/10 days	30,0	0,43	0,68	[23]	2), 3).
Cu-salt (quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	0,323	Mortality/Acute/10 days	100,0	2,08	6,46	[23]	2), 3).
Cu-salt (quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	0,345	Mortality/Acute/10 days	100,0	5,40	15,67	[23]	2), 3).

Appendix 4.7 SEM effect concentration data for copper continued.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	AVS (µmol/g dw)	Effect endpoint/ type/ Test duration	Effect size (%)	Effect conc. [SEM] (µmol/g dw)	[SEM]/ AVS-ratio	Ref.	Comments
Cu-salt (quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1). [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	0,63	Mortality/Acute/10 days	100,0	10,40	16,58	[23]	2), 3).

Experimental Methods:

1): Flow-trough exposure performed at a salinity of 28-34 ppt with adult animals from natural populations.

Protocols:

1): No reference to Experimental Protocol other than the published paper.

Chemical Analysis:

1): AVS analyzed by cold-acid purge-and-trap acc. to Di Toro et al. [22].

2): [SEM] analyzed by Graphite Furnace -AAS.

Comments:

1): Natural sediment from Long Island Sound wet-sieved trough 2 mm mesh. Total cationic [SEM] in unspiked sediment averaging 3,2 µmol/g and TOC: 0,88%.

2): Water-only exposure: $LC_{50\ 10\ days}$: 0,0205 mg/l.

3): Natural sediment from Ninigret Pond wet-sieved trough 2 mm mesh and washed several times to remove excess organic material prior to use. Total cationic [SEM] in unspiked sediment averaging 0,081 µmol/g and TOC: 0,15%.

References:

[22] Di Toro, D.M., J.D. Mahony, D.J. Hansen, K.J. Scott, M.B. Hicks, S.M. Mays and M.S. Redmond. 1990. Toxicity of cadmium in sediments: The role of acid volatile sulfide. Environ. Toxicol. Chem., 9: 1489-1504.

[23] Berry, W.J., J.D. Hansen, J.D. Mahony, D.L. Robson, D.M. Di Toro, B.P. Shipley, B. Rogers, J.M. Corbin and W.S. Bootman. 1996. Predicting the toxicity of metal-spiked laboratory sediments using acid-volatile sulphide and interstitial water normalizations. Environ. Toxicol. Chem., 15: 2067-2079.

Appendix 4.8 Bulk metal effect concentration data for mercury. References to the cited literature are listed at the end of this table.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	Effect endpoint/ type	Effect conc. (µg/g dw)	Ref.	Comments
$HgCl_2$	Experimental Method: 1), Protocol: 1)	Bulk metal analysis: 3)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	15,2	[2]	1)

Experimental Methods:

1): Static exposure performed at a salinity of 25 ppt with adult animals (0,5-1mm) collected from natural populations.

Protocols:

1): Based on Swartz *et al.* [1].

Chemical Analysis:

1): Bulk metal analysis on sediment digested with acid and analyzed by AAS.

Comments:

1): Natural sediment sieved at 0,5 mm to remove macrofauna. Total volatile solids (TVS): 1,4% on average as percentage of weight lost after ignition of dry sediment.

References:

[1] Swartz, R.C., G.R. Ditswoth, D.W. Schults and J.O. Lamberson. 1985. Sediment toxicity to a marine infaunal amphipod: Cadmium and its interaction with sewage sludge. Mar. Environ. Res., 18: 133-153.

[2] Swartz, R.C., P.F. Kemp, D.W. Scults and J.O. Lamberson. 1988. Effects of mixtures of sediment contaminants on the marine infaunal amphipod, *Rhepoxynius abronius*. Environ. Toxicol. Chem., 7: 1013-1020.

Appendix 4.9 Bulk metal effect concentration data for lead. References to the cited literature are listed at the end of this table.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	Effect endpoint/ type	Effect conc. (µg/g dw)	Ref.	Comments
Pb-salt (Quality not stated)	Experimental Method: 1) Protocol: 1)	Bulk metal analysis: 1)	*Cylindrotheca closterium* (Algae:Bacillariophyceae) Marine epi-bentic. Boreal to temperate.	$EC_{50\ 72\ hours}$ /Acute	29	[4]	1)
$PbCl_2$ (Quality not stated)	Experimental Method: 2) Protocol: 2), 3)	AVS: 2), Bulk metal analysis: 3)	*Amphiascus tenuiremis* (Crustacea: Copepoda) Marine Meio-bentic. Atlantic boreal to temperate.	$LC_{50\ 96\ hours}$ /Acute	2462	[9]	2)

Experimental Methods:

1): Algae grown in static culture in artificial seawater (American Society for Testing and Materials [1]) enriched with nutrients.

2): Static exposure performed at a salinity of 30±0,1 ppt Artificial Sea Water with adult animals collected from laboratory culture.

Protocols:

1): Based on OECD [2].

2): Based on Green *et al.* [5].

3): Based on American Society for Testing and Materials [6].

Chemical Analysis:

1): Bulk metal analysis by total decomposition method as described by Loring and Rantala [3].

2): AVS analysed by cold-acid purge-and-trap (Allen *et al.* [7].

3): Bulk metal analysis on dried sediment reflux-extracted with a mixture of HNO_3 and HCl. Analysed by low-resolution ICP-MS according to US-EPA method 200.8 (Long and Martin [8]) with indium as internal standard.

Comments:

1): Natural sediment washed with 0.1N HNO_3 and rinsed with Ultrapure H_2O (Milli-Q). More than 95% of sediment was silt (particles <63µm).

2): Natural sediment sieved at 63µm, washed 5x with deionised water, centrifuged at 11750 RCF for 6 min. and autoclaved for 15min. Reconstituted with 30 ppt ASW prior to spiking. Median sediment grain diameter 3.7±0,2µm, AVS = 0,1±0,03 µmol/g dw sed. and TOC = 2,77±0,01%.

References:

[1] ASTM. 1975. Standard Specification for Substitute Ocean Water. Designation D 1141-75.

[2] OECD. 1998. OECD Guideline for Testing of Chemicals: Alga, Growth Inhibition Test, OECD Publications, Organization for the Economic Cooperation and Development, Paris.

[3] Loring, D.H., and R.T.T. Rantala. 1992. Manual for the geochemical analyses of marine sediments and suspended particulate matter. Earth Sci. Rev., 32: 235-283.

[4] Moreno-Garrido, I., M. Hampel, L.M. Lubián and J. Blasco. 2003. Sediment toxicity tests using benthic marine microalgae *Cylindrotheca closterium* (Ehremberg) Lewin and Reimann (Bacillariophyceae). Ecotox. Environ. Safe., 54: 290-295.

[5] Green, A. S., G.T. Chandler and E.R. Blood. 1993. Aqueous, porewater and sediment phase cadmium: toxicity relationships for a meiobenthic copepod. Environ. Toxicol. Chem., 12: 1497-1506.

[6] ASTM. 1988. Standard guide for conducting acute toxicity tests with fishes, macroinvertebrates and amphibians. ASTM Standard No. E 1192-88. Philadelphia, PA. pp. 102-121.

[7] Allen, H. E., G. Fu, W. Boothman, D.M. Di Toro and J.D. Mahoney. 1991. Analytical method for determination of acid volatile sulphide and selected simultaneously extractable metals in sediment. Analytical method 821/12-91. USEPA Office of Water and Office of Science and Technology. Washington, DC.

[8] Long, S.E. and T.D. Martin. 1992. Determination of trace elements in water and wastes by inductively coupled plasma-mass spectroscopy. Method 200.8. *In*: C. K. Smoley (ed.): Methods for the determination of metals in environmental samples. Government Press Office. Washington, DC. pp. 20-35.

[9] Hagiopan-Schlekat, T., G.T. Chandler and T.J. Shaw. 2001. Acute toxicity of five sediment-associated metals, individually and in a mixture, to the estuarine meiobenthic harpactoid copepod *Amphiascus tenuiremis*. Mar. Environ. Res., 51: 247-264.

Appendix 4.10 SEM effect concentration data for lead. References to the cited literature are listed at the end of this table.

Comp.	**Experimental Methods/ Protocol**	**Chemical Analysis**	**Species/ Taxon/ Habitat/ Distribution**	**AVS (µmol/g dw)**	**Effect endpoint/ type/ Test duration**	**Effect size**	**Effect conc. [SEM] (µmol/g dw)**	**[SEM]/ AVS-ratio**	**Ref.**	**Comments**
Unspiked control	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	19,9	Mortality/Acute/10 days	10,0 %	0,23	0,01	[11]	1), 2), Unspiked control.
Pb-salt (Quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	18,6	Mortality/Acute/10 days	5,0 %	1,25	0,07	[11]	1), 2)
Pb-salt (Quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	12,8	Mortality/Acute/10 days	12,5 %	4,14	0,32	[11]	1), 2)
Pb-salt (Quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	16,4	Mortality/Acute/10 days	7,5 %	14,50	0,89	[11]	1), 2)
Pb-salt (Quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	14,9	Mortality/Acute/10 days	22,5 %	28,30	1,90	[11]	1), 2)
Pb-salt (Quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	15,5	Mortality/Acute/10 days	42,5 %	67,90	4,38	[11]	1), 2)
Pb-salt (Quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	14,2	Mortality/Acute/10 days	100,0 %	78,20	5,49	[11]	1), 2)
Pb-salt (Quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	1,2	Mortality/Acute/10 days	10,0 %	0,02	0,02	[11]	2), 3), Unspiked control
Pb-salt (Quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	1,92	Mortality/Acute/10 days	17,5 %	0,20	0,09	[11]	2), 3)

Appendix 4.10 SEM effect concentration data for lead continued.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	AVS (µmol/g dw)	Effect endpoint/ type/ Test duration	Effect size	Effect conc. [SEM] (µmol/g dw)	[SEM]/ AVS-ratio	Ref.	Comments
Pb-salt (Quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	2,23	Mortality/Acute/10 days	15,0 %	0,60	0,26	[11]	2), 3)
Pb-salt (Quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	3,1	Mortality/Acute/10 days	5,0 %	1,70	0,60	[11]	2), 3)
Pb-salt (Quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	5,75	Mortality/Acute/10 days	17,5 %	7,10	1,24	[11]	2), 3)
Pb-salt (Quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	4,08	Mortality/Acute/10 days	55,0 %	16,60	4,08	[11]	2), 3)
Pb-salt (Quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	3,37	Mortality/Acute/10 days	92,5 %	20,20	5,97	[11]	2), 3)

Experimental Methods:

1): Flow-trough exposure performed at a salinity of 28-34 ppt with adult animals from natural populations.

Protocols:

1): No reference to Experimental Protocol other than the published paper.

Chemical Analysis:

1): AVS analyzed by cold-acid purge-and-trap acc. to Di Toro *et al.* [10].

2): [SEM] analyzed by Graphite Furnace -AAS after extraction with 2M cold nitric acid.

Comments:

1): Natural sediment from Long Island Sound wet-sieved trough 2 mm mesh. Total cationic [SEM] in unspiked sediment averaging 3,2 µmol/g and TOC: 0,88%.

2): Water-only test performed in the study: $LC_{50\ 10\ days}$: 3,02 mg/l.

3): Natural sediment from Ninigret Pond wet-sieved trough 2 mm mesh and washed several times to remove excess organic material prior to use. Total cationic [SEM] in unspiked sediment averaging 0,081 µmol/g and TOC: 0,15%.

References:

[10] Di Toro, D.M., J.D. Mahony, D.J. Hansen, K.J. Scott, M.B. Hicks, S.M. Mays and M.S. Redmond. 1990. Toxicity of cadmium in sediments: The role of acid volatile sulfide. Environ, Toxicol. Chem., 9: 1489-1504.

[11] Berry, W.J., J.D. Hansen, J.D. Mahony, D.L. Robson, D.M. Di Toro, B.P. Shipley, B. Rogers, J.M. Corbin and W.S. Bootman. 1996. Predicting the toxicity of metal-spiked laboratory sediments using acid-volatile sulphide and interstitial water normalizations. Environ. Toxicol. Chem., 15: 2067-2079.

Appendix 4.11 Bulk metal effect concentration data for zinc. References to the cited literature are listed at the end of this table.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	Effect endpoint/ type	Effect conc. (µg/g dw)	Ref.	Comments
ZnSO$_4$x7H$_2$O	Experimental Method: 1), Protocol: 1), 2), 3)	Bulk metal analysis: 1)	*Corophium volutator* (Crustacea:Amphipoda) Marine infaunal. Atlantic boreal.	LC$_{50\ 10\ days}$ /Acute	31,9	[4]	1)
ZnSO$_4$x7H$_2$O	Experimental Method: 1), Protocol: 3), 4)	Bulk metal analysis: 1)	*Corophium volutator* (Crustacea:Amphipoda) Marine infaunal. Atlantic boreal.	EC$_{50\ 1hr.\ Reburial}$ /Acute	28,6	[4]	1), Effect endpoint: The ability of the test animals to rebury within 1 hour after 10 days exposure to zinc-spiked sediment
ZnSO$_4$x7H$_2$O	Experimental Method: 2), Protocol: 5)	Bulk metal analysis: 2)	*Arenicola marina* (Annelida:Polychaeta) Marine infaunal. East Atlantic boreal.	LC$_{50\ 10\ days}$ /Acute	50	[4]	2)
ZnSO$_4$x7H$_2$O	Experimental Method: 2), Protocol: 5)	Bulk metal analysis: 2)	*Arenicola marina* (Annelida:Polychaeta) Marine infaunal. East Atlantic boreal.	NOEC$_{Mortality\ 10\ days}$ /Acute	Between 23 and 52	[4]	2), Effect concentration estimated from figure 2, p. 227 in the paper
ZnSO$_4$x7H$_2$O	Experimental Method: 2), Protocol: 5)	Bulk metal analysis: 2)	*Arenicola marina* (Annelida:Polychaeta) Marine infaunal. East Atlantic boreal.	NOEC$_{Zero\ emergence\ 10\ days}$ /Acute	Between 23 and 52	[4]	2), Effect concentration estimated from figure 3, p. 229 in the paper
ZnSO$_4$x7H$_2$O	Experimental Method: 2), Protocol: 5)	Bulk metal analysis: 2)	*Arenicola marina* (Annelida:Polychaeta) Marine infaunal. East Atlantic boreal.	NOEC$_{Number\ of\ casts\ 10\ days}$ /Acute	< 23	[4]	2), Effect concentration estimated from figure 4, p. 231 in the paper
ZnSO$_4$x7H$_2$O	Experimental Method: 2), Protocol: 5)	Bulk metal analysis: 2)	*Arenicola marina* (Annelida:Polychaeta) Marine infaunal. East Atlantic boreal.	NOEC$_{Size\ of\ casts\ 10\ days}$ /Acute	Between 23 and 52	[4]	2), Effect concentration estimated from figure 5, p. 232 in the paper
ZnCl$_2$	Experimental Method: 3), Protocol: 6)	Bulk metal analysis: 3)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	LC$_{50\ 10\ days}$ /Acute	270	[7]	3)
ZnCl$_2$	Experimental Method: 4), Protocol: 7), 8)	AVS: 4), Bulk metal analysis: 5)	*Amphiascus tenuiremis* (Crustacea: Copepoda) Marine Meio-bentic. Atlantic boreal to temperate.	LC$_{50\ 96\ hours}$ /Acute	671,3	[12]	4)

Experimental Methods:

1): Static exposure performed at a salinity of 32±1ppt with adult animals (4-7mm) collected from natural populations.

2): Static exposure performed at a salinity of 32±1ppt with adult animals (aver. wet weight 4,3gr.) collected from natural populations.

3): Static exposure performed at a salinity of 25 ppt with adult animals collected from natural populations.

4): Static exposure performed at a salinity of 30±0,1 ppt Artificial Sea Water with adult animals collected from laboratory culture.

Protocols:

1): Based on American Society for Testing and Materials [1].

2): Based on US Environmental Protection Agency and US Army Corps of Engineers [2].

3): Based on Swartz *et al.* [3].

4): Based on Swartz *et al.* [5].

5): Based on Thain *et al.* [7].

6): Based on Swartz *et al.* [5].

7): Based on Green *et al.* [8].

8): Based on American Society for Testing and Materials [9].

Appendix 4.11 Bulk metal effect concentration data for zinc continued.

Chemical Analysis:

1): Bulk metal analysis on sediment fraction <63 µm. Sediment digested with conc. HNO_3 and analysed by AAS.
2): Bulk metal analysis on sediment fraction <500 µm. Sediment digested with conc. HNO_3 and analysed by AAS.
3): Bulk metal analysis on sediment digested with acid and analysed by AAS.
4): AVS analysed by cold-acid purge-and-trap acc. to Allen *et al.* [10].

5): Bulk metal analysis on dried sediment reflux-extracted with a mixture of HNO_3 and HCl. Analysed by low-resolution ICP-MS according to US-EPA method 200.8 (Long and Martin [11]) with indium as internal standard.

Comments:

1): Natural sediment sieved at 500 µm to remove macrofauna and 300 µm prior to spiking to remove particles in the size 300-500 µm. TOC=2,1±0,38%.
2): Natural sediment sieved at 500 µm to remove macrofauna and larger particles prior to spiking. TOC=1,58±0,29%.
3): Natural sediment sieved at 0,5 mm to remove macrofauna. Total volatile solids (TVS): 1,4% on average as percentage of weight lost after ignition of dry sediment.
4): Natural sediment sieved at 63 µm, washed 5x with deionised water, centrifuged at 11750 RCF for 6 min. and autoclaved for 15 min. Reconstituted with 30 ppt ASW prior to spiking. Median sediment grain diameter 3.7±0,2µm, 0,1±0,03 µmol/g dw sed. AVS and 2,77±0,01% TOC.

References:

[1] ASTM. 1990. Standard Guide for Conducting 10-day Static Sediment Toxicity Tests with Marine and Estuarine Amphipods, American Society for Testing and Materials, Philadelphia, PA, pp. 1-24.

[2] US Environmental Protection Agency and US Army Corps of Engineers. 1991. Evaluation of dredged material proposed for ocean disposal. Testing manual. EPA-503/8-91/001,Washington, DC.

[3] Swartz, R.C., W.A. DeBen, J.K.P. Jones, J.O. Lamberson and F.A. Cole. 1985. Phoxocephalid amphipod bioassay for marine sediment toxicity. *In*: R.D. Cardwell, R. Purdy and R.C. Bahner (eds.): Aquatic Toxicology and Hazard Assessment. American Society for Testing and Materials, Philadelphia, PA, pp. 284-307.

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[6] Thain, J., P. Matthiessen, S. Bifield and W. McMinn. 1994. Assessing sediment quality by bioassay in UK coastal water and estuaries. Proceedings of the Scientific Symposium on the North Sea Quality Status Report, pp. 1-10.

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[8] Green, A. S., G.T. Chandler and E.R. Blood. 1993. Aqueous, porewater and sediment phase cadmium: toxicity relationships for a meiobenthic copepod. Environ. Toxicol. Chem., 12: 1497- 1506.

[9] ASTM. 1988. Standard guide for conducting acute toxicity tests with fishes, macroinvertebrates and amphibians. ASTM Standard No. E 1192-88. Philadelphia, PA. pp. 102-121.

[10] Allen, H. E., G. Fu, W. Boothman, D.M. Di Toro and J.D. Mahoney. 1991. Analytical method for determination of acid volatile sulphide and selected simultaneously extractable metals in sediment. Analytical method 821/12-91. USEPA Office of Water and Office of Science and Technology. Washington, DC.

[11] Long, S.E. and T.D. Martin. 1992. Determination of trace elements in water and wastes by inductively coupled plasma-mass spectroscopy. Method 200.8. *In*: C. K. Smoley (ed.): Methods for the determination of metals in environmental samples. Government Press Office. Washington, DC. pp. 20-35.

[12] Hagiopan-Schlekat, T., G.T. Chandler and T.J. Shaw. 2001. Acute toxicity of five sediment-associated metals, individually and in a mixture, to the estuarine meiobenthic harpactoid copepod *Amphiascus tenuiremis*. Mar. Environ. Res., 51: 247-264.

Appendix 4.12 SEM effect concentration data for zinc. References to the cited literature are listed at the end of this table.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	AVS (µmol/g dw)	Effect endpoint/ type/ Test duration	Effect size	Effect conc. [SEM] (µmol/g dw)	[SEM]/ AVS-ratio	Ref.	Comments
Unspiked control	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	11,2	Mortality/Acute/10 days	15,0 %	1,20	0,10	[14]	1), 2), Unspiked control
Zn-salt (quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	11,7	Mortality/Acute/10 days	7,5 %	2,80	0,24	[14]	1), 2)
Zn-salt (quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	13,4	Mortality/Acute/10 days	17,5 %	5,50	0,41	[14]	1), 2)
Zn-salt (quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	15,1	Mortality/Acute/10 days	15,0 %	20,30	1,34	[14]	1), 2)
Zn-salt (quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	18,2	Mortality/Acute/10 days	77,5 %	74,30	4,09	[14]	1), 2)
Zn-salt (quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	15	Mortality/Acute/10 days	100,0 %	155,00	10,30	[14]	1), 2)
Zn-salt (quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	14	Mortality/Acute/10 days	100,0 %	140,00	9,96	[14]	1), 2)
Unspiked control	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	2,25	Mortality/Acute/10 days	5,0 %	0,01	0,00	[14]	2), 3), Unspiked control
Zn-salt (quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	2,48	Mortality/Acute/10 days	12,5 %	0,30	0,11	[14]	2), 3)
Zn-salt (quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	3	Mortality/Acute/10 days	12,5 %	0,70	0,23	[14]	2), 3)
Zn-salt (quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	2,73	Mortality/Acute/10 days	5,0 %	1,50	0,54	[14]	2), 3)
Zn-salt (quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	1,82	Mortality/Acute/10 days	35,0 %	2,00	1,09	[14]	2), 3)

Appendix 4.12 SEM effect concentration data for zinc continued.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	AVS (µmol/g dw)	Effect endpoint/ type/ Test duration	Effect size	Effect conc. [SEM] (µmol/g dw)	[SEM]/ AVS-ratio	Ref.	Comments
Zn-salt (quality not stated)	Experimental Method: 1), Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	1,31	Mortality/Acute/10 days	95,0 %	4,13	3,15	[14]	2), 3)
Zn-salt (quality not stated)	Experimental Method: 1) Protocol: 1)	AVS: 1), [SEM]: 2)	*Ampelisca abdita* (Crustacea: Amphipoda) Marine infaunal. West Atlantic boreal to temperate.	1,94	Mortality/Acute/10 days	100,0 %	8,82	4,54	[14]	2), 3)

Experimental Methods:

1): Flow-trough exposure performed at a salinity of 28-34 ppt with adult animals from natural populations.

Protocols:

1): No reference to Experimental Protocol other than the published paper.

Chemical Analysis:

1): AVS analyzed by cold-acid purge-and-trap acc. to Di Toro *et al.* [13].

2): [SEM] analyzed by Graphite Furnace -AAS after extraction with 2M cold nitric acid.

Comments:

1): Natural sediment from Long Island Sound wet-sieved trough 2 mm mesh. Total cationic [SEM] in unspiked sediment averaging 3,2 µmol/g and TOC: 0,88%.

2): Water-only test performed in the study: $LC_{50\ 10\ days}$: 0,343 mg/l.

3): Natural sediment from Ninigret Pond wet-sieved trough 2 mm mesh and washed several times to remove excess organic material prior to use. Total cationic [SEM] in unspiked sediment averaging 0,081 µmol/g and TOC: 0,15%.

References:

[13] Di Toro, D.M., J.D. Mahony, D.J. Hansen, K.J. Scott, M.B. Hicks, S.M. Mays and M.S. Redmond. 1990. Toxicity of cadmium in sediments: The role of acid volatile sulfide. Environ, Toxicol. Chem., 9: 1489-1504.

[14] Berry, W.J., J.D. Hansen, J.D. Mahony, D.L. Robson, D.M. Di Toro, B.P. Shipley, B. Rogers, J.M. Corbin and W.S. Bootman. 1996. Predicting the toxicity of metal-spiked laboratory sediments using acid-volatile sulphide and interstitial water normalizations. Environ. Toxicol. Chem., 15: 2067-2079.

Appendix 4.13 Effect concentration data for acenaphthene. References to the cited literature are listed at the end of this table.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	Effect endpoint/ type	Effect conc. (µg/g dw)	Effect conc. oc (µg/g dw)	Ref.	Comments
Acenaphthene	Experimental Method: 1), Protocol: 1)	PAH: 1) TOC: 2)	*Eohaustorius estuarius* (Crustacea:Amphipoda) Marine free-living infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	43,3	4180	[2]	1). TOC=1,23%
Acenaphthene	Experimental Method: 1), Protocol: 1)	PAH: 1) TOC: 2)	*Eohaustorius estuarius* (Crustacea:Amphipoda) Marine free-living infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	47,8	1920	[2]	2). TOC=2,49%
Acenaphthene	Experimental Method: 1), Protocol: 1)	PAH: 1) TOC: 2)	*Eohaustorius estuarius* (Crustacea:Amphipoda) Marine free-living infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	68,4	1630	[2]	3). TOC=4.21%
Acenaphthene	Experimental Method: 2), Protocol: 1)	PAH: 1) TOC: 2)	*Leptocheirus plumulosus* (Crustacea:Amphipoda) Marine tube-dwelling infaunal. West Atlantic boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	209,3	8450	[2]	2). TOC=2,52%
Acenaphthene	Experimental Method: 2), Protocol: 1)	PAH: 1) TOC: 2)	*Leptocheirus plumulosus* (Crustacea:Amphipoda) Marine tube-dwelling infaunal. West Atlantic boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	373,0	10890	[2]	3). TOC=3,66%
Acenaphthene and deuterated acenaphthene	Experimental Method: 3), Protocol: 1), 2)	PAH: 3) TOC: 4)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute		2110	[4]	4). TOC=3%
Acenaphthene and deuterated acenaphthene	Experimental Method: 3), Protocol: 1), 2)	PAH: 3) TOC: 4)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute		2310	[4]	4). TOC=3%

Experimental Methods:

1): Static exposure performed at a salinity of 28 ppt with juvenile animals (3-5mm) collected from natural populations.

2): Static exposure performed at a salinity of 28 ppt with juvenile animals (3-5mm) collected from laboratory culture originating from Queens Creek, York River, VA, USA.

3): Static exposure performed at a salinity of 28 ppt with juvenile animals (3-4mm) collected from natural populations.

Protocols:

1): Based on American Society for Testing and Materials [1].

2): Based on U.S. Environmental Protection Agency [3].

Chemical Analysis:

1): Analysis of acenaphtene was performed on GC/MS (HP 5970B) with selective ion detector in SIMS-mode.

2): TOC was analysed by combustion after removal of carbonates by acidification to pH < 2 with HCl.

3): Analysis of acenaphtene was performed on GC/MS (HP 5870).

4): TOC was analysed on a Perkin Elmer Model 2400 CHN analysator after removal of carbonates by acidification.

Appendix 4.13 Effect concentration data for acenaphthene continued.

Comments:

1): Sediment from an intertidal mud flat on the south shore of Yaquina Bay near South Beach, Oregon, wet-sieved trough 0,5mm screen and settled for 2-3 days at 4°C prior to use.

2): Sediment from an intertidal mud flat on McKinney Slough on the south shore of Alsea Bay, Oregon, wet-sieved trough 0,5mm screen and settled for 2-3 days at 4°C prior to use.

3): Sediment from an intertidal mud flat on Eckman Slough on the south shore of Alsea Bay, Oregon, wet-sieved trough 0,5mm screen and settled for 2-3 days at 4°C prior to use.

4): Sediment from McKinney Slough, Oregon wet-sieved trough 0,5mm screen for removal of macrobiota and debris and settled for 24 hours at 4°C prior to spiking. Sediment poorly sorted silt with 3% organic carbon and 40,6% solids.

References:

[1] ASTM. 1990. Standard guide for conducting solid-phase 10-day static sediment toxicity tests with marine and estuarine amphipods. E1367-90. In: Annual Book of ASTM Standards, Water and Environmental Technology. Vol. 11.04. American Society for Testing and Materials, Philadelphia, PA.

[2] Swartz, R.C., T.H. DeWitt, D.W. Schults, G.R. Ditsworth, J.O. Lamberson, J.E. Sewall and R.J. Ozretich. XXXX. Toxicity of sediment-associated acenaphtene and phenanthrene to marine benthic amphipods. Data Report. Pacific Ecosystems Branch, Environmental Research Laboratory, Narragansett, Office of Research and Development, U.S. EPA, Newport, Oregon. (Marked "Incomplete Draft"). Data also cited in: US-EPA. 1993. Sediment Quality Criteria for the Protection of Benthic Organisms: Acenapthene. United States Environmental Protection Agency, Office of Science and Technology, EPA-822-R-93-013 and US-EPA. 1992. Development of a Chronic Sediment Toxicity Test for Marine Benthic Amphipods. United States Environmental Protection Agency, EPA’s Environmental Research Laboratory, Narragansett. EPA 903-R-92-002.

[3] U.S. Environmental Protection Agency. 1994. Methods for assessing the toxicity of sediment-associated contaminants with estuarine and marine amphipods. EPA/600/R-94/025. Washington DC.

[4] Swartz, R.C., S.P. Ferraro, J.O. Lamberson, F.A. Cole, R.J. Ozretich, B.L. Boese, D.W. Schults, M. Behrenfield and G.T. Ankley. 1997. Photoactivation and toxicity of mixtures of polycyclic aromatic hydrocarbon compounds in marine sediment. Environ. Toxicol. Chem., 16: 2151-2157.

Appendix 4.14 Effect concentration data for diesel fuel. References to the cited literature are listed at the end of this table.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	Effect endpoint/ type	Effect conc. (µg/g dw)	Effect conc. oc (µg/g dw)	Ref.	Comments
Diesel fuel. Quality not stated.	Experimental Method: 1), Protocol: 1)	Diesel Fuel: 1)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	$LC_{50\ 96\ hours}$ /Acute	187		[2]	1)
Diesel fuel. Quality not stated.	Experimental Method: 2), Protocol: 1)	Diesel Fuel: 1) Radioactivity: 2)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	$IC_{50\ 30\ hours}$ /Acute	48		[2]	1). Effect endpoint: Grazing.
Diesel fuel. Quality not stated.	Experimental Method: 3), Protocol: 1)	Diesel Fuel: 3)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	$EC_{50\ 14\ days}$ /Chronic	64		[2]	1). Effect endpoint: Realised offspring produced over a 14 day period.

Experimental Methods:

1): Static exposure performed with artificial seawater at a salinity of 25 ppt with adult females collected from laboratory culture.

2): Static exposure performed with artificial seawater at a salinity of 25 ppt with adult females collected from laboratory culture. Animals fed radioactive labelled algae.

3): Static exposure performed with artificial seawater at a salinity of 25 ppt with one copulating couple in each exposure chamber. Animals collected from laboratory culture.

Protocols:

1): No reference to external protocol other than the published paper [1].

Chemical Analysis:

1): Analysis of the diesel fuel was performed on GC/MS according to Carman et al. [2].

2): Radioactivity was analysed by Liquid Scintillation Counting (LSC).

3): Analysis of the diesel fuel was performed by reverse-phase HPLC acc. to Lotufo et al. [3].

Comments:

1): Sediment collected from a mud-flat in a salt-mash in Lousiana, USA. Natural background of PAH 0,26 µg/gr. dry wt acc. to Carman et al. [2]. Test sediment wet-sieved at 125 µm sedimented overnight at 4°C before the supernatant was removed by aspiration.

References:

[1] Lotufo, G.R. 1997. Toxicity of sediment-associated PAHs to an estuarine copepod: Effects on survival, feeding, reproduction and behaviour. Mar. Environ. Res., 44: 149-166.

[2] Carman, K. R., Means, J. C. and Pomarico, S. M. 1996 Response of sedimentary bacteria in a Louisiana salt marsh to contamination by diesel fuel. Aquat. Microb. Ecol., 10: 231-241.

[3] Lotufo, G. R. and Fleeger, J. W. 1996 Toxicity of sediment-associated pyrene and phenanthrene to *Limnodrilius hoffmeisteri* (Oligochaeta.: Tubificidae). Environ. Toxicol. Chem., 15. 1508-1516.

Appendix 4.15 Effect concentration data for fluoranthene. References to the cited literature are listed at the end of this table.

Comp.	**Experimental Methods/ Protocol**	**Chemical Analysis**	**Species/ Taxon/ Habitat/ Distribution**	**Effect endpoint/ type**	**Effect conc. (µg/g dw)**	**Effect conc. oc (µg/g dw)**	**Ref.**	**Comments**
Fluoranthene	Experimental Method: 1), Protocol: 1), 2)	PAH: 1) TOC: 2)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	3,4		[4]	1). TOC = 0,18%
Fluoranthene	Experimental Method: 1), Protocol: 1), 2)	PAH: 1) TOC: 2)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	6,5		[4]	2). TOC = 0,31%
Fluoranthene	Experimental Method: 1), Protocol: 1), 2)	PAH: 1) TOC: 2)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	10,7		[4]	3). TOC = 0,48%
Fluoranthene	Experimental Method: 1), Protocol: 1), 2)	PAH: 1) TOC: 2)	*Corophium spinicorne* (Crustacea:Amphipoda) Marine infaunal. Atlantic boreal.	$LC_{50\ 10\ days}$ /Acute	5,1		[4]	1). TOC = 0,18%
Fluoranthene	Experimental Method: 1), Protocol: 1), 2)	PAH: 1) TOC: 2)	*Corophium spinicorne* (Crustacea:Amphipoda) Marine infaunal. Atlantic boreal.	$LC_{50\ 10\ days}$ /Acute		3600	[4]	4). TOC = 0,18%
Fluoranthene	Experimental Method: 1), Protocol: 1), 2)	PAH: 1) TOC: 2)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute		2100	[4]	4). TOC = 0,18%
Fluoranthene	Experimental Method: 2), Protocol: 2)	PAH: 3) TOC: 4)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	3,1		[5]	5). TOC = 0,22 and 0,26% (Data pooled from two experiments for calculation of LC_{50})
Fluoranthene	Experimental Method: 3), Protocol: 3)	PAH: 5) Radioactivity: 6) TOC: 7)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	$IC_{50\ 30\ hours}$ /Acute	94		[7]	6). TOC = 1,5%. Effect endpoint: Grazing.
Fluoranthene	Experimental Method: 4), Protocol: 3)	PAH: 5) TOC: 7)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	$EC_{50\ 14}$ days /Chronic	38		[7]	6). TOC = 1,5%. Effect endpoint: Realised offspring produced over a 14 day period.

Appendix 4.15 Effect concentration data for fluoranthene continued.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	Effect endpoint/ type	Effect conc. (µg/g dw)	Effect conc. oc (µg/g dw)	Ref.	Comments
Fluoranthene	Experimental Method: 5), Protocol: 3), 4)	PAH: 8) TOC: 9)	*Hyalella azteca* (Crustacea:Amphipoda) Freshwater infaunal. North America boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	2,3	500	[10]	7). TOC = 0,46%.
Fluoranthene	Experimental Method: 6), Protocol: 3), 4)	PAH: 8) TOC: 9)	*Chironomus tetans* (Insecta:Diptera) Freshwater Epi-faunal. North America and Europe boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	7,3	1587	[10]	7). TOC = 0,46%.
Fluoranthene	Experimental Method: 5), Protocol: 3), 4)	PAH: 8) TOC: 9)	*Hyalella azteca* (Crustacea:Amphipoda) Freshwater infaunal. North America boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	7,4	1480	[10]	8). TOC = 0,50%.
Fluoranthene	Experimental Method: 6), Protocol: 3), 4)	PAH: 8) TOC: 9)	*Chironomus tetans* (Insecta:Diptera) Freshwater Epi-faunal. North America and Europe boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	8,7	1740	[10]	8). TOC = 0,50%.
Fluoranthene	Experimental Method: 5), Protocol: 3), 4)	PAH: 8) TOC: 9)	*Chironomus tetans* (Insecta:Diptera) Freshwater Epi-faunal. North America and Europe boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	5,5	1250	[10]	9). TOC = 0,44%.
Fluoranthene	Experimental Method: 6), Protocol: 3), 4)	PAH: 8) TOC: 9)	*Chironomus tetans* (Insecta:Diptera) Freshwater Epi-faunal. North America and Europe boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	3,0	682	[10]	9). TOC = 0,44%.
Fluoranthene	Experimental Method: 7), Protocol: 2), 5)	PAH: 1) TOC: 10)	*Eohaustorius estuarius* (Crustacea:Amphipoda) Marine free-living infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	9,3		[12]	10). TOC not reported?
Fluoranthene	Experimental Method: 8), Protocol: 2), 5)	PAH: 1) TOC: 10)	*Eohaustorius estuarius* (Crustacea:Amphipoda) Marine free-living infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	10,7		[12]	10). TOC not reported?
Fluoranthene	Experimental Method: 9), Protocol: 2), 5)	PAH: 1) TOC: 10)	*Eohaustorius estuarius* (Crustacea:Amphipoda) Marine free-living infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	11,8		[12]	10). TOC not reported?

Appendix 4.15 Effect concentration data for fluoranthene continued.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	Effect endpoint/ type	Effect conc. (µg/g dw)	Effect conc. oc (µg/g dw)	Ref.	Comments
Fluoranthene	Experimental Method: 1), Protocol: 2), 5)	PAH: 1) TOC: 10)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	5,1		[12]	10). TOC not reported?
Fluoranthene	Experimental Method: 10), Protocol: 2), 5)	PAH: 1) TOC: 10)	*Hyalella azteca* (Crustacea:Amphipoda) Freshwater infaunal. North America boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	15,4		[12]	10). TOC not reported?
Fluoranthene	Experimental Method: 1), Protocol: 5), 6)	PAH: 11) TOC: 12)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	16,0	7400	[14]	11). TOC = 0,2%. Spiked sediment stored for 13 days prior to testing.
Fluoranthene	Experimental Method: 1), Protocol: 5), 6)	PAH: 11) TOC: 12)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	22,1	10200	[14]	11). TOC = 0,2%. Spiked sediment stored for 27 days prior to testing.
Fluoranthene	Experimental Method: 1), Protocol: 5), 6)	PAH: 11) TOC: 12)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	22,1	10200	[14]	11). TOC = 0,2%. Spiked sediment stored for 41 days prior to testing.
Fluoranthene	Experimental Method: 1), Protocol: 5), 6)	PAH: 11) TOC: 12)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	25,5	11800	[14]	11). TOC = 0,2%. Spiked sediment stored for 55 days prior to testing.
Fluoranthene	Experimental Method: 1), Protocol: 5), 6)	PAH: 11) TOC: 12)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	22,6	10500	[14]	11). TOC = 0,2%. Spiked sediment stored for 69 days prior to testing.
Fluoranthene	Experimental Method: 1), Protocol: 5), 6)	PAH: 11) TOC: 12)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	23,1	10700	[14]	11). TOC = 0,2%. Spiked sediment stored for 83 days prior to testing.
Fluoranthene	Experimental Method: 1), Protocol: 5), 6)	PAH: 11) TOC: 12)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	52,2	24200	[14]	11). TOC = 0,2%. Spiked sediment stored for 121 days prior to testing.

Appendix 4.15 Effect concentration data for fluoranthene continued.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	Effect endpoint/ type	Effect conc. (µg/g dw)	Effect conc. oc (µg/g dw)	Ref.	Comments
Fluoranthene	Experimental Method: 1), Protocol: 5), 6)	PAH: 11) TOC: 12)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	59,4	27600	[14]	11). TOC = 0,2%. Spiked sediment stored for 170 days prior to testing.
Fluoranthene	Experimental Method: 1), Protocol: 5), 6)	PAH: 11) TOC: 12)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	31,8	5300	[14]	12). TOC = 0,6%. Spiked sediment stored for 13 days prior to testing.
Fluoranthene	Experimental Method: 1), Protocol: 5), 6)	PAH: 11) TOC: 12)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	37,2	6200	[14]	12). TOC = 0,6%. Spiked sediment stored for 27 days prior to testing.
Fluoranthene	Experimental Method: 1), Protocol: 5), 6)	PAH: 11) TOC: 12)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	36,2	6100	[14]	12). TOC = 0,6%. Spiked sediment stored for 41 days prior to testing.
Fluoranthene	Experimental Method: 1), Protocol: 5), 6)	PAH: 11) TOC: 12)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	38,7	6500	[14]	12). TOC = 0,6%. Spiked sediment stored for 55 days prior to testing.
Fluoranthene	Experimental Method: 1), Protocol: 5), 6)	PAH: 11) TOC: 12)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	36,6	6100	[14]	12). TOC = 0,6%. Spiked sediment stored for 69 days prior to testing.
Fluoranthene	Experimental Method: 1), Protocol: 5), 6)	PAH: 11) TOC: 12)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	32,2	5400	[14]	12). TOC = 0,6%. Spiked sediment stored for 83 days prior to testing.
Fluoranthene	Experimental Method: 1), Protocol: 5), 6)	PAH: 11) TOC: 12)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	38,8	6500	[14]	12). TOC = 0,6%. Spiked sediment stored for 170 days prior to testing.
Fluoranthene	Experimental Method: 11), Protocol: 7)	PAH: 13) TOC: 14)	*Streblospio benedicti* (Annelida:Polychaeta) Marine infaunal. East Pacific, East and west Atlantic temperate.	$LC_{50\ 10\ days}$ /Acute	65,6		[16]	13). TOC = 2,04%. Normoxic exposure conditions

Appendix 4.15 Effect concentration data for fluoranthene continued.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	Effect endpoint/ type	Effect conc. (µg/g dw)	Effect conc. oc (µg/g dw)	Ref.	Comments
Fluoranthene	Experimental Method: 11), Protocol: 7)	PAH: 13) TOC: 14)	*Streblospio benedicti* (Annelida:Polychaeta) Marine infaunal. East Pacific, East and west Atlantic temperate.	$LC_{50\ 10\ days}$ /Acute	39,9		[16]	13). TOC = 2,04%. Moderately hypoxic exposure conditions
Fluoranthene	Experimental Method: 12), Protocol: 2), 5)	PAH: 11) TOC: 12)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	16,6 1)		[17]	14). TOC = 0,34%.
Fluoranthene	Experimental Method: 13), Protocol: 6), 10)	PAH: 15) TOC: 7)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute		2320	[19]	15). TOC = 3%.
Fluoranthene	Experimental Method: 13), Protocol: 6), 10)	PAH: 15) TOC: 7)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute		3310	[19]	15). TOC = 3%.
Fluoranthene	Experimental Method: 14), Protocol: 3), 5)	PAH: 13)	*Chironomus riparius* (Insecta:Diptera) Freshwater Epi-faunal. USA and Europe boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	14,69		[20]	16). TOC = 2%.
Fluoranthene	Experimental Method: 14), Protocol: 3), 5)	PAH: 13)	*Chironomus riparius* (Insecta:Diptera) Freshwater Epi-faunal. USA and Europe boreal to temperate.	$LC_{50\ 10\ days\ LOEC}$ /Acute	3		[20]	16). TOC = 2%.
Fluoranthene	Experimental Method: 15), Protocol: 3), 5)	PAH: 13)	*Hyalella azteca* (Crustacea:Amphipoda) Freshwater infaunal. North America boreal to temperate.	$LC_{50\ 14\ days}$ /Acute	5,2		[20]	16). TOC = 2%.
Fluoranthene	Experimental Method: 15), Protocol: 3), 5)	PAH: 13)	*Hyalella azteca* (Crustacea:Amphipoda) Freshwater infaunal. North America boreal to temperate.	$LC_{50\ 14\ days\ LOEC}$ /Acute	10		[20]	16). TOC = 2%.
Fluoranthene	Experimental Method: 15), Protocol: 3), 5)	PAH: 13)	*Hyalella azteca* (Crustacea:Amphipoda) Freshwater infaunal. North America boreal to temperate.	$LC_{50\ 14\ days\ NOEC}$ /Acute	3		[20]	16). TOC = 2%.

Appendix 4.15 Effect concentration data for fluoranthene continued.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	Effect endpoint/ type	Effect conc. (µg/g dw)	Effect conc. oc (µg/g dw)	Ref.	Comments
Fluoranthene	Experimental Method: 16), Protocol: 3)	PAH: 16)	*Chironomus riparius* (Insecta:Diptera) Freshwater Epi-faunal. USA and Europe boreal to temperate.	$LC_{50\ 11\ days}$ /Acute	31,7		[21]	17). TOC = 0,53%.
Fluoranthene	Experimental Method: 16), Protocol: 3)	PAH: 16)	*Chironomus riparius* (Insecta:Diptera) Freshwater Epi-faunal. USA and Europe boreal to temperate.	$LC_{50\ 11\ days}$ /Acute	29,7		[21]	18). TOC = 0,53%.
Fluoranthene	Experimental Method: 17), Protocol: 3)	PAH: 16)	*Chironomus riparius* (Insecta:Diptera) Freshwater Epi-faunal. USA and Europe boreal to temperate.	$LC_{50\ 11\ days}$ /Acute	31,9		[21]	19). TOC = 0,53%.
Fluoranthene	Experimental Method: 18), Protocol: 3)	PAH: 8) TOC: 9)	*Chironomus tetans* (Insecta:Diptera) Freshwater Epi-faunal. USA and Europe boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	7,3	1587	[22]	20). TOC = 0,46%.
Fluoranthene	Experimental Method: 18), Protocol: 3)	PAH: 8) TOC: 9)	*Chironomus tetans* (Insecta:Diptera) Freshwater Epi-faunal. USA and Europe boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	3,0	682	[22]	21). TOC = 0,50%.
Fluoranthene	Experimental Method: 18), Protocol: 3)	PAH: 8) TOC: 9)	*Chironomus tetans* (Insecta:Diptera) Freshwater Epi-faunal. USA and Europe boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	8,7	1740	[22]	22). TOC = 0,44%.
Fluoranthene	Experimental Method: 18), Protocol: 3)	PAH: 8) TOC: 9)	*Hyalella azteca* (Crustacea:Amphipoda) Freshwater infaunal. North America boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	2,3	500	[22]	20). TOC = 0,46%.
Fluoranthene	Experimental Method: 18), Protocol: 3)	PAH: 8) TOC: 9)	*Hyalella azteca* (Crustacea:Amphipoda) Freshwater infaunal. North America boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	5,5	1250	[22]	21). TOC = 0,50%.
Fluoranthene	Experimental Method: 18), Protocol: 3)	PAH: 8) TOC: 9)	*Hyalella azteca* (Crustacea:Amphipoda) Freshwater infaunal. North America boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	7,4	1480	[22]	22). TOC = 0,44%.

Appendix 4.15 Effect concentration data for fluoranthene continued.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	Effect endpoint/ type	Effect conc. (µg/g dw)	Effect conc. oc (µg/g dw)	Ref.	Comments
Fluoranthene	Experimental Method: 19), Protocol: 9)	PAH: 16) TOC: 7)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	$LC_{50\ 10\ days}$ /Chronic	213		[24]	23). TOC = 1,5%.
Fluoranthene	Experimental Method: 19), Protocol: 9)	PAH: 18) TOC: 7)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	$LC_{50\ 10\ days\ LOEC}$ /Chronic	334		[24]	23). TOC = 1,5%.
Fluoranthene	Experimental Method: 19), Protocol: 9)	PAH: 16) TOC: 7)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	$LC_{50\ 10\ days\ NOEC}$ /Chronic	132		[24]	23). TOC = 1,5%.
Fluoranthene	Experimental Method: 19), Protocol: 9)	PAH: 16) TOC: 7)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	$EC_{50\ 10\ days}$ /Chronic	55		[24]	23). TOC = 1,5%. Effect endpoint: Realized offspring as all nauplii and copepodites/copepods present in the different exposure vessels at day 10 divided on the number of surviving females.
Fluoranthene	Experimental Method: 19), Protocol: 9)	PAH: 16) TOC: 7)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	$EC_{50\ 10\ days\ LOEC}$ /Chronic	47		[24]	23). TOC = 1,5%. Effect endpoint: Realized offspring as all nauplii and copepodites/copepods present in the different exposure vessels at day 10 divided on the number of surviving females.
Fluoranthene	Experimental Method: 19), Protocol: 9)	PAH: 16) TOC: 7)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	$EC_{50\ 10\ days\ NOEC}$ /Chronic	18		[24]	23). TOC = 1,5%. Effect endpoint: Realized offspring as all nauplii and copepodites/copepods present in the different exposure vessels at day 10 divided on the number of surviving females.
Fluoranthene	Experimental Method: 19), Protocol: 9)	PAH: 16) Radioactivity: 6) TOC: 7)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	$IC_{50\ 23\ hours}$ /Acute	34		[24]	23). TOC = 1,5%. Effect endpoint: Grazing.

Appendix 4.15 Effect concentration data for fluoranthene continued.

Comp.	**Experimental Methods/ Protocol**	**Chemical Analysis**	**Species/ Taxon/ Habitat/ Distribution**	**Effect endpoint/ type**	**Effect conc. (µg/g dw)**	**Effect conc. oc (µg/g dw)**	**Ref.**	**Comments**
Fluoranthene	Experimental Method: 19), Protocol: 9)	PAH: 16) Radioactivity: 6) TOC: 7)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	$IC_{50\ 23\ hours\ LOEC}$ /Acute	18		[24]	23). TOC = 1,5%. Effect endpoint: Grazing.
Fluoranthene	Experimental Method: 19), Protocol: 9)	PAH: 16) Radioactivity: 6) TOC: 7)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	$IC_{50\ 23\ hours\ NOEC}$ /Acute	5		[24]	23). TOC = 1,5%. Effect endpoint: Grazing.
Fluoranthene	Experimental Method: 19), Protocol: 9)	PAH: 16) TOC: 7)	*Coullana* sp. (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	$LC_{50\ 10\ days}$ /Chronic	132		[24]	23). TOC = 1,5%.
Fluoranthene	Experimental Method: 19), Protocol: 9)	PAH: 16) TOC: 7)	*Coullana* sp. (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	$LC_{50\ 10\ days\ LOEC}$ /Chronic	132		[24]	23). TOC = 1,5%.
Fluoranthene	Experimental Method: 19), Protocol: 9)	PAH: 16) TOC: 7)	*Coullana* sp. (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	$LC_{50\ 10\ days\ NOEC}$ /Chronic	47		[24]	23). TOC = 1,5%.
Fluoranthene	Experimental Method: 19), Protocol: 9)	PAH: 16) TOC: 7)	*Coullana* sp. (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	$EC_{50\ 10\ days\ LOEC}$ /Chronic	132		[24]	23). TOC = 1,5%. Effect endpoint: Realized offspring as all nauplii and copepodites/copepods present in the different exposure vessels at day 10 divided on the number of surviving females.
Fluoranthene	Experimental Method: 19), Protocol: 9)	PAH: 16) TOC: 7)	*Coullana* sp. (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	$EC_{50\ 10\ days\ NOEC}$ /Chronic	47		[24]	23). TOC = 1,5%. Effect endpoint: Realized offspring as all nauplii and copepodites/copepods present in the different exposure vessels at day 10 divided on the number of surviving females.

Appendix 4.15 Effect concentration data for fluoranthene continued.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	Effect endpoint/ type	Effect conc. (µg/g dw)	Effect conc. oc (µg/g dw)	Ref.	Comments
Fluoranthene	Experimental Method: 19), Protocol: 9)	PAH: 16) Radioactivity: 6) TOC: 7)	*Coullana* sp. (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	$IC_{50\text{ 23 hours}}$ /Acute	35		[24]	23). TOC = 1,5%. Effect endpoint: Grazing.
Fluoranthene	Experimental Method: 19), Protocol: 9)	PAH: 16) Radioactivity: 6) TOC: 7)	*Coullana* sp. (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	$IC_{50\text{ 23 hours LOEC}}$ /Acute	47		[24]	23). TOC = 1,5%. Effect endpoint: Grazing.
Fluoranthene	Experimental Method: 19), Protocol: 9)	PAH: 16) Radioactivity: 6) TOC: 7)	*Coullana* sp. (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	$IC_{50\text{ 23 hours NOEC}}$ /Acute	18		[24]	23). TOC = 1,5%. Effect endpoint: Grazing.

1) Effect-concentration value calculated by non-linear regression based on data in the paper.

Experimental Methods:

1): Static exposure performed at a salinity of 28 ppt with adult animals collected from natural populations.

2): Static exposure performed at a salinity of 25 ppt with adult animals collected from natural populations.

3): Static exposure performed with artificial seawater at a salinity of 25 ppt with adult females collected from laboratory culture. Animals fed radioactive labelled algae.

4): Static exposure performed with artificial seawater at a salinity of 25 ppt with one copulating couple in each exposure chamber. Animals collected from laboratory culture.

5): Static exposure performed in pond water (fresh water) with juvenile animals (0,6 - 1,0 mm; 2 - 3 weeks old) collected from laboratory culture.

6): Static exposure performed in pond water (fresh water) with juvenile animals (second instar, 10-12 days post hatching) collected from laboratory culture.

7): Static exposure performed in natural seawater diluted to a salinity of 2 ppt with distilled water. Exposure performed with adult animals (3-5mm body length) collected from natural populations.

8): Static exposure performed in natural seawater diluted to a salinity of 10 ppt with distilled water. Exposure performed with adult animals (3-5mm body length) collected from natural populations.

9): Static exposure performed in natural seawater diluted to a salinity of 28 ppt with distilled water. Exposure performed with adult animals (3-5mm body length) collected from natural populations.

10): Static exposure performed in natural seawater diluted to a salinity of 2 ppt with distilled water. Exposure performed with juvenile animals (3-6mm body length) collected from natural populations.

11): Static exposure performed in natural seawater at a salinity of 29,2 ppt with animals collected from laboratory culture.

12): Static exposure performed at a salinity of 28 ppt with animals collected from natural populations.

13): Static exposure performed at a salinity of 28 ppt with juvenile animals (body length 3 - 4 mm) collected from natural populations.

14): Static exposure performed with artificial freshwater with 48 hours old larvae collected from laboratory culture.

15): Static exposure performed with artificial freshwater with juvenile animals (animals passing trough 1,0 mm sieve, but retained on 0,5 mm sieve; age approx. 2-3 weeks) collected from laboratory culture.

16): Static exposure performed with artificial freshwater with juvenile animals less than 24 hours post-hatch collected from laboratory culture.

Appendix 4.15 Effect concentration data for fluoranthene continued.

17): Static exposure performed with natural pond water (freshwater) with juvenile animals in their second instar stage (10-12 days post-hatch) collected from laboratory culture.
18): Static exposure performed with natural pond water (freshwater) with juvenile animals (animals passing trough 1,0 mm sieve, but retained on 0,6 mm sieve; age approx. 2-3 weeks) collected from laboratory culture.
19): Static exposure performed with artificial seawater at a salinity of 25 ppt with adult non-ovigerous females collected from laboratory culture.

Protocols:

1): Protocol for spiking of sediment based on Swartz et al. [1].
2): Protocol for exposure based on Swartz et al. [2].
3): No reference to external protocol other than the published paper.
4): Sediment handling, storage and characterisation acc. to Plumb [9].
5): Protocol for spiking of sediment based on Ditsworth et al. [11].
6): Protocol for exposure based on ASTM [13].
7): Protocol for exposure based on ASTM [15].
8): Protocol for exposure based on US-EPA [18].
9): Protocol for exposure based on previous work of Lotufo [23].

Chemical Analysis:

1): Analysis of fluoranthene was performed on a capillary gas chromatograph with FID-detector.
2): Total organic content (TOC) analysed using a LECO model WR-12 induction furnace after acidification to pH <2 with HCl to remove carbonates acc. to Plumb [3].
3): Analysis of fluoranthene was performed on a capillary gas chromatograph.
4): Total organic content (TOC) was not analysed per se, but estimated as 17,3% of the total volatile solids (TVS) lost after combustion of the samples at 550°C for 1 hour.
5): Analysis of fluoranthene was performed by reverse-phase HPLC acc. to Lotufo et al. [6].
6): Radioactive activity by liquid scintillation counting (LSC).
7): Sediment organic carbon (SOC) was measured on a Perkin-Elmer 2400 CHN Elemental Analyzer after acidification with HCl to remove inorganic carbonate.
8): Analysis of fluoranthene was performed on a spektrofluorometer after extraction in hexane.
9): Total organic content (TOC) was determined using a Dohrmann model DC-80 analyser after acidification of sediment samples with 0,1N H_3PO_4 to remove inorganic carbon.
10): Total organic content (TOC) estimated as % weight loss after ignition of the sample at 550°C for 1 hour.
11): Analysis of fluoranthene was performed on a Hewlett-Packard 5988A capillary gas chromatograph coupled with a mass spectrometer.
12): Total organic content (TOC) was determined using high temperature combustion coulometric titration with a Coulometrics Model 110 carbon analyser.
13): Fluoranthene was quantified by reversed phase HPLC.
14): The sediment organic carbon (SOC) was measured on a Perkin-Elmer CHNS/O Analyzer model 2400/Series II.
15): Fluoranthene was quantified on a HP 5870 capillary gas chromatograph coupled with a mass spectrometer.
16): Fluoranthene was quantified by liquid scintillation counting (LSC) after spiking the fluoranthene with [3-^{14}C]fluorantene.

Comments:

1): Natural sediment defaunated by sieving at 0,5 mm before removal of fines by twice stirring and siphoning off the supernatant after 1 minute settling by mixing 5 L sediment in 60 L seawater. The resulting fine sand was mixed with fine sediment rich in organic carbon (OC). Sand content in final sediment > 90%, fines (silt + clay) 2,8%.
2): Natural sediment treated as in 1) above. Sand content in final sediment > 90%, fines (silt + clay) 6,0%.
3): Natural sediment treated as in 1) above. Sand content in final sediment > 90%, fines (silt + clay) 9,1%.
4): Natural sediment treated as in 1) above. Sand content in final sediment > 90%, fines (silt + clay) 2,8 - 9,1%.
5): Natural sediment defaunated by sieving at 1,0 mm to remove adult *R. abronius* before resieving at 0,5 mm to remove juvenile *R. abronius* and adjust the salinity of the sediment to 25 ppt.
6): Natural sediment collected from a mud-flat in a salt-mash in Lousiana, USA. Natural background of PAH 0,26 µg/dry g acc. to Carman et al. [8]. Test sediment wet-sieved at 45 µm sedimented overnight at 4°C before the supernatant was removed by aspiration. The remaining sediment was defaunated by autoclaving.
7): Natural sediment collected from Water Research Station, University of Texas. Sediment collected at <1m depth by an Ekman dredge, background of fluoranthene < 1.0 µg/kg and no detectable background toxicity. Sediment consisting of 1,36% clay, 55,98% silt and 42,66% sand.
8): Natural sediment collected from Lake Fork Reservoir near Quitman, Texas. Sediment collected at <1m depth by an Ekman dredge, background of fluoranthene < 1.0 µg/kg and no detectable background toxicity. Sediment consisting of 0,94% clay, 55,10% silt and 43,96% sand.
9): Natural sediment collected from Trinity River near Ennis, Texas. Sediment collected at <1m depth by an Ekman dredge, background of fluoranthene < 1.0 µg/kg and no detectable background toxicity. Sediment consisting of 0,93% clay, 46,32% silt and 52,75% sand.

Appendix 4.15 Effect concentration data for fluoranthene continued.

10): Natural sediment collected from Yaquina Bay, Oregon. Sediment sieved at 0,5 mm and into prefiltered (<5 µm) Yaquina Bay water adjusted to given salinity by distilled water for removal of macrofauna, larger debris and to equilibrate with exposure salinity.

11): Natural sediment collected from an tidal area with fine sand at Yaquina Bay, Oregon. Sediment wet sieved at 0,5 mm for removal of macrofauna, larger debris and to equilibrate with exposure salinity. Sediment consisting of 97% sand and 3% silt + clay.

12): Natural sediment collected from an tidal area with fine sand at Yaquina Bay, Oregon. Sediment wet sieved at 0,5 mm for removal of macrofauna, larger debris and to equilibrate with exposure salinity. Sediment consisting of 75,8% sand and 24,2% silt + clay.

13): Natural sediment collected from a tidal creek-saltmash. Larger debris and fauna removed by wet sieving to 500µm prior to freezing. Particle distribution acc. to a modification of Plumb [17]: 49,6% sand, 18,4% silt and 32,1% clay.

14): Base sediment with low organic content (0,03% particulate organic carbon – POC), 178,0 µm median particle diameter and 98,8% sand was collected intertidally from Ona Beach, Oregon. The sediment was screened for debris and macroinvertebrates by sieving at 500 µm and stored at 4°C for 3 days prior to use. The sediment was amended to a nominal POC concentration of 0,4%with natural suspended solids rich in organic matter sieved trough 250 µm screen.

15): Natural sediment from McKinney Slough, Oregon wet-sieved trough 0,5mm screen for removal of macrobiota and debris and settled for 24 hours at 4°C prior to spiking. Sediment a poorly sorted silt with 3% organic carbon and 40,6% solids.

16): Artificial sediment was reconstituted using 65% sand (Silice et Kaolin) washed and sieved between 0,5 and 2mm, 30% kaolin clay (Prolabo), 4.85% alfa-cellulose (Sigma), 0.15% TetraMin and 0.1% calcium carbonate (Prolabo). The resulting Total Organic Carbon (TOC) was 2%. All % on dry weight basis.

17): Natural sediments from the River Frome, Dorset, England. Fluoranthene was spiked into wet sediment by adding required amount of stock solution in acetone and mixed by rolling for 20 hours without evaporation of acetone prior to mixing.

18): Natural sediments from the River Frome, Dorset, England. Fluoranthene was spiked into wet sediment by coating the inside of mixing jars with the PAH stock solution and evaporation to dryness before adding of wet sediment and mixing.

19): Natural sediments from the River Frome, Dorset, England. Fluoranthene was spiked into the wet sediment by coating it on predried sediment. This were performed by adding the required amount of stock solution in acetone to an predried aliquot (approx. 20%) of sediment and evaporating the sample to dryness before introducing it into the remainding of the wet sediment in mixing jars before mixing.

20): Natural sediments were collected in <1 m water depth with an Eckman dredge from the University of North Texas (UNT) Water Research Field Station (WRFS), in Denton County, Texas.Upon collection, sediments were stored at 4°C until tested, within four weeks storage time. Sediment characteristics: Organic carbon: 0,46%, sand: 42,66%, silt: 55,98% and clay: 1,36%.

21): Natural sediments were collected in <1 m water depth with an Eckman dredge from the Trinity River at river mile 408.5, near Ennis, Texas. Upon collection, sediments were stored at 4°C until tested, within four weeks storage time. Sediment characteristics: Organic carbon: 0,50%, sand: 43,96%, silt: 55,10% and clay: 0,94%.

22): Natural sediments were collected in <1 m water depth with an Eckman dredge from the Lake Fork Reservoir near Quitman, Texas. Upon collection, sediments were stored at 4°C until tested, within four weeks storage time. Sediment characteristics: Organic carbon: 0,44%, sand: 52,72%, silt: 46,32% and clay: 0,93%.

23): Natural sediment collected from a *Spartina alterniflora* mudflat near Cocodrie, LA, USA. Particle size of test-sediment was less than 45 µm, and the sediment organic carbon (SOC) was 1.5% acc. to Lotufo [28].

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Appendix 4.15 Effect concentration data for fluoranthene continued.

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Appendix 4.16 Effect concentration data for phenanthrene. References to the cited literature are listed at the end of this table.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	Effect endpoint/ type	Effect conc. (µg/g dw)	Effect conc. oc (µg/g dw)	Ref.	Comments
Phenanthrene	Experimental Method: 1), Protocol: 1)	PAH: 1) TOC: 2)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	LC$_{50\ 94\ \mathrm{hours}}$ /Acute	524		[1]	1). TOC = 1,5%.
Phenanthrene	Experimental Method: 2), Protocol: 1)	PAH: 1) Radioactivity: 3) TOC: 2)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	IC$_{50\ 30\ \mathrm{hours}}$ /Acute	51		[1]	1). TOC = 1,5%. Effect endpoint: Grazing.
Phenanthrene	Experimental Method: 3), Protocol: 1)	PAH: 1) TOC: 2)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	EC$_{50\ 14}$ days /Chronic	952		[1]	1). TOC = 1,5%. Effect endpoint: Realised offspring produced over a 14 day period.
Phenanthrene	Experimental Method: 4), Protocol: 1)	PAH: 1) TOC: 2)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	LC$_{50\ 10\ \mathrm{days}}$ /Chronic	84	5600	[4]	1). TOC = 1,5%.
Phenanthrene	Experimental Method: 4), Protocol: 1)	PAH: 1) TOC: 2)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	LC$_{50\ 10\ \mathrm{days\ LOEC}}$ /Chronic	45		[4]	1). TOC = 1,5%.
Phenanthrene	Experimental Method: 4), Protocol: 1)	PAH: 1) TOC: 2)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	LC$_{50\ 10\ \mathrm{days\ NOEC}}$ /Chronic	22		[4]	1). TOC = 1,5%.
Phenanthrene	Experimental Method: 5), Protocol: 1)	PAH: 1) TOC: 2)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	LC$_{50\ 10\ \mathrm{days}}$ /Chronic	172		[4]	1). TOC = 1,5%.
Phenanthrene	Experimental Method: 5), Protocol: 1)	PAH: 1) TOC: 2)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	LC$_{50\ 10\ \mathrm{days\ LOEC}}$ /Chronic	177		[4]	1). TOC = 1,5%.
Phenanthrene	Experimental Method: 5), Protocol: 1)	PAH: 1) TOC: 2)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	LC$_{50\ 10\ \mathrm{days\ NOEC}}$ /Chronic	90		[4]	1). TOC = 1,5%.
Phenanthrene	Experimental Method: 6), Protocol: 1)	PAH: 1) TOC: 2)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	LC$_{50\ 10\ \mathrm{days}}$ /Chronic	349	26800	[4]	1). TOC = 1,5%.

Appendix 4.16 Effect concentration data for phenanthrene continued.

Comp.	**Experimental Methods/ Protocol**	**Chemical Analysis**	**Species/ Taxon/ Habitat/ Distribution**	**Effect endpoint/ type**	**Effect conc. (µg/g dw)**	**Effect conc. oc (µg/g dw)**	**Ref.**	**Comments**
Phenanthrene	Experimental Method: 6), Protocol: 1)	PAH: 1) TOC: 2)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	$LC_{50\ 10\ days\ LOEC}$ /Chronic	492		[4]	1). TOC = 1,5%.
Phenanthrene	Experimental Method: 6), Protocol: 1)	PAH: 1) TOC: 2)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	$LC_{50\ 10\ days\ NOEC}$ /Chronic	217		[4]	1). TOC = 1,5%.
Phenanthrene	Experimental Method: 1), Protocol: 1)	PAH: 1) TOC: 2)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	$LC_{50\ 10\ days}$ /Chronic	345		[4]	1). TOC = 1,5%.
Phenanthrene	Experimental Method: 1), Protocol: 1)	PAH: 1) TOC: 2)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	$LC_{50\ 10\ days\ LOEC}$ /Chronic	492		[4]	1). TOC = 1,5%.
Phenanthrene	Experimental Method: 1), Protocol: 1)	PAH: 1) TOC: 2)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	$LC_{50\ 10\ days\ NOEC}$ /Chronic	217		[4]	1). TOC = 1,5%.
Phenanthrene	Experimental Method: 7), Protocol: 1)	PAH: 1) TOC: 2)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	$EC_{50\ 10\ days\ LOEC}$ /Chronic	22		[4]	1). TOC = 1,5%. Effect endpoint: Mean realized offspring production was calculated on a per-surviving-female basis based on number of nauplii and copepodites produced.
Phenanthrene	Experimental Method: 7), Protocol: 1)	PAH: 1) TOC: 2)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	$EC_{50\ 10\ days\ NOEC}$ /Chronic	11		[4]	1). TOC = 1,5%. Effect endpoint: Mean realized offspring production was calculated on a per-surviving-female basis based on number of nauplii and copepodites produced.
Phenanthrene	Experimental Method: 7), Protocol: 1)	PAH: 1) TOC: 2)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	$EC_{50\ 10\ days\ LOEC}$ /Chronic	22		[4]	1). TOC = 1,5%. Effect endpoint: Mean time in days for eggs carried by ovigerous females to hatch into nauplii from the beginning of the observation period.
Phenanthrene	Experimental Method: 7), Protocol: 1)	PAH: 1) TOC: 2)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	$EC_{50\ 10\ days\ NOEC}$ /Chronic	11		[4]	1). TOC = 1,5%. Effect endpoint: Mean time in days for eggs carried by ovigerous females to hatch into nauplii from the beginning of the observation period.

Appendix 4.16 Effect concentration data for phenanthrene continued.

Comp.	**Experimental Methods/ Protocol**	**Chemical Analysis**	**Species/ Taxon/ Habitat/ Distribution**	**Effect endpoint/ type**	**Effect conc. (µg/g dw)**	**Effect conc. oc (µg/g dw)**	**Ref.**	**Comments**
Phenanthrene	Experimental Method: 7), Protocol: 1)	PAH: 1) TOC: 2)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	$EC_{50\ 10\ days\ LOEC}$ /Chronic	45		[4]	1). TOC = 1,5%. Effect endpoint: Hatching success expressed as number of nauplii produced per female.
Phenanthrene	Experimental Method: 7), Protocol: 1)	PAH: 1) TOC: 2)	*Schizopera knabeni* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America boreal to temperate.	$EC_{50\ 10\ days\ NOEC}$ /Chronic	22		[4]	1). TOC = 1,5%. Effect endpoint: Hatching success expressed as number of nauplii produced per female.
Phenanthrene	Experimental Method: 4), Protocol: 1)	PAH: 1) TOC: 2)	*Nitocra lacustris* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America and Europe temperate.	$LC_{50\ 10\ days}$ /Chronic	71	2867	[4]	1). TOC = 1,5%.
Phenanthrene	Experimental Method: 4), Protocol: 1)	PAH: 1) TOC: 2)	*Nitocra lacustris* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America and Europe temperate.	$LC_{50\ 10\ days\ LOEC}$ /Chronic	45		[4]	1). TOC = 1,5%.
Phenanthrene	Experimental Method: 4), Protocol: 1)	PAH: 1) TOC: 2)	*Nitocra lacustris* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America and Europe temperate.	$LC_{50\ 10\ days\ NOEC}$ /Chronic	22		[4]	1). TOC = 1,5%.
Phenanthrene	Experimental Method: 5), Protocol: 1)	PAH: 1) TOC: 2)	*Nitocra lacustris* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. USA and Europe temperate.	$LC_{50\ 10\ days}$ /Chronic	43		[4]	1). TOC = 1,5%.
Phenanthrene	Experimental Method: 5), Protocol: 1)	PAH: 1) TOC: 2)	*Nitocra lacustris* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America and Europe temperate.	$LC_{50\ 10\ days\ LOEC}$ /Chronic	22		[4]	1). TOC = 1,5%.
Phenanthrene	Experimental Method: 5), Protocol: 1)	PAH: 1) TOC: 2)	*Nitocra lacustris* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America and Europe temperate.	$LC_{50\ 10\ days\ NOEC}$ /Chronic	11		[4]	1). TOC = 1,5%.
Phenanthrene	Experimental Method: 6), Protocol: 1)	PAH: 1) TOC: 2)	*Nitocra lacustris* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America and Europe temperate.	$LC_{50\ 10\ days}$ /Chronic	72	7000	[4]	1). TOC = 1,5%.
Phenanthrene	Experimental Method: 6), Protocol: 1)	PAH: 1) TOC: 2)	*Nitocra lacustris* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America and Europe temperate.	$LC_{50\ 10\ days\ LOEC}$ /Chronic	90		[4]	1). TOC = 1,5%.

Appendix 4.16 Effect concentration data for phenanthrene continued.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	Effect endpoint/ type	Effect conc. (µg/g dw)	Effect conc. oc (µg/g dw)	Ref.	Comments
Phenanthrene	Experimental Method: 6), Protocol: 1)	PAH: 1) TOC: 2)	*Nitocra lacustris* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America and Europe temperate.	$LC_{50\ \text{10 days NOEC}}$ /Chronic	45		[4]	1). TOC = 1,5%.
Phenanthrene	Experimental Method: 1), Protocol: 1)	PAH: 1) TOC: 2)	*Nitocra lacustris* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America and Europe temperate.	$LC_{50\ \text{10 days}}$ /Chronic	105		[4]	1). TOC = 1,5%.
Phenanthrene	Experimental Method: 1), Protocol: 1)	PAH: 1) TOC: 2)	*Nitocra lacustris* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America and Europe temperate.	$LC_{50\ \text{10 days LOEC}}$ /Chronic	177		[4]	1). TOC = 1,5%.
Phenanthrene	Experimental Method: 1), Protocol: 1)	PAH: 1) TOC: 2)	*Nitocra lacustris* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America and Europe temperate.	$LC_{50\ \text{10 days NOEC}}$ /Chronic	90		[4]	1). TOC = 1,5%.
Phenanthrene	Experimental Method: 8), Protocol: 1)	PAH: 1) TOC: 2)	*Nitocra lacustris* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America and Europe temperate.	$EC_{50\ \text{10 days LOEC}}$ /Chronic	90		[4]	1). TOC = 1,5%. Effect endpoint: Mean realized offspring production was calculated on a per-surviving-female basis based on number of nauplii and copepodites produced.
Phenanthrene	Experimental Method: 8), Protocol: 1)	PAH: 1) TOC: 2)	*Nitocra lacustris* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America and Europe temperate.	$EC_{50\ \text{10 days NOEC}}$ /Chronic	45		[4]	1). TOC = 1,5%. Effect endpoint: Mean realized offspring production was calculated on a per-surviving-female basis based on number of nauplii and copepodites produced.
Phenanthrene	Experimental Method: 8), Protocol: 1)	PAH: 1) TOC: 2)	*Nitocra lacustris* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America and Europe temperate.	$EC_{50\ \text{10 days LOEC}}$ /Chronic	45		[4]	1). TOC = 1,5%. Effect endpoint: Mean time in days for eggs carried by ovigerous females to hatch into nauplii from the beginning of the observation period.
Phenanthrene	Experimental Method: 8), Protocol: 1)	PAH: 1) TOC: 2)	*Nitocra lacustris* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America and Europe temperate.	$EC_{50\ \text{10 days NOEC}}$ /Chronic	22		[4]	1). TOC = 1,5%. Effect endpoint: Mean time in days for eggs carried by ovigerous females to hatch into nauplii from the beginning of the observation period.
Phenanthrene	Experimental Method: 8), Protocol: 1)	PAH: 1) TOC: 2)	*Nitocra lacustris* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America and Europe temperate.	$EC_{50\ \text{10 days LOEC}}$ /Chronic	90		[4]	1). TOC = 1,5%. Effect endpoint: Hatching success expressed as number of nauplii produced per female.

Appendix 4.16 Effect concentration data for phenanthrene continued.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	Effect endpoint/ type	Effect conc. (µg/g dw)	Effect conc. oc (µg/g dw)	Ref.	Comments
Phenanthrene	Experimental Method: 8), Protocol: 1)	PAH: 1) TOC: 2)	*Nitocra lacustris* (Crustacea:Copepoda Harpactoida) Marine Epi-faunal. North America and Europe temperate.	$EC_{50\ 10\ days\ NOEC}$ /Chronic	45		[4]	1). TOC = 1,5%. Effect endpoint: Hatching success expressed as number of nauplii produced per female.
Phenanthrene	Experimental Method: 9), Protocol: 2)	PAH: 4) TOC: 2)	*Limnodrilus hoffmeisteri* (Annelida:Oligochaeta) Freshwater infaunal. North America and Europe boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	297,5	42500	[6]	2). TOC = 0,7%.
Phenanthrene	Experimental Method: 9), Protocol: 2)	PAH: 4) TOC: 2)	*Limnodrilus hoffmeisteri* (Annelida:Oligochaeta) Freshwater infaunal. North America and Europe boreal to temperate.	$EC_{50\ 10\ days\ LOEC}$ /Acute	47		[6]	2). TOC = 0,7%. Effect endpoint: Reduction in the production of fecal pellets.
Phenanthrene	Experimental Method: 9), Protocol: 2)	PAH: 4) TOC: 2)	*Limnodrilus hoffmeisteri* (Annelida:Oligochaeta) Freshwater infaunal. North America and Europe boreal to temperate.	$EC_{50\ 10\ days\ NOEC}$ /Acute	20		[6]	2). TOC = 0,7%. Effect endpoint: Reduction in the production of fecal pellets.
Phenanthrene	Experimental Method: 10), Protocol: 2)	PAH: 4) TOC: 2)	*Limnodrilus hoffmeisteri* (Annelida:Oligochaeta) Freshwater infaunal. North America and Europe boreal to temperate.	$EC_{50\ 28\ days\ LOEC}$ /Chronic	102		[6]	2). TOC = 0,7%. Effect endpoint: Mean realized offspring production calculated on a per-surviving-female basis based on number of unhatched cocoons and juveniles at end of exposure.
Phenanthrene	Experimental Method: 10), Protocol: 2)	PAH: 4) TOC: 2)	*Limnodrilus hoffmeisteri* (Annelida:Oligochaeta) Freshwater infaunal. North America and Europe boreal to temperate.	$EC_{50\ 28\ days\ NOEC}$ /Chronic	47		[6]	2). TOC = 0,7%. Effect endpoint: Mean realized offspring production calculated on a per-surviving-female basis based on number of unhatched cocoons and juveniles at end of exposure.
Phenanthrene	Experimental Method: 11), Protocol: 3)	PAH: 5) TOC: 6)	*Eohaustorius estuarius* (Crustacea:Amphipoda) Marine free-living infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	39,2	4060	[8]	3). TOC = 1,02%
Phenanthrene	Experimental Method: 11), Protocol: 3)	PAH: 5) TOC: 6)	*Eohaustorius estuarius* (Crustacea:Amphipoda) Marine free-living infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	92,6	3760	[8]	4). TOC = 2,47 %
Phenanthrene	Experimental Method: 11), Protocol: 3)	PAH: 5) TOC: 6)	*Eohaustorius estuarius* (Crustacea:Amphipoda) Marine free-living infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	134,1	4210	[8]	5). TOC = 3,33 %

Appendix 4.16 Effect concentration data for phenanthrene continued.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	Effect endpoint/ type	Effect conc. (µg/g dw)	Effect conc. oc (µg/g dw)	Ref.	Comments
Phenanthrene	Experimental Method: 12), Protocol: 3)	PAH: 5) TOC: 6)	*Leptocheirus plumulosus* (Crustacea:Amphipoda) Marine tube-dwelling infaunal. West Atlantic boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	91,9	8080	[8]	3). TOC = 1,02%
Phenanthrene	Experimental Method: 12), Protocol: 3)	PAH: 5) TOC: 6)	*Leptocheirus plumulosus* (Crustacea:Amphipoda) Marine tube-dwelling infaunal. West Atlantic boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	170,1	6870	[8]	4). TOC = 2,47 %
Phenanthrene	Experimental Method: 12), Protocol: 3)	PAH: 5) TOC: 6)	*Leptocheirus plumulosus* (Crustacea:Amphipoda) Marine tube-dwelling infaunal. West Atlantic boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	254,8	8180	[8]	5). TOC = 3,33 %
Phenanthrene	Experimental Method: 13), Protocol: 4), 5)	PAH: 7) TOC: 2)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute		3080	[11]	6). TOC = 3%.
Phenanthrene	Experimental Method: 13), Protocol: 4), 5)	PAH: 7) TOC: 2)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	$LC_{50\ 10\ days}$ /Acute		2220	[11]	6). TOC = 3%.
Phenanthrene	Experimental Method: 14), Protocol: 1), 6)	PAH: 4)	*Chironomus riparius* (Insecta:Diptera) Freshwater Epi-faunal. USA and Europe boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	14,7		[13]	7). TOC = 2%.
Phenanthrene	Experimental Method: 14), Protocol: 1), 6)	PAH: 4)	*Chironomus riparius* (Insecta:Diptera) Freshwater Epi-faunal. USA and Europe boreal to temperate.	$LC_{50\ 10\ days\ LOEC}$ /Acute	30		[13]	7). TOC = 2%.
Phenanthrene	Experimental Method: 14), Protocol: 1), 6)	PAH: 4)	*Chironomus riparius* (Insecta:Diptera) Freshwater Epi-faunal. USA and Europe boreal to temperate.	$LC_{50\ 10\ days\ NOEC}$ /Acute	10		[13]	7). TOC = 2%.
Phenanthrene	Experimental Method: 14), Protocol: 1), 6)	PAH: 4)	*Chironomus riparius* (Insecta:Diptera) Freshwater Epi-faunal. USA and Europe boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	15,83		[13]	7). TOC = 2%.
Phenanthrene	Experimental Method: 14), Protocol: 1), 6)	PAH: 4)	*Chironomus riparius* (Insecta:Diptera) Freshwater Epi-faunal. USA and Europe boreal to temperate.	$LC_{50\ 10\ days\ LOEC}$ /Acute	30		[13]	7). TOC = 2%.

Appendix 4.16 Effect concentration data for phenanthrene continued.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	Effect endpoint/ type	Effect conc. (µg/g dw)	Effect conc. oc (µg/g dw)	Ref.	Comments
Phenanthrene	Experimental Method: 14), Protocol: 1), 6)	PAH: 4)	*Chironomus riparius* (Insecta:Diptera) Freshwater Epi-faunal. USA and Europe boreal to temperate.	$LC_{50\ 10\ days\ NOEC}$ /Acute	10		[13]	7). TOC = 2%.
Phenanthrene	Experimental Method: 14), Protocol: 1), 6)	PAH: 4)	*Chironomus riparius* (Insecta:Diptera) Freshwater Epi-faunal. USA and Europe boreal to temperate.	$LC_{50\ 10\ days}$ /Acute	13,63		[13]	7). TOC = 2%.
Phenanthrene	Experimental Method: 14), Protocol: 1), 6)	PAH: 4)	*Chironomus riparius* (Insecta:Diptera) Freshwater Epi-faunal. USA and Europe boreal to temperate.	$LC_{50\ 10\ days\ LOEC}$ /Acute	30		[13]	7). TOC = 2%.
Phenanthrene	Experimental Method: 14), Protocol: 1), 6)	PAH: 4)	*Chironomus riparius* (Insecta:Diptera) Freshwater Epi-faunal. USA and Europe boreal to temperate.	$LC_{50\ 10\ days\ NOEC}$ /Acute	10		[13]	7). TOC = 2%.
Phenanthrene	Experimental Method: 15), Protocol: 3), 5)	PAH: 4)	*Hyalella azteca* (Crustacea:Amphipoda) Freshwater infaunal. North America boreal to temperate.	$LC_{50\ 14\ days}$ /Acute	20,54		[13]	7). TOC = 2%.
Phenanthrene	Experimental Method: 15), Protocol: 3), 5)	PAH: 4)	*Hyalella azteca* (Crustacea:Amphipoda) Freshwater infaunal. North America boreal to temperate.	$LC_{50\ 10\ days\ LOEC}$ /Acute	30		[13]	7). TOC = 2%.
Phenanthrene	Experimental Method: 15), Protocol: 3), 5)	PAH: 4)	*Hyalella azteca* (Crustacea:Amphipoda) Freshwater infaunal. North America boreal to temperate.	$LC_{50\ 10\ days\ NOEC}$ /Acute	10		[13]	7). TOC = 2%.

Appendix 4.16 Effect concentration data for phenanthrene continued.

Experimental Methods:

1): Static exposure performed with artificial seawater at a salinity of 25 ppt with adult females collected from laboratory culture.

2): Static exposure performed with artificial seawater at a salinity of 25 ppt with adult females collected from laboratory culture. Animals fed radioactive labelled algae.

3): Static exposure performed with artificial seawater at a salinity of 25 ppt with one copulating couple in each exposure chamber. Animals collected from laboratory culture.

4): Static exposure performed with artificial seawater at a salinity of 25 ppt with juvenile animals (naupliar stage, 1-2 days post-hatch) collected from laboratory culture.

5): Static exposure performed with artificial seawater at a salinity of 25 ppt with sub-adult animals (copepodite stage, 8-9 days post-hatch) collected from laboratory culture.

6): Static exposure performed with artificial seawater at a salinity of 25 ppt with adult males collected from laboratory culture.

7): Static exposure performed with artificial seawater at a salinity of 25 ppt with 10 copulating couples in each exposure chamber. Animals collected from laboratory culture.

8): Static exposure performed with artificial seawater at a salinity of 25 ppt with 10 animals of each sex in separate exposure chambers. Animals collected from laboratory culture.

9): Static exposure performed with artificial pond water with adult animals collected from laboratory culture.

10): Semi-static exposure performed with artificial pond water with 8 mature adult animals collected from laboratory culture in each exposure vessel.

11): Static exposure performed at a salinity of 28 ppt with juvenile animals (3-5mm) collected from natural populations.

12): Static exposure performed at a salinity of 28 ppt with juvenile animals (3-5mm) collected from laboratory culture originating from Queens Creek, York River, VA, USA.

13): Static exposure performed at a salinity of 28 ppt with juvenile animals (body length 3 - 4 mm) collected from natural populations.

14): Static exposure performed with artificial freshwater with 48 hours old larvae collected from laboratory culture.

15): Static exposure performed with artificial freshwater with juvenile animals (animals passing trough 1,0 mm sieve, but retained on 0,5 mm sieve; age approx. 2-3 weeks) collected from laboratory culture.

Protocols:

1): No reference to external protocol other than the published paper.

2): Protocol for exposure based on Kaster et al. [5].

3): Based on ASTM E1367-90 [7].

4): Protocol for exposure based on ASTM E 1367-92 [9].

5): Protocol for exposure based on US-EPA [10].

6): Protocol for spiking of sediment based on Ditsworth et al. [12].

Chemical Analysis:

1): Analysis of phenanthrene was performed by reverse-phase HPLC acc. to Lotufo et al. [2].

2): Sediment organic carbon (SOC) was measured on a Perkin-Elmer 2400 CHN Elemental Analyzer after acidification with HCl to remove inorganic carbonate.

3): Radioactive activity by liquid scintillation counting (LSC).

4): Analysis of phenanthrene was performed by reverse-phase HPLC.

5): Analysis of phenanthrene was performed on GC/MS (HP 5970B) with selective ion detector in SIMS-mode.

6): TOC was analysed by combustion after removal of carbonates by acidification to pH < 2 with HCl.

7): Phenanthrene was quantified on a HP 5870 capillary gas chromatograph coupled with a mass spectrometer.

Comments:

1): Natural sediment collected from a mud-flat in a salt-mash in Lousiana, USA. Natural background of PAH 0,26 µg/dry g acc. to Carman and Todaro [3]. Test sediment wet-sieved at 45 µm sedimented overnight at 4°C before the supernatant was removed by aspiration. The remaining sediment was defaunated by autoclaving.

2): Natural sediment collected from a local drainage system, wet-sieved to < 125 µm and settled for one week at 4°C. Overlaying water siphoned off and replaced with Arificial Pond Water (APW) before resuspension and spiking.

3): Natural sediment from an intertidal mud flat on the south shore of Yaquina Bay near South Beach, Oregon, wet-sieved trough 0,5mm screen and settled for 2-3 days at 4°C prior to use.

4): Natural sediment from an intertidal mud flat on McKinney Slough on the south shore of Alsea Bay, Oregon, wet-sieved trough 0,5mm screen and settled for 2-3 days at 4°C prior to use.

5): Natural sediment from an intertidal mud flat on Eckman Slough on the south shore of Alsea Bay, Oregon, wet-sieved trough 0,5mm screen and settled for 2-3 days at 4°C prior to use.

6): Natural sediment from McKinney Slough, Oregon wet-sieved trough 0,5mm screen for removal of macrobiota and debris and settled for 24 hours at 4°C prior to spiking. Sediment a poorly sorted silt with 3% organic carbon and 40,6% solids.

7): Artificial sediment was reconstituted using 65% sand (Silice et Kaolin) washed and sieved between 0,5 and 2mm, 30% kaolin clay (Prolabo), 4.85% alfa-cellulose (Sigma), 0.15% TetraMin and 0.1% calcium carbonate (Prolabo). The resulting Total Organic Carbon (TOC) was 2%. All % on dry weight basis.

Appendix 4.16 Effect concentration data for phenanthrene continued.

References:

[1] Lotufo, G.R. 1997. Toxicity of sediment-associated PAHs to an estuarine copepod: Effects on survival, feeding, reproduction and behaviour. Mar. Environ. Res., 44: 149-166.

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[3] Carman, K.R. and M.A. Todaro. 1996. Influence of polycyclic aromatic hydrocarbons on the meiobenthic copepod community of a Louisiana salt marsh. J. Exp. Mar. Biol. Ecol. 198: 37-54.

[4] Lotufo, G.R. and J.W. Fleeger. 1997. Effects of sediment-associated phenanthrene on survival, development and reproduction of two species of meiobenthic copepods. Mar. Ecol.-Prog. Ser., 151: 91-102.

[5] Kaster, J.L., J.V. Klump, J. Meyer, J. Krezoski and M.E. Smith. 1984. Comparison of defecation rates of *Limnodrilus hoffmeisteri* Cleparede (Tubificidae) using two different methods. Hydrobiologia, 111: 181-184.

[6] Lotufo, G.R. and J.W. Fleeger. 1996. Toxicity of sediment-associated pyrene and phenanthrene to *Limnodrilus hoffmeisteri* (Oligochaeta:Tubificidae). Environ. Toxicol. Chem., 15: 1508-1516.

[7] ASTM. 1990. Standard guide for conducting solid-phase 10-day static sediment toxicity tests with marine and estuarine amphipods. E1367-90. In: Annual Book of ASTM Standards, Water and Environmental Technology. Vol. 11.04. American Society for Testing and Materials, Philadelphia, PA.

[8] Swartz, R.C., T.H. DeWitt, D.W. Schults, G.R. Ditsworth, J.O. Lamberson, J.E. Sewall and R.J. Ozretich. XXXX. Toxicity of sediment-associated acenaphtene and phenanthrene to marine benthic amphipods. Data Report. Pacific Ecosystems Branch, Environmental Research Laboratory, Narragansett, Office of Research and Development, U.S. EPA, Newport, Oregon. (Marked "Incomplete Draft"). Data also cited in US-EPA. 1993. Sediment Quality Criteria for the Protection of Benthic Organisms: Phenanthrene. United States Environmental Protection Agency, Office of Science and Technology, EPA-822-R-93-014 and US-EPA. 1992. Development of a Chronic Sediment Toxicity Test for Marine Benthic Amphipods. United States Environmental Protection Agency, EPA's Environmental Research Laboratory, Narragansett. EPA 903-R-92-002.

[9] ASTM. 1993. Guide for conducting 10-day static sediment toxicity tests with marine and estuarine amphipods. E 1367-92. In: Annual Book of ASTM Standards. Vol 11.04. Philadelphia, PA, pp 1138-1163.

[10] U.S. Environmental Protection Agency. 1994. Methods for assessing the toxicity of sediment-associated contaminants with estuarine and marine amphipods. EPA/600/R-94/025. Washington DC.

[11] Swartz, R.C., S.P. Ferraro, J.O. Lamberson, F.A. Cole, R.J. Ozretich, B.L. Boese, D.W. Schults, M. Behrenfield and G.T. Ankley. 1997. Photoactivation and toxicity of mixtures of polycyclic aromatic hydrocarbon compounds in marine sediment. Environ. Toxicol. Chem., 16: 2151-2157.

[12] Ditsworth, G.R., D.W Schults and J.K.P. Jones. 1990. Preparation of benthic substrates for sediment toxicity testing. Environ. Toxicol. Chem. 9: 1523-1529.

[13] Verrhiest, G., B. Clement and G. Blake. 2001. Single and combined effects of sediment-associated PAHs on three species of freshwater macroinvertebrates. Ecotoxicology, 10: 363-372.

Appendix 4.17 Effect concentration data for pyrene. References to the cited literature are listed at the end of this table.

Comp.	Experimental Methods/ Protocol	Chemical Analysis	Species/ Taxon/ Habitat/ Distribution	Effect endpoint/ type	Effect conc. (µg/g dw)	Effect conc. oc (µg/g dw)	Ref.	Comments
Pyrene	Experimental Method: 1), Protocol: 1	PAH: 1) TOC: 2)	*Diporeia* sp. (Crustacea:Amphipoda) Freshwater infaunal. North America boreal to temperate.	LC$_{50\ 28\ days}$ /Chronic	147		[1]	1). TOC=0,46%
Pyrene	Experimental Method: 2), Protocol: 1	PAH: 3) TOC: 2)	*Lumbriculus variegatus* (Annelida:Oligochaeta) Freshwater infaunal. USA and Europe boreal to temperate.	EC$_{50\ 7\ days}$ /Acute	226		[3]	2). TOC=0,44%. Effect endpoint: Sediment avoidance.
Pyrene	Experimental Method: 3), Protocol: 2)	PAH: 1) TOC: 2)	*Limnodrilus hoffmeisteri* (Annelida:Oligochaeta) Freshwater infaunal. USA and Europe boreal to temperate.	EC$_{50\ 10\ days\ LOEC}$ /Acute	91		[5]	3). TOC = 0,7%. Effect endpoint: Reduction in the production of fecal pellets.
Pyrene	Experimental Method: 3), Protocol: 2)	PAH: 1) TOC: 2)	*Limnodrilus hoffmeisteri* (Annelida:Oligochaeta) Freshwater infaunal. USA and Europe boreal to temperate.	EC$_{50\ 10\ days\ NOEC}$ /Acute	46		[5]	3). TOC = 0,7%. Effect endpoint: Reduction in the production of fecal pellets.
Pyrene	Experimental Method: 4), Protocol: 3), 4)	PAH: 4) TOC: 2)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	LC$_{50\ 10\ days}$ /Acute		1220	[8]	4). TOC = 3%.
Pyrene	Experimental Method: 4), Protocol: 3), 4)	PAH: 4) TOC: 2)	*Rhepoxynius abronius* (Crustacea:Amphipoda) Marine infaunal. East Pacific boreal to temperate.	LC$_{50\ 10\ days}$ /Acute		2810	[8	4). TOC = 3%.

Experimental Methods:

1): Static exposure performed in Lake Michigan water (freshwater) with juvenile animals (4-8 mg wet-weight) collected from natural populations.

2): Static exposure performed in Lake Michigan water (freshwater) with adult animals collected from laboratory culture.

3): Static exposure performed with artificial pond water with adult animals collected from laboratory culture.

4): Static exposure performed at a salinity of 28 ppt with juvenile animals (body length 3 - 4 mm) collected from natural populations.

Protocols:

1): No reference to external protocol other than the published paper.

2): Protocol for exposure based on Kaster et al. [4].

3): Protocol for exposure based on ASTM E 1367-92 [6].

4): Protocol for exposure based on US-EPA [7].

Chemical Analysis:

1): Analysis of pyrene was performed by reversed phase HPLC.

2): TOC was analysed on a Perkin Elmer Model 2400 CHN analysator after removal of carbonates by acidification.

3): Analysis of pyrene was performed by determination of radioactive activity by liquid scintillation counting (LSC) after spiking pyrene with [^{3}H]pyrene.

4): Pyrene was quantified on a HP 5870 capillary gas chromatograph coupled with a mass spectrometer.

Comments:

1): Natural sediment collected at 45m depth in Lake Michigan, screened to 1mm and kept at 4°C prior to use. Background of approx. 70 ng g^{-1} pyrene in the exposure sediment acc. to Eadie et. al. [2]. Percent fines (<63 µm) 38±1.2%.

Appendix 4.17 Effect concentration data for pyrene continued.

2): Natural sediment collected at 45m depth in Lake Michigan, screened to 1mm and kept at 4°C prior to use. Background of approx. 250 ng g^{-1} pyrene in the exposure sediment acc. to Eadie et. al. [2]. 80% of the sediment particles was in the range 43 - 420 µm.

3): Natural sediment collected from a local drainage system, wet-sieved to < 125 µm and settled for one week at 4°C. Overlaying water siphoned off and replaced with Arificial Pond Water (APW) before resuspension and spiking.

4): Natural sediment from McKinney Slough, Oregon wet-sieved trough 0,5mm screen for removal of macrobiota and debris and settled for 24 hours at 4°C prior to spiking. Sediment a poorly sorted silt with 3% organic carbon and 40,6% solids.

References:

[1] Landrum, P.F., W.S. Dupuis and J. Kukkonen. 1994. Toxicokinetics and toxicity of sediment-associated pyrene and phenanthrene in *Diporeia* spp.: Examination of equilibrium-partitioning theory and residue-based effects for assessing hazard. Environ. Toxicol. Chem., 13: 1769-1780.

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[5] Lotufo, G.R. and J.W. Fleeger. 1996. Toxicity of sediment-associated pyrene and phenanthrene to *Limnodrilus hoffmeisteri* (Oligochaeta:Tubificidae). Environ. Toxicol. Chem., 15: 1508-1516.

[6] ASTM. 1993. Guide for conducting 10-day static sediment toxicity tests with marine and estuarine amphipods. E 1367-92. In: Annual Book of ASTM Standards. Vol 11.04. Philadelphia, PA, pp. 1138-1163.

[7] U.S. Environmental Protection Agency. 1994. Methods for assessing the toxicity of sediment-associated contaminants with estuarine and marine amphipods. EPA/600/R-94/025. Washington DC.

[8] Swartz, R.C., S.P. Ferraro, J.O. Lamberson, F.A. Cole, R.J. Ozretich, B.L. Boese, D.W. Schults, M. Behrenfield and G.T. Ankley. 1997. Photoactivation and toxicity of mixtures of polycyclic aromatic hydrocarbon compounds in marine sediment. Environ. Toxicol. Chem., 16: 2151-2157.

8.3. Appendix - Chapter 5

Appendix 5-1 Log barite/water partition coefficients (log K_p) for metals in the three barite samples in Table 5.2. Barite samples were incubated in 10:1 or 4:1 dilutions at pH 2,3 - 6 phthalate buffer for 15 minutes to 48 hours. K_p is the concentration ratio, µg/g metal in barite/µg/g metal in solution in water equilibrated with barite. Data fromTrefry and Trocine (2005). The Kp values recommended applied for metals in the sediments is also presented.

Metal/pH	Low Trace Metal	High Trace Metal	Laboratory Blend
Barium			
2.3	4.58	5.49	5.32
3	4.62	5.30	6.27
4	4.57	5.23	5.79
5	4.62	5.15	5.79
6	4.59	5.09	5.81
Cadmium			
2.3	0.84	1.03	1.31
3	0.94	1.26	1.36
4	1.19	1.33	1.48
5	1.30	1.57	1.70
6	1.46	1.70	1.99
Chromium			
2.3	2.74	2.17	2.67
3	3.12	2.45	2.82
4	3.21	2.71	2.91
5	3.37	3.06	3.07
6	3.85	3.43	3.24
Copper			
2.3	1.71	1.31	1.51
3	1.79	1.39	1.61
4	1.88	1.42	1.70
5	1.92	1.49	1.86
6	2.20	1.64	2.10
Iron			
2.3	2.92	2.64	2.79
3	3.10	2.81	4.45
4	3.29	3.02	4.81
5	3.83	3.63	4.86
6	4.92	4.85	4.66
Mercury			
2.3	6.54	5.25	7.48
3	6.94	5.31	7.58
4	>5.54	>4.77	>7.08
5	>5.54	>4.77	>7.08
6	6.7	5.77	7.78
Lead			
2.3	2.11	2.89	2.17
3	1.88	2.97	2.28
4	1.83	2.28	2.44
5	1.81	2.13	2.70
6	1.90	2.17	2.98
Zinc			
2.3	1.69	1.43	1.65
3	1.80	1.51	1.72

4	1.83	1.52	1.75
5	2.00	1.64	1.89
6	2.24	1.84	2.08

Estimation of Koc

Non-polar organic chemicals, such as PAH, partition between the particulate phase of the drilling discharge and the ambient water according to their relative affinities for the two phases. The main adsorbtive phase for PAH/aliphatics in sediment, drilling mud solids, or cuttings particles is the organic phase of the solids. Equilibrium between the organic phase of the waste particles and the water is expressed by the sediment organic carbon/water partition coefficient (K_{oc}). K_{oc} can be estimated from the octanol/water partition coefficient (K_{ow}), for which abundant data have been published, by the Equation from Di Toro et al. (2000):

$$\text{Log}\ (K_{oc}) = 0.00028 + 0.983\ \log\ (K_{ow})$$

K_{ow} values have been measured or calculated for these compounds; approximate K_{oc} values can be estimated from K_{ow} as described above. Values for log K_{oc} for a large number of PAH are summarized in Table 8.2. As indicated by the Equation, values for log K_{oc} are slightly lower than values of log K_{ow}.

Appendix 5-2. Log K_{ow} and log K_{oc} (US-EPA, 2003b).

PAH	Log K_{ow}	Log K_{oc}
Naphthalene	3.356	3.299
C1-Naphthalene	3.8	3.736
C2-Naphthalene	4.3	4.227
C3-Naphthalene	4.8	4.719
C4-Naphthalene	5.3	5.21
Fluorene	4.208	4.137
C1-Fluorene	4.72	4.64
C2-Fluorene	5.2	5.112
C3-Fluorene	5.7	5.603
Anthracene	4.534	4.457
Phenanthrene	4.571	4.494
C1-Phenanthrene/anthracene	5.04	4.955
C2-Phenanthrene/anthracene	5.46	5.367
C3-Phenanthrene/anthracene	5.92	5.82
C4-Phenanthrene/anthracene	6.32	6.213
Pyrene	4.922	4.839
Fluoranthene	5.084	4.998
C1-Pyrene/Fluoranthene	5.287	5.197
Benz(a)anthracene	5.673	5.577
Chrysene	5.713	5.616
C1-Benzanthracene/Chrysene	6.14	6.036
C2-Benzanthracene/Chrysene	6.429	6.32
C3-Benzanthracene/Chrysene	6.94	6.822
C4-Benzanthracene/Chrysene	7.36	7.235
Benzo(e)pyrene	6.135	6.031
Benzo(a)pyrene	6.107	6.003
Perylene	6.135	6.031
Benzo(b)fluoranthene	6.266	6.16
Benzo(k)fluoranthene	6.291	6.184
Benzo(g,h,i)perylene	6.507	6.397
Indeno(1,2,3-cd)pyrene	6.722	6.608

Appendix 5-3. Values for metals based on Crommentuijn, et al. 1997. Maximum Permissible Concentrations and Negligible Concentrations for Metals, taking Background Concentrations into Account. Report No. 601501001. National Institute of Public Health and the Environment Bilthoven, the Netherlands.

Metals (assume 10% organic matter)	**MPA_{water} (ug/L)**	**Log $K_{p\ (sed/water)}$[a] (L/kg)**	**MPA_{sed} (mg/kg)**	**Cb_{sed} (mg/kg)**	**MPC_{sed} (mg/kg)**
Arsenic	24	3,82	160	29	190
Barium	150	3	150	155	300
Cadmium	0,34	4,93	29	0,8	30
Chromium	8,5	5,28	1620	100	1720
Copper	1,1	4,53	37	36	73
Lead	11	5,63	4700	85	4800
Mercury (inorganic)	0,23	5,05	26	0,3	26
Mercury (methyl)	0,01	5,05	1,1	0,3	1,4
Nickel	1,8	3,72	9,4	35	44
Zinc	6,6	4,86	480	140	620

a. Log $K_{p\ (sed/water)}$: Partition coefficient between sediment and water based on monitoring data in marine surface water and sediment at different locations in the North Sea and Wadden Sea during 1995 (Yland, 1996).

8.4. Appendix - Chapter 7

8.4.1. An example of data analysis for derivation of ERL and ERM values for naphthalene from Long and Morgan (1990)

Appendix 7-1. Effects range-low (ERL) and effects range-median (ERM) values for naphthalene based on 28 mean effects concentrations arranged in ascending order. From Long and Morgan (1990).

Concentration (µg/kg dry wt: ppb)	End Pointa
77	Southern California bioassay (COA)
127	San Francisco Bay, CA, bioassay (COA
340	**ERL**
343	Puget Sound, WA, bioassay (COA)
414	Marine SLC
500	99 percentile EP chronic marine @ 1 % TOC
593	Commencement Bay, WA, bioassay (COA)
594	Commencement Bay, WA, bioassay (COA)
720	95 percentile EP chronic marine @ 1 % TOC
973	Commencement Bay, WA, bioassay (COA)
1501	Eagle Harbor, WA, bioassay (COA)
1564	Commencement Bay, WA, bioassay (COA)
2100	Puget Sound, WA, AET – amphipod
2100	Puget Sound, WA, AET - oyster
2100	**ERM**
2100	Puget Sound, WA, AET – benthic
2100	Puget Sound, WA, AET - Microtox™
2375	Elizabeth River, VA, bioassay COA
2400	Puget Sound, WA, AET - amphipod
2700	Puget Sound, WA, AET – benthic
3670	Marine SLC
3934	Puget Sound, WA, bioassay (COA)
6200	SSB with flounder
7370	SSB with flounder
10710	SSB with flounder
11500	Trinity River, TX, benthos (COA)
40000	Lake Union, WA, bioassay (COA)
42000	EP acute marine threshold @ 4 % TOC
53200	Elizabeth River, VA, bioassay (COA)
95000	Elizabeth River, VA bioassay (COA)

[a] AET, apparent effects threshold; COA, bioeffects/contaminant co-occurrence analysis; EP, equilibrium partitioning; SLC, screening level concentration; SSB, spiked sediment bioassay.

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

MUST, Multivariate Strategies as www.must.as Centre of Technology and Innovation Kjølnes Ring 30 N-3918 Porsgrunn, NORWAY Enterprise No.: NO 982768772MVA Phone: +47 35 57 40 00 Fax: +47 35 57 40 10		MEMO TITLE **Field Validation part II;-** **Comparing the results from the two approaches; Species Sensitivity Distribution and the Mowing Window Approach including operational implications.** AUTHOR(s) Frode Brakstad, MUST Anders Bjørgesæter, University of Oslo Salve Dahle, Akvaplan-niva CLIENT ERMS project / Ivar Singsas, SINTEF	
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Summary

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

Both methods have their limitations when it comes to decalines and THC, as these components are rapidly weathered and biodegraded at the seafloor. All data on the organic chemicals in MOD are probably considerably lower than the concentration at the time for exposure and impacting the benthic fauna. As the MWM method delivers pure FTV values, i.e. isolated FTV values for individual chemical toxic stressors, the problem of degrading of decaline and THC becomes pronounced, resulting in too low values. The SSD delivers f-PNEC values that are influenced by the presence of a combination of organic stressors and different ranges of pollution. As a consequence the rapid degrading of THC and decaline, becomes less pronounced and evident in the fPNEC estimates from the SSD method. This may explain a less good agreement between the pure FTV and the f-PNEC for the THC and decalines. The degrading of NPD and PAH is less rapid, resulting in a better agreement between the two methods.

By comparing the results from the field validation with the values derived from literature according to the Equilibrium Partitioning Method (EqP) (task 1), there is a fair agreement with only Mercury and Chromium as exceptions. The PNECs from field data are recommended used as model input for Mercury and Chromium.

CONTENT

1. Introduction

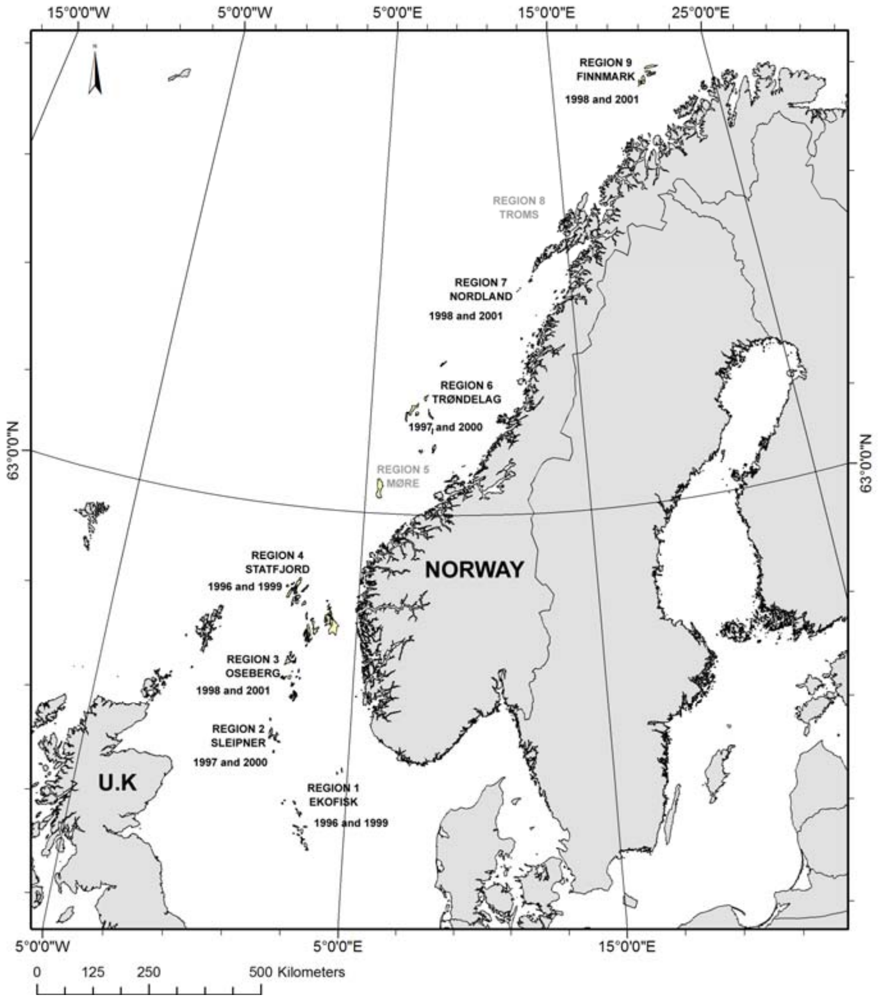
This memo compares and discusses the results from the two different approaches used in the field validation of the literature values. The f-SSD method shows the response of all the sensitive species (macro fauna) to the given contaminant in the presence of other contaminants. Thus, the f-SSDs account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

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

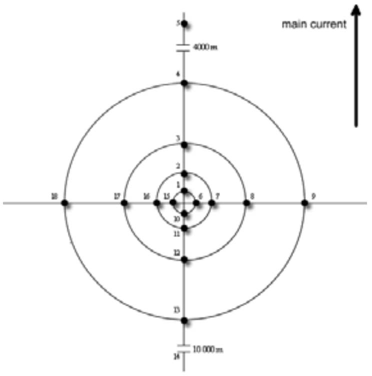
The methods have been described in detail in separate reports [1, 2].

Methods

Although the two approaches have used the same MOD data, they have collected the samples into different grain size intervals. Thus some simplifications are necessary in order to compare the TELs from the MWM and SSD method. The MWM TELs have been “averaged” by calculating the average for each of the 6 grain size intervals weighted by the number of stations, while the SSDs TELs have been averaged over 3 grain size intervals (Table 1). Note that these are values for comparison of the TELs from the two methods only.



Sampling design:



Taxa (1990 – 2001):

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

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

3. Comparison of field TELs

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

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

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

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

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

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

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

4. Discussion

4.1 Barium and the trace elements

There is a fairly good agreement between the average FTV and the f-PNEC values for the metals. As expected the FTV values calculated by the MWM approach are lower than the f-PNECs calculated from the SSD approach (on average 2.3 times lower in the range of 19 % for Hg to 104 % for Cr; Table 1). One exception is the Chromium where the f-PNEC and FTV values are almost the same (104%). Taking into account the inherent analytical variation[2] in the MOD and the uncertainties in estimating TELs (two quite different approaches), the agreement between the MWM and the SSD approaches for the trace elements may be considered to be fairly good as the relative ratio are on same level (19%-104%).

The organic compounds

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

The larger differences between the TELs for organic compounds than for metals may be partly explained by the uncertainties introduced by the time delay between the discharges to the sea floor and the sampling. Sampling takes place every three years, while the discharges to the sea floor from drilling operations and accidental spill (over time 12 % of the discharges all together) and produced water (88 %) may happen during the whole lifespan of an oil field [3]. The effect on the benthic macro communities are accumulated over all these years. Weathering and biodegradation of the organic compounds starts as soon as they are discharged. Within some days as much as 90% of the THC may be weathered (e.g. Grahl-Nielsen and Brakstad, 1986 [4]). Thus, at the time of sampling the concentration in the sediments of the organic compounds may be much lower than originally, however, their negative impact of the fauna may still be registered. This is illustrated in Figure 2:

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

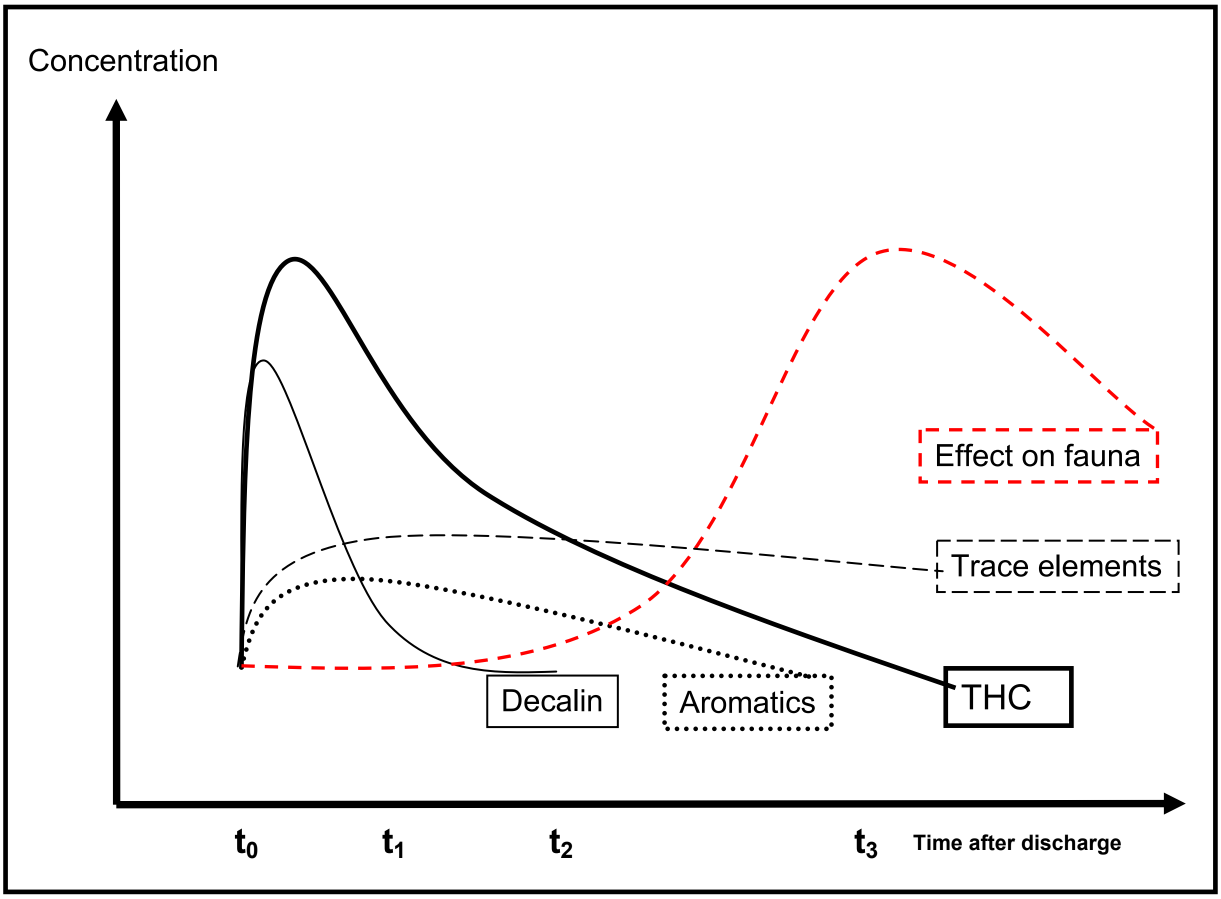

Figure 2: Illustration of the effect of time span between discharges of rapid degradable organics as THC and decaline and sampling time, while comparing concentrations in sediments and impacts on the benthic fauna.

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

Both methods have their clear limitation as they tend to correlate the concentration level of a specific organic compound (decalins) or group or organic compounds (THC, NPD and PAH) *at sampling time*

to a certain level at exposure time i.e. there is a time delay between the decrease in chemical concentrations and the restitution time of the biological community.
This suggests that most or all of the data on concentrations of organic compounds in sediments in MOD are lower than initially, and that the benthic fauna has been exposed to higher concentration of stressors than are measured at the time of sampling. As a result, our calculations from the SSD and the MWM will give too low TELs for the organics.

Comparison with literature and EqP values (task 1)

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

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

toxicity x equilibrium constants

resulting in the values as reported in Table 2.

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

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

* Background concentrations
** Based on samples from about 150 reference stations (extraction with nitric acid)
*** Based on total concentration of Hg. Also used as background concentration for Hg methyl
▪ Calculated from mean background concentrations from NCS
◊ Data from A. Bjørgesæter 2004
◊◊ Data from B. Grung et al 2005
b ER-L (Effects Range-Low) and ER-M (Effects Range-Median)
d TEL (Threshold Effect Level) and PEL (Probable Effect level)
TEL is a concentration which adverse effects to sediment-dwelling fauna would be observed infrequently. PELs represent concentrations above which adverse effects are likely to occur.

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

Thus we recommend that the field data for Mercury and Chromium to be used as PNECs for sediment, instead of the reported values from task 1. When discrepancies are as large as the ones for Chromium and Mercury, we suggest to trust the field data more than the theoretical ones. We could also argue that because both the methods gave more or less the same values, this is underlying the credibility of the field values.
Thus our recommendations for PNEC sediments are the one as reported below (operational implications).

5. Operational implications

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

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

Table 3: Recommended sediment PNECs for the metals

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

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

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

Conclusion

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

The outcome from the MWM analysis showed that the FTV values vary with grain size. This observation was not observed by the SSD approach for the f-PNECs, but may be supported from literature. Task 1 has also concluded that availability of toxic stressors adsorbed on sediment particles is dependent on fraction of water available[3].

Both methods have their limitations when it comes to decalines and THC, as these stressors are rapidly degraded. All concentration data on organic compounds in MOD represent the concentration at <u>sampling time</u>, and are probably considerably lower than the concentration at the time of discharge. The registered observed impacts on the benthic fauna from the hydrocarbons will in most samples correspond to significant higher values than the one registered in the MOD database.
As the MWM approach delivers “pure” FTV values , e.g. isolated FTV values for individual chemical toxic stressors (derived independent on the other chemical stressors), the rapid degrading of decaline and THC results in too low values. The SSD delivers f-PNEC values that are influenced by the presence of a number of other compounds, possibly being stressors. As a consequence the rapid degrading of THC and decaline becomes les pronounced and evident in the f-PNEC estimates from the SSD method. This may explain a less good agreement between the pure FTV and the f-PNEC for the

THC and decalines. The degrading of NPD and PAH is less rapid than the ones for THC and decalines [4], resulting in a better agreement between the two methods.

As a result of the degradation of organic compounds, the FTV values from the MWM approach will be too conservative. The effect on the quality of the f-PNEC values is not so simple to estimate, but these values will also probably be too conservative as an estimate related to 5% risk.
Consequently, we recommend to use the estimated PNECs from Task 1 as input to the EIF sediment model for *i*) hydrocarbons[4], *ii*) chemicals and *ii*) trace elements with the exception of Mercury and Chromium.

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[3] "*Bioavailability of metals in sediments and hence toxicity is related to* <u>*chemical activity*</u> *in the sediment-pore-water system, and can therefore better be expressed by toxicity in the pore-water*", from pp presentation Task 1

[4] *When values for organic components are provided through Task 1. We do not recommend that the field PNEC for the hydrocarbons are used as input to the EIF sediment model.*

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