report

ERMS

Environmental Risk Management System

B&O-DH-R2005/181 Open
Date 29.05.2005

ERMS Report no. 10

From PEC_PNEC ratio to quantitative risk level using Species Sensitivity Distribution

M.G.D. Smit, K.I.E. Holthaus, J.E. Tamis, C.C. Karman

Program participants: - Agip - Conoco Phillips - Exxon Mobil - Hydro - Petrobras - Shell - Statoil - Total

TOTAL

BR

Eni

HYDRO

ConocoPhillips

ExxonMobil

STATOIL

onderzoek / Netherlands Organisation
for Applied Scientific Research

Laan van Westenenk 501
Postbus 342
7300 AH Apeldoorn
The Netherlands

www.tno.nl

T +31 55 549 34 93
F +31 55 549 32 01
info@mep.tno.nl

TNO-report

B&O-DH - R 2005/181

From PEC_PNEC ratio to quantitative risk level using Species Sensitivity Distributions;

Methodology applied in the Environmental Impact Factor

Date	June 29, 2005
Authors	M.G.D. Smit K.I.E. Holthaus J.E. Tamis C.C. Karman
Order no.	33981
Keywords	Species Sensitivity Distributions, PEC:PNEC, Risk assessment, Produced water, EIF
Intended for	ERMS project group

Summary

Part I

Although the definitions of risk differ among users of risk assessment methodologies, the basics of risk assessment related to the aquatic environment are universal. They comprise a comparison of the exposure of (a part of) the ecosystem to a chemical with the sensitivity of the ecosystem for this chemical. The exposure is often represented by the PEC (Predicted Environmental Concentration). The sensitivity is often expressed in a PNEC (Predicted No Effect Concentration). A comparison of the PEC and the PNEC; the PEC_PNEC ratio, is a widely accepted and applied endpoint in aquatic risk assessment models intended for screening and hazard characterisation.

With the PEC_PNEC ratio as endpoint for risk assessment, the definition of risk is related to the definition of the PNEC. At PEC_PNEC ratios higher than 1, unacceptable effects on organisms are likely to occur. The higher the ratio, the more likely it is, that unacceptable effects may occur. According to the definitions of risk, the endpoint of a risk assessment should include a quantification of the likelihood and a characterisation of the extent of effects. The PEC_PNEC ratio does not comply with this definition. It does not provide any characterisation of the expected impact and is just an indication of the likelihood and no quantification. This is adequate for identification of the possibility of occurring impacts and for prioritisation, but not for real impact assessment.

The EU-TGD provides **one** definition of the PNEC, and **two** methods to derive its value. The first method uses assessment factors to establish the level of the PNEC from the lowest available EC50 or NOEC value. The second method uses a cut-off value (usually 5%) of a Species Sensitivity Distribution (SSD) based on chronic NOECs. Theoretically the two methods should give the same result. This implies that irrespective what procedure is used to derive the PNEC, its value will always correspond to a probability of 5% of a random species being exposed above its chronic no effect concentration (which can be statistically tested and be regarded as a confidence interval).

With the PNEC being the 5 percentile of a SSD based on chronic NOECs, the PEC_PNEC ratio together with the slope of the SSD do give a quantification of the likelihood (probability estimate) and a characteristic of the extent of effects (fraction of species having effects caused by the toxicant). Therefore, when the PEC_PNEC ratio is translated to a quantified risk value using the SSD, the endpoint of the risk assessment will be in accordance with the accepted definition of risk (quantification of the likelihood and a characterisation of the extent of effects). The challenge that remains for ecotoxicologists and policymakers is the definition of what effects are acceptable (or unacceptable) related to ecosystem health.

Part II

Produced water may contain natural components and added chemicals. In order to characterise this complex mixture 11 groups of substances have been defined (Johnson *et al.*, 2000). The groups are based on chemical structure of the components. It is assumed that the chemical and toxic properties of the components within the same group are comparable. Based on available toxicity data for the components in the different groups, one representative PNEC value and one representative Species Sensitivity Distribution (SSD) is defined for each group. Based on the results of a statistical analysis of the average toxicity per component within one group, grouping of these components can not be justified. However, it is practical to keep this classification as it is also based on analytical methods, methods for treatment and physical properties. It is decided to use the precautionary principle in the derivation of the PNEC for one group (PNEC for one group of components is derived from toxicity data of the most toxic component within that group). The classification of substances based on chemical structure can still be applied.

Based on the defined PNEC values and the constructed SSDs, concentration-to-risk curves (a curve describing the relationship between exposure concentration and risk) and PEC_PNEC-to-risk curves (a curve describing the relationship between PEC_PNEC ratio and risk) are derived for all groups. These separate PEC_PNEC-to-risk curves show that there is a wide range of variation in species sensitivity which is component-group specific. This means that the likelihood of effects occurring at a certain PEC_PNEC ratio differs per component group. This is also the reason why PEC_PNEC ratios for different groups should not be added.

The defined average PEC_PNEC-to-risk curve from this study is not significantly different from the PEC_PNEC-to-risk curve which was derived by Karman & Reerink (1997). This old curve was based on toxicity data for 17 components which are only a small selection of the components present in produced water discharges. This curve has been used in the calculation of the EIF (Environmental Impact Factor) for produced water releases (Johnson *et al.*, 2000). In this study risk calculations on four produced water profiles are carried out in order to identify effects of replacing this old PEC_PNEC-to-risk curve by the new average curve or by the separate curves for the different groups as established in this study.

From the calculations it is observed that differences in the cumulative risk value calculated with the different PEC_PNEC-to-risk curves for four realistic produced water profiles depend mainly on the dilution of the produced water release. At a dilution where the PEC is close to the PNEC there is hardly any difference in the value of the cumulative risk present. At higher and lower dilutions the observed differences in the cumulative risk increase. However the difference in the cumulative risk stays within the same range, well within the expected uncertainty limits.

At PEC_PNEC ratios higher than 1, the small differences in the calculated contributions of the 11 substances to the overall risk indicate that, the choice of the PEC_PNEC-to-risk curve applied has only a limited influence on the contribution distribution of the separate components.

Therefore it can be concluded that replacing the old PEC_PNEC-to-risk curve by the separate curves for the different component groups is a refinement of the PEC_PNEC-to-risk calculation. However, this will not change the results of the EIF calculations nor the contributions to risk of separate components in a large extent. It is suggested to update the EIF calculation with the new average curve for added chemicals and the separate curves for the different groups as derived in this study.

Index

PART I From PEC:PNEC to risk; quantification of risk

1. Introduction

1.1 Definition of Environmental Risk Assessment (ERA)

Environmental Risk Assessment (ERA) has become a generally used tool in the evaluation of the potential environmental impact of chemical products or activities. According to ISO (ISO, 2002) the term risk can be interpreted as "*the combination of the probability of an event and the consequences of this event*". In the case of environmental risk assessment applied to operational discharges the probability of occurrence of the event is often equal to 1 (discharges are taking place). Therefore the definition of risk in ERA mainly focuses on the consequences.

The more widely accepted definition of risk related to the procedure of risk assessment was formulated in 1983 by the US National Research Council (USEPA): "*the characterisation of the potential adverse health effects of human exposure to environmental hazards*''. The UK Department of Environment defines risk assessment as "*the structured gathering of the information available about risks and the forming of a judgement about them*". Risk assessment has since developed into a series of guidelines for conducting ecological risk assessment (USEPA, 1998).

Within the EU, risk assessment is defined as: "*A process of evaluation including the identification of the attendant uncertainties, of the likelihood and severity of (an) adverse effect(s) / event(s) occurring to man or the environment following exposure under defined conditions to (a) risk source(s)*". A risk assessment comprises hazard identification, hazard characterisation, exposure assessment and risk characterisation, and is an integrated part of the risk management procedure (Figure 1). These four steps of the risk assessment process were first elaborated by the US national research council (USEPA, 1993) and are adopted by the EU (EC, 2003). A summery of EC guidance and practice was published in 1998 (EC, 1998).

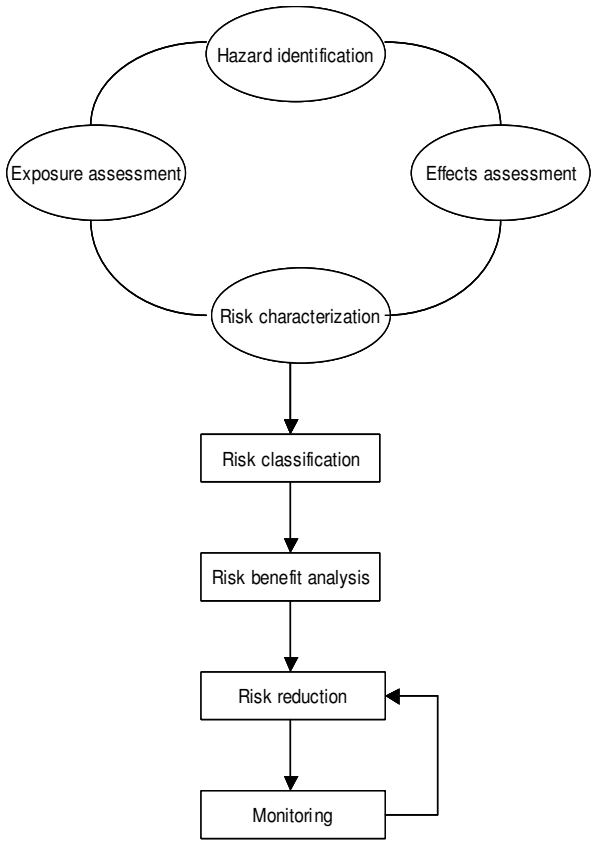


Figure 1 Steps in the risk management process.

The guidance on and requirements for environmental risk assessment for US Naval Operations has explicitly included the marine environment. Recently (2003) the EU has published the updated Technical Guidance Document (EU-TGD) on risk assessment containing a technical guidance specified to marine risk assessments (EC, 2003). OSPAR[1] agreed to adopt the guidelines for risk assessment as described in the EU-TGD as the common EU/OSPAR approach on risk assessment methodology for the marine environment (OSPAR agreement 20-2003).

From the sources and definitions of risk as mentioned above, the following general characteristics of the assessment endpoint of ERA can be derived:

- The assessment endpoint of risk assessment should include a quantification of the likelihood and severity of biological effects.

[1] The OSPAR Convention entered into force on 25 March 1998. It replaces the Oslo and Paris Conventions, but Decisions, Recommendations and all other agreements adopted under those Conventions will continue to be applicable, unaltered in their legal nature, unless they are terminated by new measures adopted under the 1992 OSPAR Convention.

Comparison of the results of the assessment with criteria set on the likelihood and severity of effects in carried out to check whether the risk is within acceptable limits.

1.2 Basics of ERA and chemical exposure

If the process of Environmental Risk Assessment (ERA) is applied to chemical exposure, the assessment is based on a comparison of the exposure of (a part of) the ecosystem to a chemical with the sensitivity of (the same part of) the ecosystem for this chemical (through this specific exposure-route) (Suter, 1993) (see Figure 2 for a schematic overview). The exposure is represented by the PEC (Predicted Environmental Concentration), and can be obtained by actual field measurements (monitoring data) or by estimations using environmental fate models. The toxicity threshold (PNEC; predicted No Effect Concentration) represents the sensitivity of the ecosystem, and is usually derived from standardised toxicity tests. The EU-TGD (EC, 2003) prescribes the use of a PEC:PNEC approach (comparison of PEC and PNEC) as a general tool for environmental risk assessment.

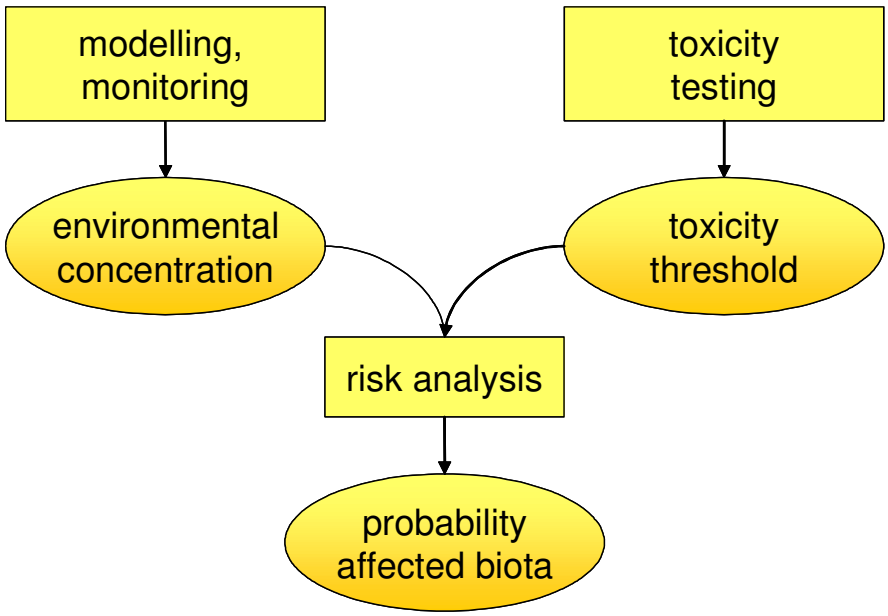


Figure 2 *The above scheme represents the general framework for environmental risk assessment, based on the comparison of an environmental concentration with the sensitivity of the environment.*

Part I of the current report describes the use of the PEC_PNEC ratio in ERA. Estimation procedures and definitions for the PNEC are presented together with the strengths and weaknesses of the PEC_PNEC ratio. The use of two different estimation methodologies for the PNEC is discussed together with the possibility to quantify the endpoint of risk assessment when these methodologies are integrated. Chapter 3 describes how the PEC_PNEC ratio can be translated to a quantitative

risk estimate, which is more in line with the general definition of risk. Approaches to be followed when limited data are available, are described in chapter 4. Chapter 5 presents an overview of the main conclusions of part I.

2. The use of the PNEC in ERA

One of the challenges in environmental risk assessment is to have an adequate estimation of the sensitivity of the environment towards the toxicant. Usually one fixed value is derived to represent the sensitivity of the environment to a specific toxicant. This threshold value is often referred to as the PNEC (Predicted No Effect Concentration). The definition of the PNEC according to the EU Technical Guidance Document (TGD) (EC, 2003) is:

The concentration below which unacceptable effects on organisms will most likely not occur.

When the ratio of PEC and PNEC (often referred to as the PEC_PNEC ratio or the RCR - Risk Characterisation Ratio) exceeds 1, unacceptable effects on organisms will most likely occur as a result of exposure to the specific chemical. It does, however, not provide a quantification of the environmental risk. (See also Scholten *et al*., 2000). The exact meaning of 'unacceptable effects' (or acceptable effects) is not presented and the uncertainty level of 'most likely' is not defined.

Typical risk assessment models, based on the PEC:PNEC approach, which are applied for the use of chemicals by the oil and gas industry, are EUSES (European Union System for the Evaluation of Substances) and CHARM (Chemical Hazard Assessment and Risk Management). Both models are specially developed for use in protective hazard assessments and prioritizing of chemicals and are adopted by regulators in the EU. EUSES is developed in the EC for risk assessment of new and existing substances and pesticides (Vermeire *et al*., 1997) and based on the Dutch USES model (Jager & Visser, 1994). Within OSPAR the hazard assessment module of CHARM is the mandatory tool for selecting the most environmental friendly production, drilling, or work-over chemical (Thatcher *et al.*, 1999).

2.1 Estimation of the PNEC

The TGD provides two ways to estimate the value of the PNEC. One is making use of assessment factors. The second uses a Species Sensitivity Distribution (SSD). As a result of scarce data the first method is most commonly used.

2.1.1 Assessment factors

Assumptions are made concerning the aquatic environment which allow, however uncertain, an extrapolation to be made from single-species short-term toxicity data to ecosystem effects. It is assumed that:

- Ecosystem sensitivity depends on the most sensitive species, and;
- The protection level for ecosystem structure is sufficient for the protection of community function.

These two assumptions have important consequences. By establishing which species is the most sensitive to the toxic effects of a chemical in the laboratory, extrapolation can subsequently be based on the data from that species. Furthermore, the functioning of any ecosystem in which that species exists is protected, provided the structure is not sufficiently distorted as to cause an imbalance. It is generally accepted that protection of the most sensitive species should protect structure, and hence function. For most substances, the pool of data from which to predict ecosystem effects is very limited. In general, only short-term toxicity data are available. In these circumstances, it is recognized that, while not having a strong scientific validity, empirically derived assessment factors must be used. Assessment factors have also been proposed by the US-EPA and OECD. In applying such factors, the intention is to predict a concentration below which any unacceptable effect will most likely not occur. It is not intended to be a level below which the chemical is considered to be completely safe. However, again, it is likely that an unacceptable effect will not occur (EC, 2003).

In principle, the PNEC is calculated by dividing the lowest LC_{50}/EC_{50} or NOEC value for three trophic groups of marine organisms by an appropriate assessment factor in accordance with the TGD. The assessment factors are applied to extrapolate from laboratory single-species toxicity data to multi-species ecosystem effects. When only short-term toxicity data are available, an assessment factor of 1000 will be applied on the lowest LC_{50}/EC_{50} of the relevant available toxicity data, irrespective of whether or not the species tested is a standard test organism. A smaler assessment factor will be applied on the lowest NOEC derived in long-term tests with a relevant test organism (EC, 2003).

The assessment factors address a number of uncertainties:
- interspecies variation (biological variance);
- short-term to long-term toxicity extrapolation;
- laboratory data to field impact extrapolation.

Table 1 The assessment factor scheme as used for calculating PNEC values (EC, 2003)

Available toxicity data	**Assessment factors**
At least one short-term EC_{50} from each of three trophic levels (algae, crustaceans and fish)	1000
Long-term NOEC from one trophic level (either fish or crustaceans)	100
Long-term NOEC from species representing two trophic levels (fish and/or crustaceans and/or algae)	50
Long-term NOEC from at least three trophic levels (fish, crustaceans and algae)	10
Field data or model ecosystem	Reviewed on a case to case basis

2.1.2 Species Sensitivity Distributions

A second method to define a PNEC value is the use of statistical extrapolation methods using the variation in species sensitivity (see Aldenberg & Jaworska (2000) for a review). If a large data set with NOECs from long-term experiments for different taxonomic groups is available, these values can be used to draw a distribution. This distribution that describes the variability of hazard of a substance to organisms is called a Species Sensitivity Distribution (SSD). This distribution can be presented as a frequency distribution (cumulative normal distribution curves or other similar distribution curves) of NOEC values for species. In general the method works as follows: toxicity data are log transformed and fitted to a distribution function. For the description of dose-effect curves, several distribution functions have been proposed for this; Weibull distribution (Kodell & Felton, 1991), log-logistic (Kooijman, 1987), lognormal (Wagner & Løkke, 1991) etc. It has however been shown that the choice of a distribution is quite arbitrary and is mostly done based on best fit results (Kooijman, 1981; Newman *et al*., 2000; Smit *et al*., 2001; Van der Hoeven, 2001 and Wheeler *et al*., 2002;). In this report we chose to use the log-normal distribution. For this cumulative log-normal distribution, NOEC values for species are fitted to a logarithmic scale. The mean (Xm) of this curve represents the position of the distribution on the x-axis and the standard deviation (Sm) determines the slope of the curve. In terms of the sensitivity of species, the Xm gives an indication of the *mean toxicity* expressed as the mean NOEC value of a substance. The Sm represents the *toxicity range* or *variation in sensitivity* of a substance. The main assumption on the use of SSDs in risk assessment is that the distribution based on a selection of species (tested in laboratory experiments) are representative for all species (in the field) (Aldenberg & Jaworska, 2000; Posthuma *et al*., 2002; Forbes & Calow, 2002a and 2002b). Figure 3 presents a Species Sensitivity Distribution described by a log-normal distribution.

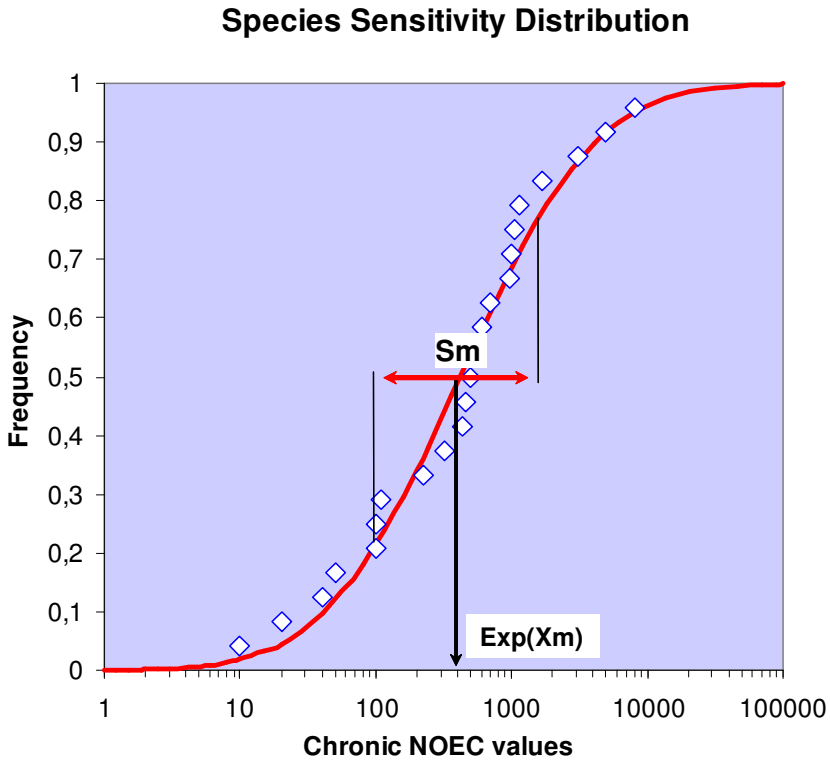


Figure 3 *Species Sensitivity Distribution for one toxic compound based on chronic NOEC values, described by the variation in sensitivity (Sm) and the median sensitivity (Xm).*

Statistical extrapolation methods may be used to derive a PNEC from a SSD by taking a prescribed percentile of this distribution. For pragmatic reasons it has been decided that the concentration corresponding with the point in the SSD profile below which 5% of the species occur, should be derived as an intermediate value in the determination of a PNEC. This 5% point in the SSD is also identified as a hazardous concentration (HC) at which a certain percentage (in this case 5%) of all species is assumed to be affected (e.g. Van Straalen & Denneman, 1989, Aldenberg & Slob, 1993; Newman *et al.*, 2000; Van der Hoeven, 2001; EC, 2003). Attempts to validate this choice of the 5th percentile have been made, however the choice remains quite arbitrary (Okkerman *et al.*, 1993; Versteeg *et al.*, 1999).

This methodology can only be applied in cases where sufficient NOECs of good quality for sufficient species are available. Confidence can be associated with a PNEC derived by statistical extrapolation if the database contains at least 10 NOECs (preferably more than 15) for different species covering at least 8 taxonomic groups (EC, 2003; Posthuma *et al.*, 2002). If this is not the case the estimation of the PNEC and the variation between species is unreliable and assessment factors or other approaches should be used (see paragraph 4). When

sufficient data is available the PNEC is calculated according to Aldenberg & Slob (1993):

$$PNEC = 5\%\ SSD\ (50\%\ \ c.i.) based\ on\ chronic\ \ NOECs \qquad (1)$$

Figure 4 presents a graphical overview of the relation between the value of the PNEC and the SSD based on chronic NOEC values.

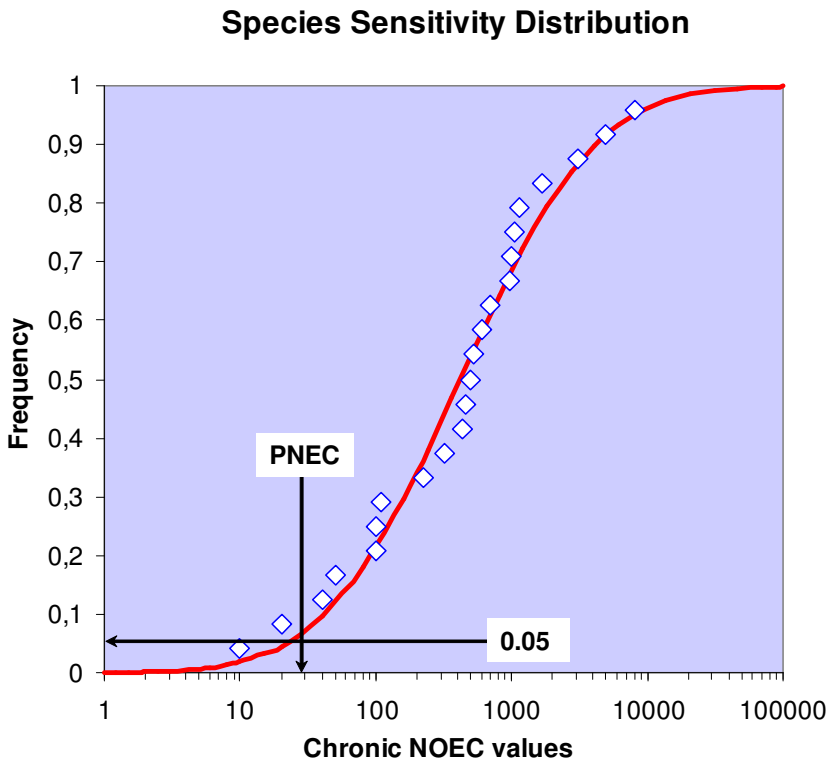


Figure 4 *Estimating the PNEC from a SSD based on chronic NOECs for most sensitive endpoints per species.*

When the PNEC is derived in this way, “unacceptable effects” are related to the effects for which the NOECs apply. The TGD prescribes that the most sensitive endpoint should be used as representative for a species. This implies that the SSD describes effect levels of the most sensitive endpoints for all species in the ecosystem. The term “most likely” in the definition of the PNEC can statistically be tested using the SSD based on chronic NOECs. This is because the PNEC level is set at a value of 5%. This can be regarded as a confidence interval, below which the effect is regarded as insignificant.

2.2 Interpretation of PNEC and risk

The EU-TGD provides **one** definition of the PNEC, and **two** methods to derive this value (as described in the previous paragraph). As the result of both calculations is interpreted in the same way, theoretically the two methods should give the same result. This implies that also the PNEC calculated with assessment factors should correspond to a probability of 5% of a random species being exposed above its chronic no effect concentration (which can be statistically tested and be regarded as a confidence interval) (e.g. Van Straalen & Denneman, 1989; Aldenberg & Slob, 1993; Newman *et al.*, 2000; Van der Hoeven, 2001; Aldenberg & Jaworska, 2000)).

With the PEC_PNEC ratio as endpoint for risk assessment it will be obvious that the definition of risk is related to the definition of the PNEC. A PEC_PNEC ratio higher than 1 indicates that unacceptable effects on organisms are likely to occur; the higher the ratio, the more likely that unacceptable effects may occur. According to the definitions of risk as mentioned in chapter 1, risk should include a quantification of the likelihood and a characterisation of the extent of effects. It becomes clear that the PEC_PNEC ratio does not comply with this definition. The PEC_PNEC ratio is just an indication of the likelihood and no quantification. This is adequate for identification of possible impacts and for prioritisation. However, it does not provide any characterisation of the expected impact.

With this interpretation of the PNEC as being the 5^{th} percentile of a SSD based on chronic NOECs, the PEC_PNEC ratio together with the slope of the SSD do give a quantification of the likelihood and a characteristic of the extent of effects. Therefore the endpoint of the risk assessment is in accordance with the definition of risk. However, even in this revised state there are limitations when one considers the lack of ecosystem dynamics, such as food web relationships, incorporated into the assessment model, with the major focus at the species level of organisation. Besides that the question was raised how representative the species are, on which the SSD is based, for specific environments (Forbes & Calow 2002a and 2002b). The challenge that still remains for ecologist and ecotoxicologists is the definition of what effects on the ecosystem are acceptable or unacceptable in relation to the most sensitive endpoints on the species level. Thus developments in risk assessment models should focus on the translation from laboratory species to field communities. In addition, these uncertainties in the risk assessment procedure should always be stated clearly (Calow & Forbes, 2003).

3. From risk indicator to risk level

3.1 From PEC-to-risk level

Taking into account the definition of the PNEC and the two defined ways to derive the value of the PNEC as described in the previous chapter, it can be stated that when the PEC is equal to PNEC (PEC_PNEC ratio =1); the probability that a random species is effected by the toxicant is equal to 5% and that the risk on adverse effects is equal to 5%. At any other level of exposure the probability that a species is affected by the toxicant is equal to the respective frequency in the Species Sensitivity Distribution. This probability is defined as the risk at that level of exposure. Figure 5 presents this procedure for a specific PEC value. The x-axis in this figure is defined as a concentration –axis. On this axis the NOEC values, the PNEC and the PEC are plotted.

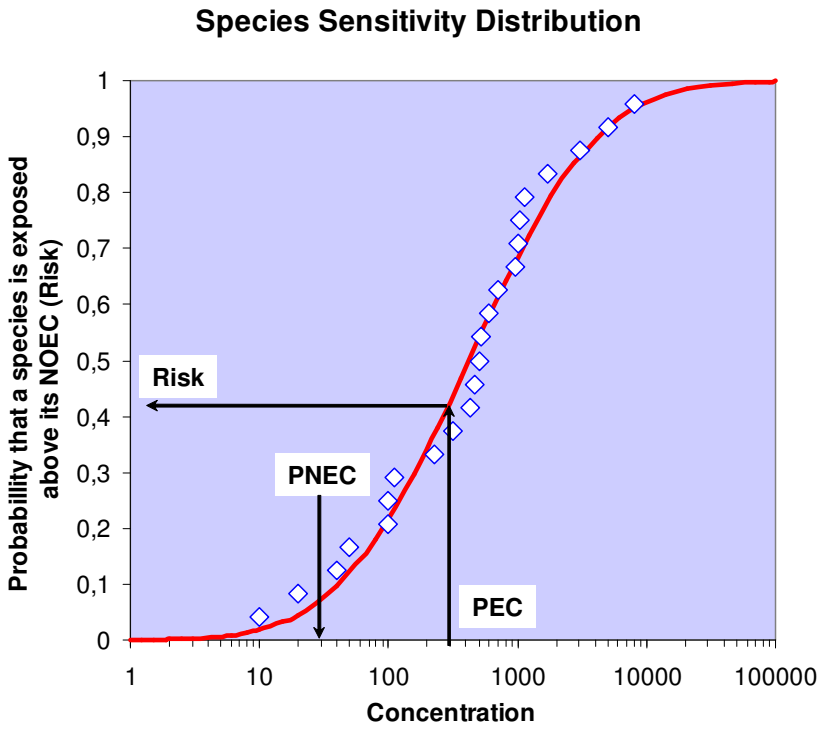


Figure 5 Use of SSD for translating PEC values to risk values.

With this PEC-to-risk curve, which is based on the empirically estimated variation in sensitivity amongst marine biota, the PEC can be translated into a quantitative risk measure (i.e. the probability that an organism will be affected).

The information needed for this translation of PEC to quantitative risk level, is the description of the SSD (Xm and Sm from Figure 3). The relationship between PEC and risk can be calculated according to the following formula:

$$R = \int_{0}^{\ln PEC} \left\{ \frac{1}{S_m * \sqrt{2 * \pi}} * e^{\frac{-(\ln PEC - X_m)^2}{2 * S_m^{\,2}}} \right\} \quad \text{.....} \qquad (2)$$

in which:
R = *risk (probability that a species will be affected)*
Xm = *mean of the logarithmically transformed data*
Sm = *standard deviation of the logarithmically transformed data*
PEC = *exposure concentration*

The values for Xm and Sm can only be obtained from a dataset with sufficient chronic NOEC values for sufficient species (Posthuma *et al*., 2002; EC, 2003). However, the availability of chronic NOECs is usually low. This complicates the estimation of Xm and Sm. The SSD can also be described by The PNEC and the Sm. For these two parameters estimation procedures are available. An estimation procedure for the PNEC using assessment factors and single toxicity values was already described in section 2.1 of this report. An estimation procedure for the Sm is described in section 4 of this report.

3.2 From PEC_PNEC ratio to risk level

The concentration scale on the x-axis of the graph in Figure 5 can be translated into a PEC_PNEC ratio scale when the values on the axis are divided by the (constant) value of the PNEC. This will result in a shift of the total curve until the value PEC:PNEC = 1 corresponds to a risk value of 5%. Mathematically this will mean a change in the value of the Xm. The Sm will keep the same value.

When the x-axis is transformed from concentration-axis to PEC_PNEC ratio-axis, the value of the PNEC is not longer required to define the resulting PEC_PNEC-to-risk curve. For example in the case of industrial chemicals, for which the toxicity data may be confidential, the value of the PNEC is unknown. For the determination of the PEC_PNEC-to-risk curve only the value of the Sm of the SSD is needed. The Xm is obtained by shifting the distribution with this Sm until a x-value of 1 corresponds to a risk of 5%. This 5% is chosen as a cut-off criterion. The exposure of organisms to substances in their aquatic environment is considered acceptable is case less than 5% of the species is at risk at a PEC_PNEC ratio of 1 (e.g. Van Straalen & Denneman, 1989, Aldenberg & Slob, 1993; Newman *et al.*, 2000; Van der Hoeven, 2001; EC, 2003). Figure 6 presents an example of a PEC_PNEC-to-risk curve.

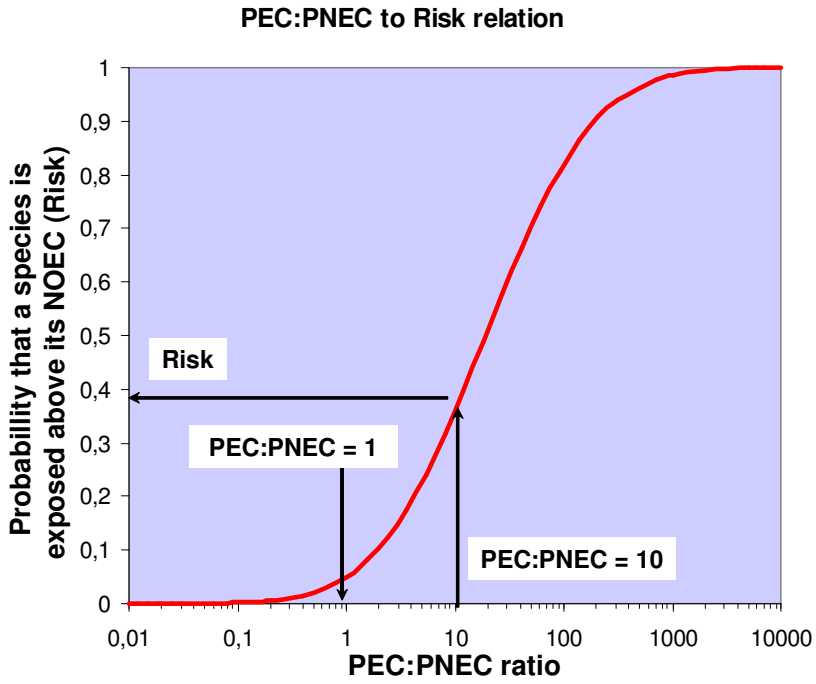


Figure 6 *Species Sensitivity Distribution scaled to the PNEC resulting in a PEC_PNEC-to-risk curve.*

The information needed for this translation of PEC:PNEC to quantitative risk level, is the Sm value from the SSD (Figure 3). The relationship between PEC_PNEC ratio and risk can be calculated according to the following formula:

$$R = \int_{0}^{\ln PEC:PNEC} \left\{ \frac{1}{S_m * \sqrt{2 * \pi}} * e^{\frac{-(\ln PEC:PNEC - X_m)^2}{2 * S_m^{\,2}}} \right\} \ldots \qquad (2)$$

in which:

R = *risk (probability that a species will be affected)*
Xm = *mean of the distribution for which PEC_PNEC ratio =1; risk = 5%*
Sm = *standard deviation of the logarithmically transformed data*
PEC = *exposure concentration*

The Xm value in the PEC_PNEC-to-risk curve is different from the Xm value from the PEC-to-risk curve. The value for the Sm is the same. This value for Sm can be obtained from a dataset with sufficient chronic NOEC values for sufficient species (Posthuma *et al*., 2002; EC, 2003). However, as mentioned earlier, the availability of chronic NOECs is usually low. This complicates the estimation of Sm. For the Sm estimation procedures are available, which are described in section 4 of this report.

3.3 Mixture toxicity estimated by combining probabilities

When the environment is exposed to a mixture of different toxicants, the corresponding risk values (probabilities) can, unlike PEC_PNEC ratios, be combined. For all components in the mixture the variation of sensitivity of species is taken into account and the affected fraction of species per component can be summarised assuming independency. It is assumed that when combining many chemicals synergistic and antagonistic effects cancel each other out. Formula 3 is used to calculate the overall (cumulative) risk for a mixture of two substances:

$$R(A+B) = R(A) + R(B) - R(A) * R(B) \quad (3)$$

with,
R(A) = *probability that a species will be affected due to an exposure to chemical A,*
R(B) = *probability that a species will be affected due to an exposure to chemical B,*
R(A+B) = *probability that a species will be affected due to both chemicals A and B.*

4. Unavailability of data

As presented in the previous chapter the PEC can be translated into a quantified risk level by using the SSD based on chronic NOECs for many species. In practice, the number of data needed to construct the SSD is hardly available (Posthuma *et al*., 2002). Two parameters are needed to construct the SSD; The PNEC or the Xm and the Sm. For the PNEC and the Sm estimation procedures are available in the case not sufficient NOECs are available. These procedures are making use of acute toxicological data. The availability of (acute) E(L)C50 values is much higher than the one for chronic NOECs and also for much more species data is available. A way to derive the value of the PNEC from acute toxicity data by applying safety factors is already presented in section 2.1.1. The next section will describe procedures to estimate the variation in species sensitivity.

4.1 Estimation of the variation in species sensitivity

4.1.1 Using SSD based on acute data

In the ideal situation the variation in species sensitivity is derived from a large dataset of chronic NOEC values. A distribution can then be fit on this data (as explained in section 2.2). The variation of this distribution (the standard deviation for the log-normal distribution) is a measure for the variation in sensitivity between the species (Figure 3). The uncertainty in the value of this parameter depends on the availability of data. The more data are available the better the estimation for this value will be. However the availability of chronic NOECs is very low. In Posthuma *et al.* (2002) a comparison is presented of variation in species sensitivity based on chronic NOECs and based on acute EC50 values. From this comparison it is concluded that variation in species sensitivity is comparable based on either NOECs or EC50 values. The more data points are available the more the two estimates of variation in species sensitivity are alike (Posthuma *et al*., 2002). This implies that the variation of species sensitivity (the Sm from the SSD) based on the more available EC50 values can be used for constructing the PEC_PNEC-to-risk relationship (Figure 7).

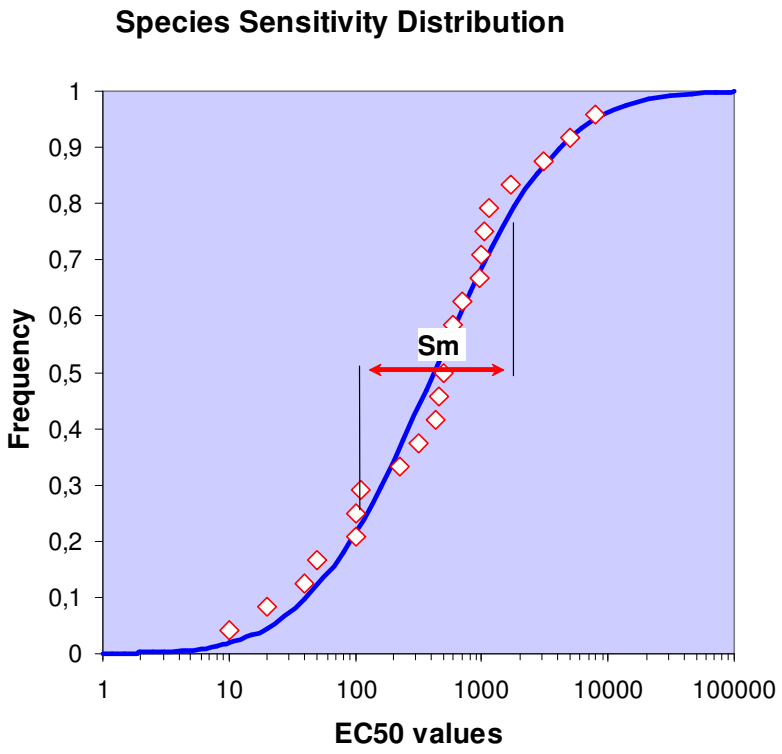


Figure 7 *Variation in species sensitivity based on EC50 values can be used as an estimate for the variation in species sensitivity based on chronic NOECs.*

4.1.2 Using species variation based on mode of action

Also the mode of toxic action of the toxic compound can be used to derive the variation in sensitivity between species. It is assumed that chemicals with the same mode of action have comparable values for the variation between species (Sm). In Posthuma *et al*. (2002) the results of a comparison study are presented. From this study it is observed that for chemicals tested on many species, the value of Sm converged to a fixed value related to the toxic mode of action of that component. The variation in sensitivity between species is smaller for chemicals with a narcotic mode of action than for chemicals with a specific mode of action. This was reflected in the Sm.

Table 2 *Mode of action related to the variation in sensitivity between species. Taken from Posthuma* et al. *(2002) (Sm is calculated from reported β values using relationship taken from Smit et al., 2001)*

Toxic mode of action	Number of chemicals	Average Sm
Nonpolar narcosis	34	0.66
Polar narcosis	13	0.53
Organophosphates	27	1.21
Diesters	6	0.71
Carbonyl compounds	2	0.48

As the availability of chronic NOECs for most substances is low, estimation procedures based on acute toxicity data are useful. The procedures for the estimation of the PNEC and the Sm presented in this report, can easily be applied. With the values of PNEC and Sm, the PEC-to-risk and the PEC_PNEC-to-risk curves can be constructed. With these curves exposure estimates and PEC_PNEC ratios can easily be translated in to quantified risk values.

5. Conclusions of part I

The PEC_PNEC ratio is commonly reported as endpoint of risk assessment. This ratio indicates whether the exposure is expected to be higher (or lower) than the defined threshold (PNEC). The PNEC is the concentration below which unacceptable effects on organisms will likely not occur. Toxicants with equal PEC_PNEC ratios (e.g. for a toxicant with a generic mode of action and a toxicant with a specific mode of action) can have different impacts on the environment (Jager *et al*., 2001). PEC_PNEC ratios are just indicators of risk and do not provide a quantification of the environmental risk (Scholten *et al*., 2000). Indicators should not be added.

Risk can be expressed as the probability that a random selected species is exposed above its chronic NOEC. This probability equals the fraction of affected species at a certain exposure concentration. With the PNEC defined as the 5^{th} percentile of the SSD (e.g. Van Straalen & Denneman, 1989, Aldenberg & Slob, 1993; Newman *et al.*, 2000; Van der Hoeven, 2001; Aldenberg & Jaworska, 2000) the PEC_PNEC ratio can be converted into the fraction of effected species using the Species Sensitivity Distribution based on chronic NOECs for the selected toxicant. Unlike indicators, probabilities can be added and compared to indicate the stressor with the highest contribution to the overall impact. The PNEC and Sm of the SSD are required to go from exposure to PEC_PNEC ratio to quantified risk value (probability). Both parameters can be obtained from the SSD based on chronic NOECs. However estimation procedures are available which use acute toxicity data as well. The PNEC can be estimated using assessment factors, The SSD can be based on EC50 values or the mode of action of a toxicant.

Combining the assessment factor approach and SSD approach does not solve the issue of uncertainty in risk assessment. It is questioned how representative the SSD based on laboratory species is for all species (Forbes & Calow 2002a and 2002b). For this study this discussion is not limited to the PNEC derived from the SSD but also to the variation among species. In Posthuma *et al*. (2002) the results of a comparison between laboratory-based SSDs and field-based SSDs is presented. From this study it can be concluded that laboratory-based SSDs can be used to represent field species, however uncertainty in the assessment is associated with the explicit absence of ecological interactions in the assessment using SSDs. However the EU defines risk assessment as; “A process of evaluation including the identification of the attendant uncertainties, of the likelihood and severity of adverse effects. ..”. (EC, 1998). Therefore, SSDs can be helpful in combining risks of different stressors, as long as the uncertainties of the outcome are an explicit part of the assessment. However this becomes less important when the methodology is applied in risk assessment for prioritising purposes for which two assessments with the same level of uncertainty are compared.

PART II PEC:PNEC to risk; application in the EIF

1. Introduction

The discharge of produced water to the sea results in an input of a mixture of contaminants into the water column. Concern exists on the impacts and risks resulting from these releases. Therefore the discharge of produced water is regulated and evaluated using environmental management systems. One of the recent developed environmental managements systems is the Environmental Impact Factor for produced water (EIF) (Johnson *et al.*, 2000; Grini *et al*., 2002). The calculation of the environmental impact factor is based on the guidelines for risk assessment as prescribed by the EU- technical Guidance Document for risk assessment (EU-TGD; EC, 2003). This implies that a PEC_PNEC ratio is used to indicate whether a risk is present or not.

In addition to the standard risk assessment procedure the methodology to quantify risk described in Part II is applied in order to compare and combine the contribution of the single components to the overall risk of the mixture. This is done in order to identify the main contributor to the overall risk. Reducing this contributor is most effective in the reduction of the risk. The data that is needed for this risk assessment procedure are the PNEC values and the slopes of the SSDs (Sm) for the most important chemical groups in produced water as well as for added chemicals.

For this purpose, EC_{50} and NOEC data have been collected to determine the PNEC and the slope of the SSD. With this information PEC_PNEC-to-risk curves for *each* of the 11 groups of substances and the 'mean' PEC_PNEC-to-risk curve for *all* the 11 groups of substances are defined. Chapter 2 of this part of the report describes the data collection and analysis. PEC_PNEC-to-risk relationships will be defined and presented. In the final chapter of this part, risk calculations are presented based on four discharges profiles. Different relationships are used to calculate the risk and the contribution to risk and results are presented and discussed.

2. PNECs and SSD-slopes (Sm) for the component groups as defined for the EIF

2.1 Data collection

Produced water contains natural components from the reservoir and added (production) chemicals to facilitate the production process (e.g. fluid separation, corrosion inhibition, oxygen scavenging). In order to characterise this complex mixture 11 groups of substances have been defined (Johnson *et al.*, 2000). The components are grouped based on their chemical structure. Table 3 gives an overview of these groups. Additional to components in these groups production chemicals are included.

Table 3 Composition of the defined groups of substances in produced water

Group no.	Main group	Substances
1	BTEX	Benzene, toluene, ethylbenzene, xylene
2	Naphthalenes	Naphtalene + C1-C3 Alkylhomologues
3	PAH 2-3 ring	Substances on the EPA 16 PAH list with 2-3 rings
4	PAH 4-ring+	Substances on the EPA 16 PAH list with 4 ring or more
5	Alkylphenols C0-C3	Phenol + C1-C3 alkylphenols, incl. Alkyl-homologues
6	Alkylphenols C4-C5	C4-C5 alkylphenols, incl. Alkylhomologues
7	Alkylphenols C6+	C6-phenol and higher, incl. Alkylhomologues
8	Aliphatic hydrocarbons	
9	Metals 1	Zn, Cu and Ni
10	Metals 2	Hg, Cd and Pb
11	Organic acids	Total organic acids (<C6)

For this analysis for 11 defined groups of substances in produced water (Table 3) acute EC_{50} and chronic NOEC values for fresh water and marine aquatic organisms were obtained from Frost (2002). Additional toxicity data for substances in these groups were extracted from the TNO database MEDUSA's Head.

For most chemicals, i.e. the chemicals belonging to the 11 defined groups, the available data are primarily acute, whereas regulators and assessors are primarily concerned with chronic effects. Most EC_{50} data were obtained for BTEX and for the metals Zn, Cu and Ni (Figure 8). Very few NOEC data (less than 10 data) were available for groups of substances, except for the >C6 alkylphenols. For the metals Hg, Cd and Pb and the organic acids (groups 10 and 11, respectively) NOEC data were lacking. Figure 8 and Figure 9 present the total amount of EC_{50}s and NOECs for each chemical group. Table 21 in Annex 1 presents details of the available EC_{50} data per component per group. Most toxicity data concerned crustacean, mollusc and fish species.

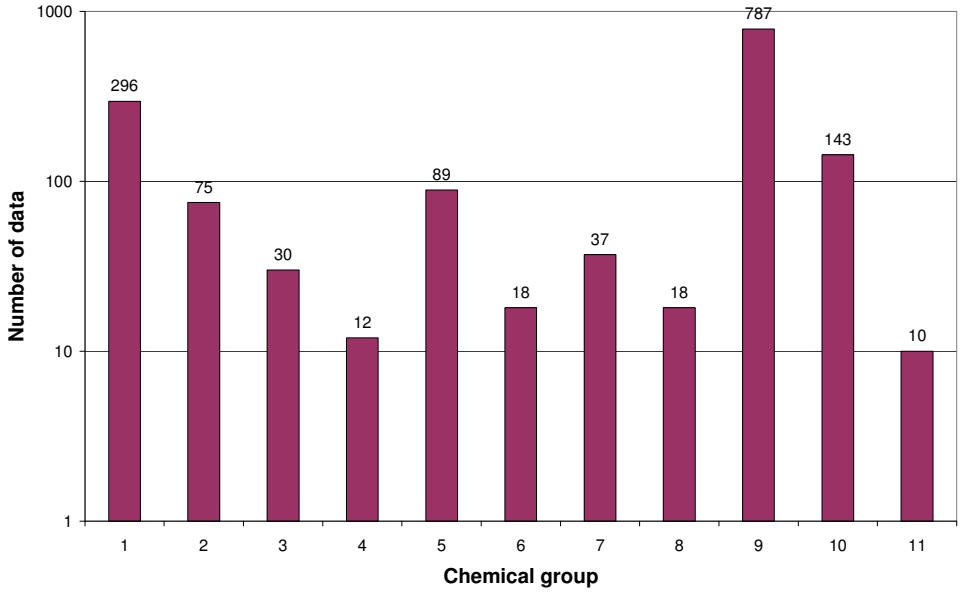


Figure 8 Number of EC_{50}s specified per chemical group.

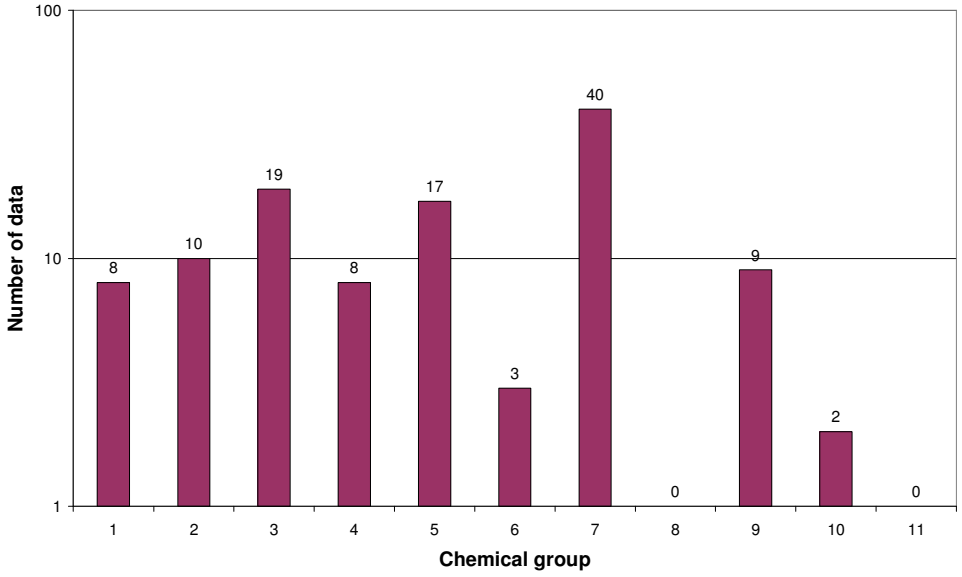


Figure 9 Number of NOECs specified per chemical group

For the added production chemicals the only toxicity data that is available is acute data delivered on the HOCNF (Harmonised Offshore Chemical Notification Format) (OSPAR Recommendation 2000-5 and OSPAR Reference 2003-1). For most chemicals this data is confidential.

2.2 Derivation of a PNEC per group

In order to represent the toxicity of the components in the group one PNEC value for the group is derived. This PNEC can be based on all collected toxicity data of the components within one group when it is assumed that the chemical and toxic properties of the components within the same group are comparable. To check this assumption, it was statistically tested if the average EC_{50} of a component within one group is not significantly different from the average EC_{50} of another component in the same group. The set of EC_{50}s was selected for this because of the scare NOEC data for some groups.

An 1-way ANOVA is performed for all defined group(s) of substances in produced water using the statistical software package Graphpad Prism for Windows version 2 (1995). Also the influence of other parameters that might influence the value of the average EC_{50} value were included in this analysis (e.g. trophic groups, fresh or salt water, type of endpoints (mortality, photosynthesis, growth, behaviour, immobilisation, reproduction or biochemical effect), exposure duration (<1, 1-3 and >3 days for EC_{50} values). The results of the statistical analysis on the logarithmically transformed EC_{50} values with a 1-way ANOVA or t-test are shown in Table 22 in Annex 2.

From the statistical analysis can be concluded that, in general, the components within one group do not have a comparable toxicity. In 7 of the 11 groups there is a significant difference in the average EC_{50} values for components within one group. Only for group 5, 7, 8 and 11 this significance cannot be determined.

Based on the results of the statistical analysis of the average toxicity per component within one group, it can be stated that grouping of these components can not be justified. However it is practical to keep this classification as it is also based on analytical methods, methods for treatment and physical properties of the components in the produced water effluent. It was decided to use the precautionary principle in the derivation of the PNEC for one group. This means that the PNEC for a group is based on the toxicity data of the most toxic component within that group. Now the classification of substances based on chemical structure can still be applied.

As for added production chemicals the number of available toxicity data is low (maximum of 3 values). This implies that an SSD for these chemicals cannot be constructed. The PNEC must be derived using assessment factors as described in section 2.1.1. As the final results from the risk calculations for the added chemicals and the natural components from the 11 defined groups will be compared, the assessment factor approach is also used to derive a PNEC for the natural components. Frost (2002) calculated PNEC values from acute and/or chronic toxicity data by using assessment factors according to the methodology for effect assessment described in the TGD (EC, 2003). The calculated PNECs are listed in

Table 4. The data sets for metals were so large that it was decided not to group the metals (Frost, 2002). Risk assessment for each metal is performed separately.

Table 4 Calculated PNEC values (Frost, 2002) for the 11 defined groups of substances in produced water.

Group no.	Group of substances	PNEC (µg/l) Frost (2002)
1	BTEX	17
2	Naphthalenes	2.1
3	PAH 2-3 ring	0.15
4	PAH 4-ring +	0.05
5	Alkylphenols C0-C3	2
6	Alkylphenols C4-C5	0.36
7	Alkylphenols C6+	0.04
8	Aliphatic hydrocarbons	40.4
9	Metals 1 (Cu, Ni and Zn)	0.046, 0.02, 1.22#
10	Metals 2 (Cd, Hg and Pb)	0.028, 0.182, 0.008$
11	Organic acids	n.a.

n.a. not available
PNEC values respectively for Cu, Ni and Zn
$ PNEC values respectively for Cd, Hg and Pb

2.3 Derivation of SSD-slopes (Sm) per group

The second parameter (next to the PNEC) needed to translate the PEC_PNEC ratio into a quantified risk endpoint is the slope of the SSD (Sm). An often-mentioned disadvantage of SSDs is that they require relatively large data sets for each substance. Discussions of numbers of data that are required continue to this date. In the TGD (2003) it is proposed to use at least 10 toxicity data representing at least eight taxa. As produced water will be discharged into the pelagic environment, a limited number of taxa (i.e. algae, crustaceans, fish) are representative for this environment. Therefore, a minimum of data for 10 species within these taxonomic groups is considered to be in good agreement with other authors, for aquatic risk assessment (Wheeler *et al.,* 2002). For comparison, the minimum data set in the Netherlands is currently four data representing four taxa. From a scientific perspective, and in relation to the analysis of fundamental statistical features of the data set, the number of data that is required for a profitable assessment is not fixed (Posthuma *et al.,* 2002). Because of the low availability of chronic NOECs for some groups, the slope of the SSD based on EC_{50} values is used to represent the slope of the SSD based on chronic NOECs (See part I, chapter 4).

Figure 10 shows the Species Sensitivity Distributions (SSD) based on EC_{50} values for 9 groups of substances when toxicity data of all components within one group is combined.

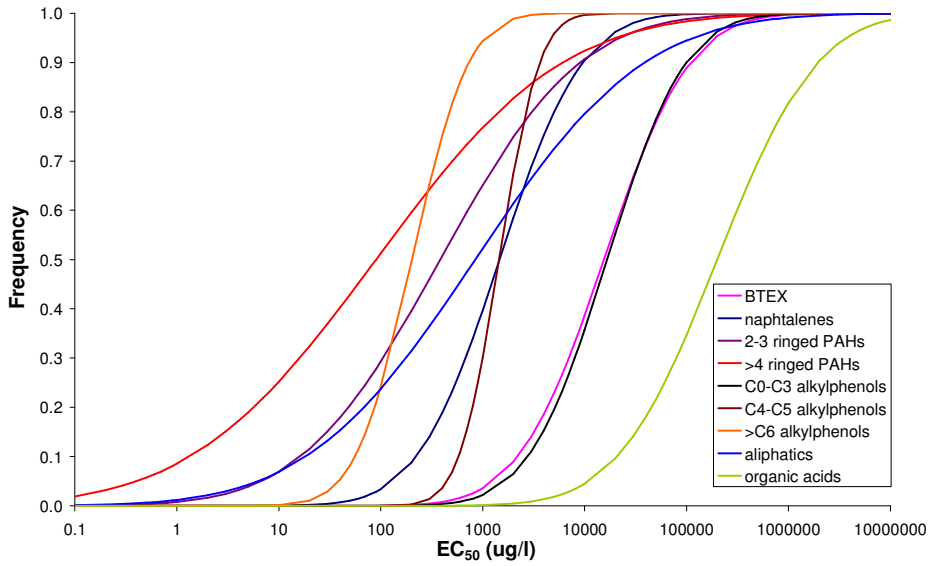


Figure 10 The Species Sensitivity Distributions (SSD) for 9 groups of substances in produced water based on EC50 values (on a logarithmic scale).

The SSDs show that species are the most sensitive for one or more components in the group of ≥ 4 ringed PAH and the least sensitive for the group of organic acids (as shown by the position of the curves on the x-axis). The SSD for the naphthalene's, C0-C3 alkylphenols, C4-C5 alkylphenols and >C6 alkylphenols have the steepest slopes (a low value for the Sm), indicating that EC_{50} values for species in the dataset are in the same order of magnitude for these groups of substances.

Combining the toxicity values of the different components can be defended when the components within one group have a comparable median toxicity and comparable variance in the EC_{50} values (i.e. both the average EC_{50}s as the slopes of the SSDs for single components should be comparable if the components are in the same group). However, the results of the statistical analysis of the logarithmically transformed EC_{50} values with a 1-way ANOVA or t-test, as shown in Table 22, indicate that, for 7 of the 11 groups, the average EC_{50} of the components in one group are significantly different from each other. This implies that the toxicity values of the components within one group cannot be combined in order to construct the SSD.

From the results of the 1-way ANOVA can also be observed that a significant difference in the value of the Sm for different components within one group could not be indicated. It can be concluded that the slopes of the SSDs for the single components in the groups are comparable. Based on this similarity the grouping of components can be defended.

As the median toxicity of components within one group differs, the Sm values from Figure 10 cannot be used as a representative for the group SSD. In order to define the Sm value representative for a group, the SSDs for the single components within one group are constructed (See Annex 1). The average of the Sm values for the single components within one group is used to represent the Sm value for the group. Table 5 presents an overview of the average Sm values per group.

Table 5 Average Sm values for the 11 groups of produced water components based on the Sm values for a presented number of components within one group

Group no.	Main Group	Group Sm
1	BTEX	1.16
2	Naphthalenes	1.43
3	PAH 2-3 ring	1.30
4	PAH 4-ring+	2.01
5	Alkylphenols C0-C3	1.28
6	Alkylphenols C4-C5	0.37
7	Alkylphenols C6+	0.77
8	Aliphatic hydrocarbons	1.37
9	Metals 1	
	Cu	1.99
	Ni	2.26
	Zn	1.83
10	Metals 2	
	Cd	2.42
	Hg	1.96
	Pb	2.08
11	Organic acids	2.06

As the metals are treated separately, the Sm can directly be derived from the SSD based on the EC_{50} values. Figure 11 presents the SSD for the six metals separately.

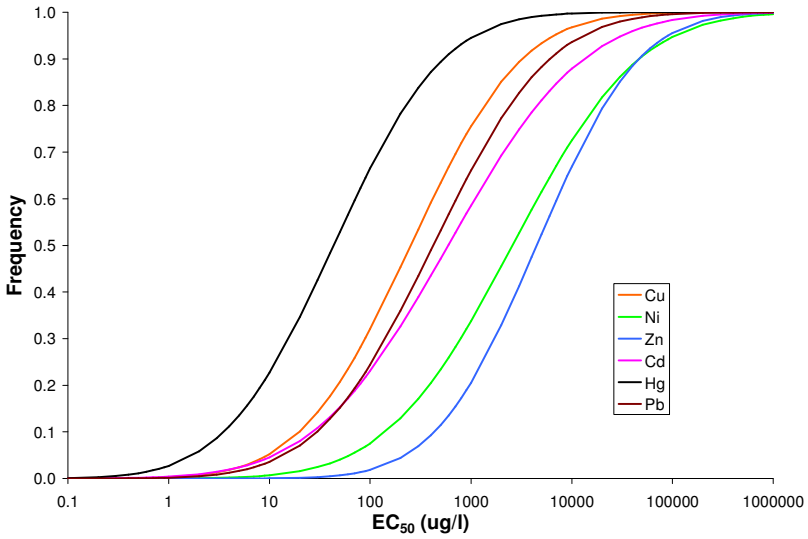


Figure 11 *The Species Sensitivity Distributions (SSD) for metals of group 9 (Cu, Ni and Zn) and 10 (Cd, Hg and Pb) based on EC50 values (on a logarithmic scale).*

The slopes (Sm) of the SSD for metals are roughly equal, which indicates that the variation in EC_{50} values for these substances is similar for all substances.

2.4 PEC-to-risk curves

As explained in part I of this document the estimated PNEC from the toxicity data and the Sm from the SSD based on EC_{50} values can be used to construct the PEC-to-risk curve. For each component group the value of the estimated PNEC (representative for the most toxic compound in the group) from Frost (2002) is scaled to a risk value of 5%. The average Sm per group is used to construct the curve presenting the relation between concentration and risk. *Figure 12* presents these concentration-to-risk relationships for 8 groups of produced water components. Figure 13 presents the same relationships for the six metals.

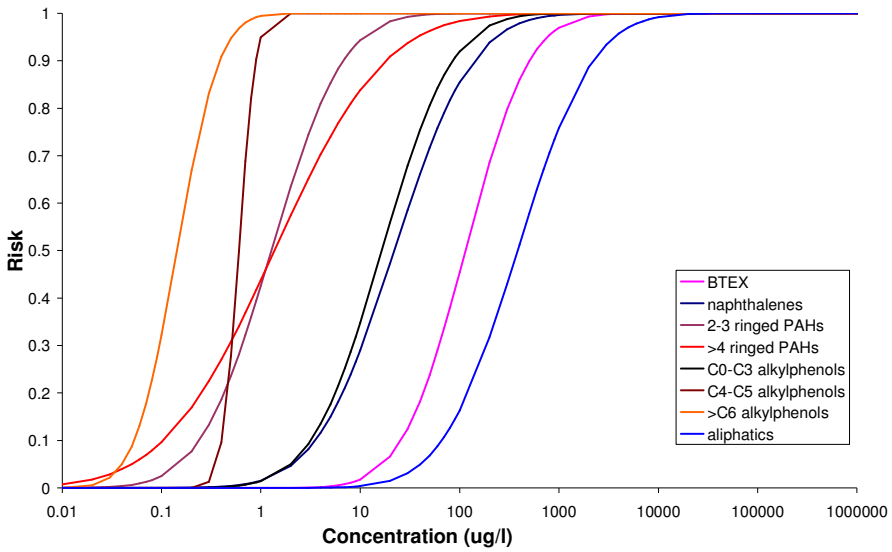


Figure 12 *PEC-to-risk curves, describing the relationship between concentration (µg/l) and risk (probability) for 8 groups of substances in produced water (on logarithmic scale).*

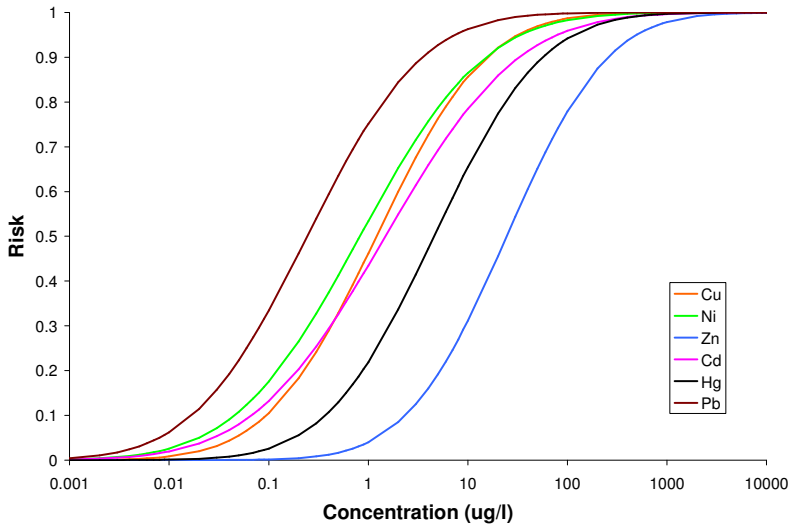


Figure 13 *PEC-to-risk curves, describing the relationship between concentration (µg/l) and risk (probability) for metals of group 9 (Cu, Ni and Zn) 10 (Cd, Hg and Pb) in produced water (on logarithmic scale).*

Table 6 provides an overview of the Sm and Xm values for the concentration-to-risk relationships. Because of the low PNEC values and the comparable values for the Sm, Pb is the most toxic and Zn the least toxic metal compound.

Table 6 Xm and Sm values for the concentration-to-risk curves for the 11 defined groups of substances in produced water. Xm values apply for the distribution with a risk of 5% at the PNEC.

Group.	Main Group	Group Sm	Xm (PNEC at 5% risk
1	BTEX	1.16	4.74
2	Naphthalenes	1.43	3.09
3	PAH 2-3 ring	1.30	0.24
4	PAH 4-ring+	2.01	0.32
5	Alkylphenols C0-C3	1.28	2.80
6	Alkylphenols C4-C5	0.37	-0.51
7	Alkylphenols C6+	0.77	-1.95
8	Aliphatic hydrocarbons	1.37	5.95
9	Metals 1		
	Cu	1.99	0.19
	Ni	2.26	-0.19
	Zn	1.83	3.20
10	Metals 2		
	Cd	2.42	0.40
	Hg	1.96	1.52
	Pb	2.08	-1.41
11	Organic acids	2.06	n.a.

n.a. not available

From the curves for the non-metal components, it can be concluded that aliphatics are the least toxic and have a relative high variation in species sensitivity. However, the impact related to aliphatics exposure will, as for all other components, depend on the concentration (PEC). Of the non-metals, the PAHs with >4 rings are the most toxic components in the produced water (effects might occur at very low concentrations), however at higher concentrations the risk level of exposure to > C6 alkylated phenols will be higher.

2.5 PEC_PNEC-to-risk curves

As described in part I of this document, the concentration-to-risk curve can be translated to a curve describing the relationship between a PEC_PNEC ratio and risk probability. The position of each distribution as presented in the previous paragraph has to be recalibrated. After recalibration the PEC_PNET-to-risk curves cross at: PEC_PNEC ratio = 1; and a risk value = 5%. Figure 14 presents the PEC_PNEC-to-risk curve for 8 component groups as defined in the EIF. The PEC_PNEC-to-risk curves for metals of group 9 (Cu, Ni and Zn) and group 10 (Cd, Hg and Pb) are shown in Figure 15.

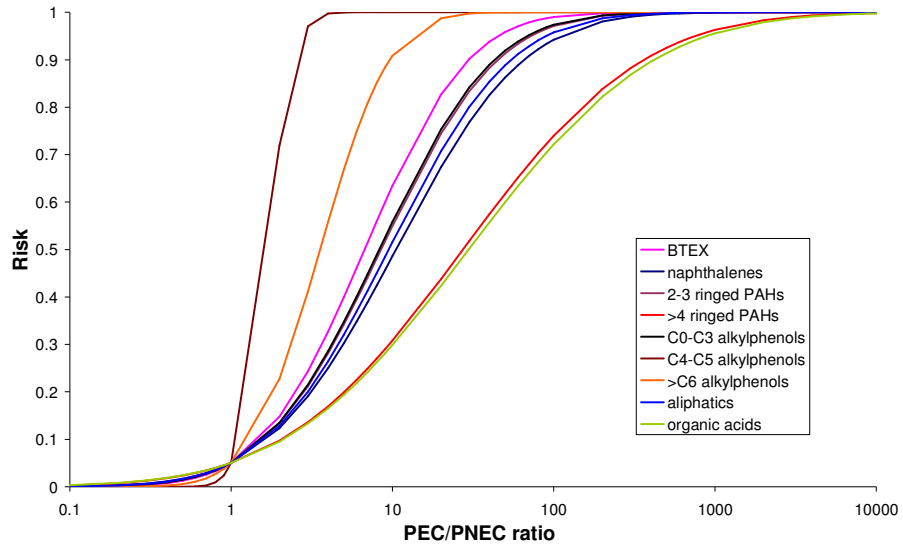


Figure 14 *PEC_PNEC-to-risk curves, describing the relationship between PEC_PNEC ratio and risk (probability) for 9 groups of substances in produced water (on logarithmic scale).*

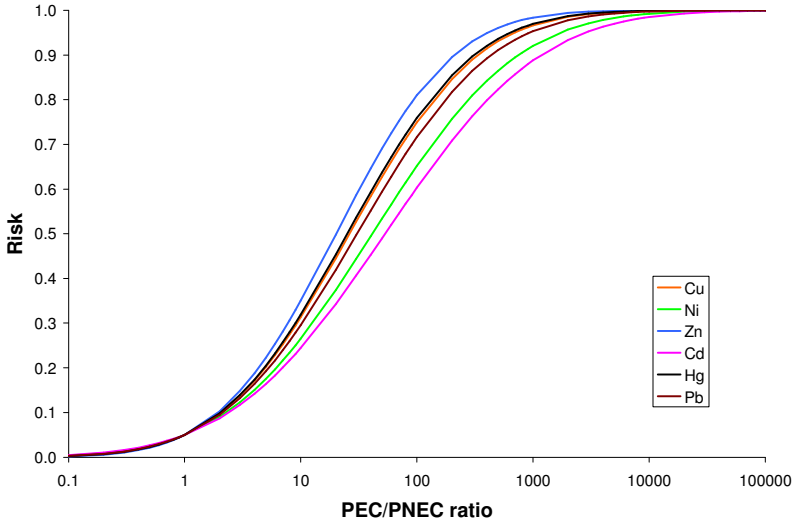


Figure 15 *PEC_PNEC-to-risk curves, describing the relationship between PEC_PNEC ratio and risk (probability) for metals of group 9 (Cu, Ni and Zn) 10 (Cd, Hg and Pb) in produced water (on logarithmic scale).*

The different Sm values of the different groups result in a steep or shallow PEC_PNEC-to-risk curves. For metals there is only a relative small difference between the values of the Sm, resulting in comparable PEC_PNEC-to-risk curves. Table 7 provide an overview of the corresponding Sm and Xm values.

Table 7 Xm and Sm values for the PEC_PNEC-to-risk curves for the 11 defined groups of substances in produced water. Xm values apply for the distribution with a risk of 5%. At the PEC_PNEC ratio of 1.

Group	Main Group	Group Sm	Xm (PEC/PNEC of 1 at 5% risk)
1	BTEX	1.16	1.90
2	Naphthalenes	1.43	2.35
3	PAH 2-3 ring	1.30	2.14
4	PAH 4-ring+	2.01	3.31
5	Alkylphenols C0-C3	1.28	2.11
6	Alkylphenols C4-C5	0.37	0.51
7	Alkylphenols C6+	0.77	1.27
8	Aliphatic hydrocarbons	1.37	2.25
9	Metals 1		
	Cu	1.99	3.27
	Ni	2.26	3.72
	Zn	1.83	3.00
10	Metals 2		
	Cd	2.42	3.97
	Hg	1.96	3.23
	Pb	2.08	3.47
11	Organic acids	2.06	3.39

2.6 Comparison of different PEC_PNEC-to-risk curves

The relationship presently used in the EIF to calculate the PEC_PNEC ratio into a risk measure for the different components in produced water is based on toxicity data for 17 different substances. Karman and Reerink (1997) presented an overview of the data and the derivation of the relationship. The 17 chemicals, for which the SSD was constructed, cover a range of different chemical groups including heavy metals, aromatic hydrocarbons, alkylated phenols, and pesticides. The substances have simply been selected because sufficient data values were available for the derivation of SSDs based on acute toxicity (EC_{50}s). However, the substances only partly reflect the composition of produced water. Figure 16 presents the different SSDs of the 17 components of the Karman & Reerink (1997) study. From these separate SSDs one average SSD with a generic value for Sm (variation in sensitivity between species) has been derived. This Sm value (1.74) was used to define the relationship between the PEC_PNEC ratio and the quantitative risk value as explained in Chapter 2 (Xm value of this curve is 2.85).

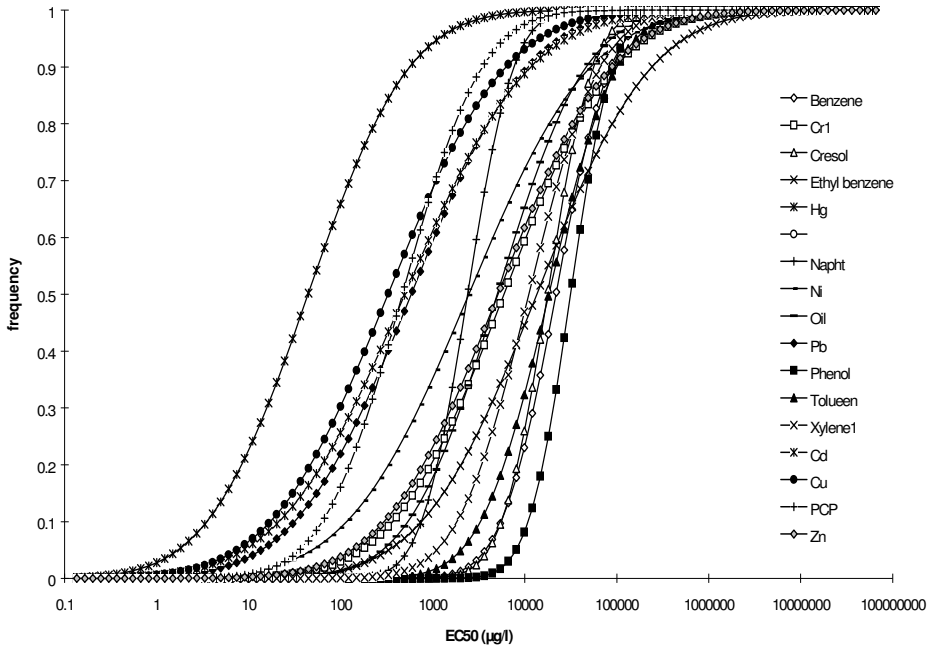


Figure 16 The PEC-to-risk curves for 17 substances defined by Karman and Reerink (1997).

In the current study separate PEC_PNEC-to-risk curves based on the SSDs for relevant (groups of) substances of produced water are defined. It is suggested to replace the *old* -Karman & Reerink (1997) - *average* PEC_PNEC-to-risk curve by the *separate* PEC_PNEC-to-risk curves for the different component groups, when this result in significant different results. Figure 17 shows, the 'average' PEC_PNEC-to-risk curve derived from this study, compared to the *old* curve from Karman and Reerink (1997). It is indicated that the *new average* curve is somewhat steeper than the *old* curve. The Sm and Xm values of the new average curve are 1.39 and 2.28 respectively)

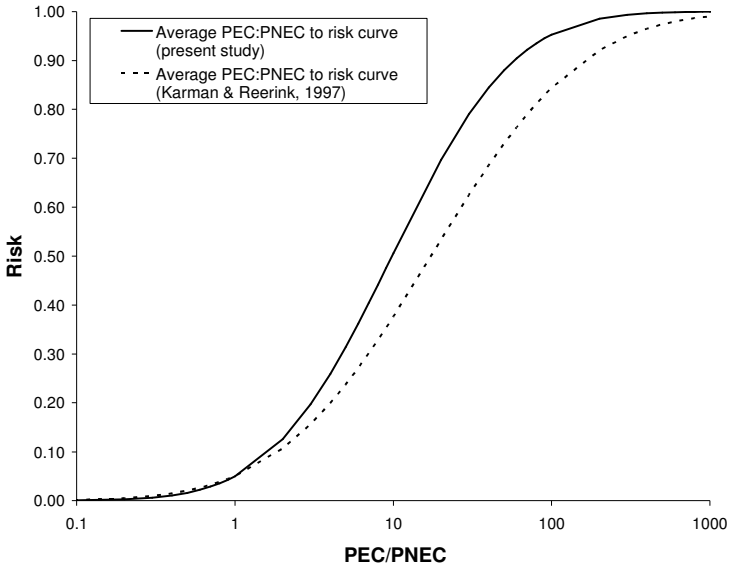


Figure 17 *The average PEC_PNEC-to-risk curve for 17 substances in produced water defined by Karman and Reerink (1997), describing the relationship between PEC_PNEC ratio and risk, compared to average PEC_PNEC-to-risk curve of the current database of the 11 defined groups of substances in produced water.*

3. Risk calculations with different PEC_PNEC –to-risk curves

3.1 Introduction

In order to investigate the consequences of updating the PEC_PNEC-to-risk curves in the EIF calculation rules, risk calculations are carried out based on realistic produced water discharges and realistic dilutions. The results of the use of three different PEC_PNEC-to-risk curves are compared:

- Calculation of risk using *separate* PEC_PNEC-to-risk curves for the different groups (this study).
- Calculation of risk using the new *average* PEC_PNEC-to-risk curve for all groups (this study).
- Calculation of risk using the *old* PEC_PNEC-to-risk curves taken from Karman & Reering (1997) for all groups.

Four produced water profiles where obtained from Grini *et al*. (2002). These four profiles differ in composition. In each of the profiles, one or more groups of substances are dominant. No data for the group of organic acids were available for these profiles and were therefore left out the analysis (Table 8).

Table 8 Four Norwegian produced water profiles (Grini et al., 2002).

Group of substances	Profile 1 (µg/l)	Profile 2 (µg/l)	Profile 3 (µg/l)	Profile 4 (µg/l)
BTEX	11600	166000	30000	10800
Naphthalenes	1780	6430	2100	1090
PAH 2-3 ring	1600	980	170	76
PAH 4-ring+	3	0.2	60	1
Alkylphenols C0-C3	5800	12500	15500	3800
Alkylphenols C4-C5	220	140	240	120
Alkylphenols C6+	1	0.2	3	0.3
Aliphatic hydrocarbons	40000	10000	23300	10000
Metals 1 (Zn, Cu, Ni)	140	5	51	5
Metals 2 (Hg, Cd and Pb)	0.4	5	2	0.4
Organic acids	n.a.	n.a.	n.a.	n.a.

n.a. not available

The PNEC values as reported in this document are taken from Frost (2002) and were used to calculate the PEC_PNEC ratios for the different groups (Table 4). This calculation step was performed at different dilutions (1,000; 10,000 and 100,000). As an indication of the total stress on the environment the sum of the PEC_PNEC ratios of the different groups within one profile is calculated. This sum of the PEC_PNEC ratios has no ecological relevance. The different PEC_PNEC-

to-risk curves were used to translate the PEC_PNEC ratio into a quantitative risk value for each component group.

The overall risk is calculated using the combination rule of joint probabilities (section 3.3, part I). The cumulative risk level is reported together with a transformed PEC_PNEC ratio for the mixture. To calculate this mixture PEC_PNEC ratio, the cumulative risk value is translated back into a PEC_PNEC ratio using the average curve for the 11 groups (The reason for this is that policymakers are more used to communicate in PEC_PNEC ratios than in risk probabilities).

Finally the contribution of the different groups to the overall risk is calculated and presented in a pie-chart. In order to identify the differences in the results of the application of the different PEC_PNEC-to-risk curves, these pie-charts, as well as the total risk values, are compared.

3.2 Results of the cumulative risk calculations

3.2.1 Profile 1

Profile 1 is characterized by a high level of aliphatics, PAHs and metals. Table 9, Table 10 and Table 11 present the results of the calculation procedure as described in 3.1 for produced water profile 1, applying a dilution factor of 1,000, 10,000 and 100,000 respectively.

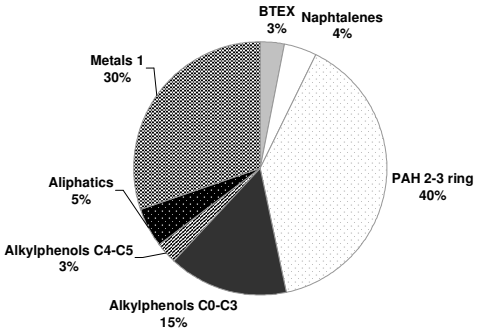
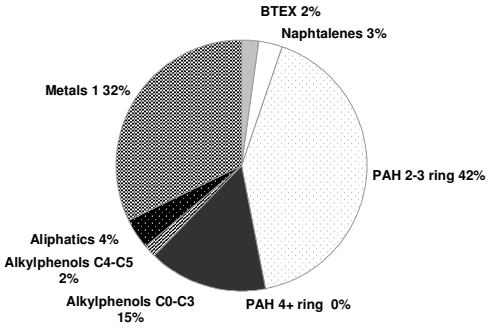
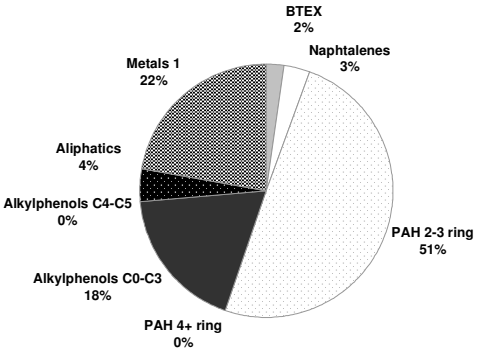
At relative high risk values (risk >>5%; dilution is low) the total risk value is the lowest when the old curve is applied. This is caused by the fact that the *old* curve is somewhat shallower than the new *average* curve (higher risk values at PEC_PNEC ratios higher than 1). Profile 1 contains groups with a relative shallow PEC_PNEC-to-risk curve, therefore, when dilution is low, the total risk value is lower when the *separate* curves are applied. At relative high risk values the difference in the contribution to risk pie-charts for the different curves applied is small (Table 9).

At intermediate risk values (risk around 5%) the total risk value is equal irrespective which curve is applied. This is caused by the fact that all curves cross at the 5% value. At intermediate risk values the difference in the contribution to risk pie-charts for the different curves applied is small (Table 10).

At relative low risk values (risk < 5%) the total risk value is the lowest when the *average* curve is applied. This is caused by the fact that the *average* curve is some what steeper than the *old* curve and the curves for the dominant groups of this profile (lower risk values at PEC_PNEC ratios below 1). At relative low risk values the contribution of groups with a shallow PEC_PNEC-to-risk curve, like the metals, are higher (Table 11).

In Annex 3 Table 23 (PEC_PNEC ratios) and Table 24 (risk values) present detailed results of the risk calculations for the different groups.

Table 9 *Contribution to risk, cumulative risk and corresponding mixture PEC_PNEC ratio at a dilution of 1,000 of produced water profile 1, for the three different curves.*

Produced water profile 1, dilution = 1,000 x	
	Contribution to the overall risk of the different groups using the *old* PEC_PNEC-to-risk curve. Risk = 69% Mixture PEC:PNEC = 41
	Contribution to the overall risk of the different groups using the *average* PEC_PNEC-to-risk curve. Risk = 80% Mixture PEC:PNEC = 32
	Contribution to the overall risk of the different groups using the *separate* PEC_PNEC-to-risk curves. Risk = 77% Mixture PEC:PNEC = 28

.

Table 10 Contribution to risk, cumulative risk and corresponding mixture PEC_PNEC ratio at a dilution of 10,000 of produced water profile 1, for the three different curves.

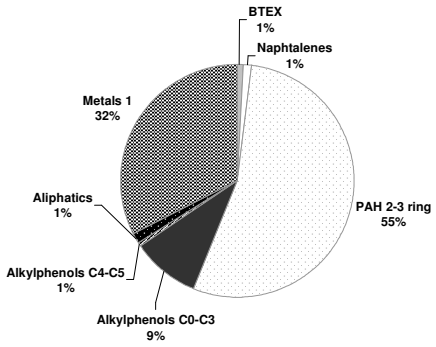
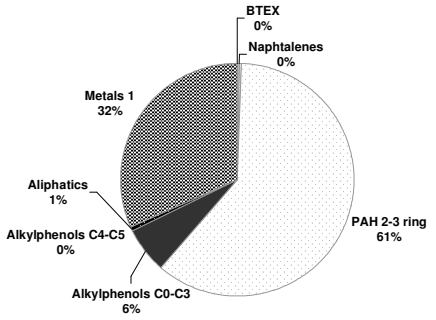
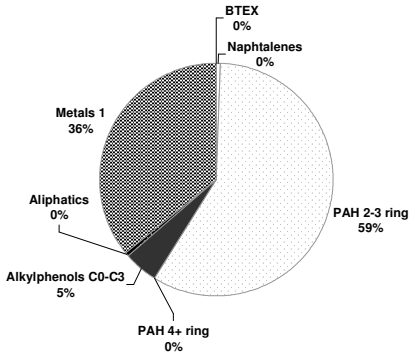
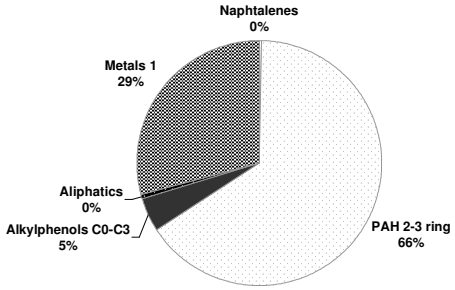
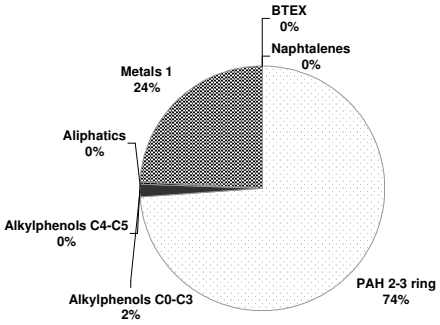
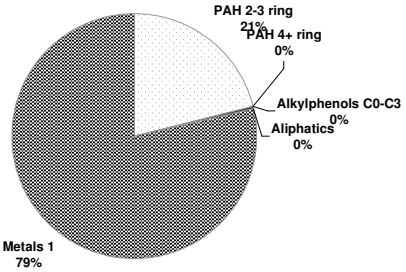
Produced water profile 1, dilution = 10,000 x	
	Contribution to the overall risk of the different groups using the *old* PEC_PNEC-to-risk curve. Risk = 10% Mixture PEC:PNEC = 1.8
	Contribution to the overall risk of the different groups using the *average* PEC_PNEC-to-risk curve. Risk = 9% Mixture PEC:PNEC = 1.5
	Contribution to the overall risk of the different groups using the *separate* PEC_PNEC-to-risk curves. Risk = 9% Mixture PEC:PNEC = 1.6

Table 11 Contribution to risk, cumulative risk and corresponding mixture PEC_PNEC ratio at a dilution of 100,000 of produced water profile 1, for the three different curves.

Produced water profile 1, dilution = 100,000 x	
	Contribution to the overall risk of the different groups using the *old* PEC_PNEC-to-risk curve. Risk = 0.26% Mixture PEC:PNEC = 0.13
	Contribution to the overall risk of the different groups using the *average* PEC_PNEC-to-risk curve. Risk = 0.08% Mixture PEC:PNEC = 0.12
	Contribution to the overall risk of the different groups using the *separate* PEC_PNEC-to-risk curves. Risk = 0.18% Mixture PEC:PNEC = 0.17

3.2.2 Profile 2

Profile 2 is characterised by a high level of BTEX and naphthalenes. Table 12, Table 13 and Table 14 present the results of the calculation procedure as described in 3.1 for produced water profile 2 for a dilution factor of 1,000, 10,000 and 100,000 respectively.

At relative high risk values (risk >>5%) the total risk value is the highest when the *separate* curves are applied. This is caused by the fact that the *separate* curves of dominant groups in profile 2 are steeper than the *average* curve (higher risk values at PEC_PNEC ratios higher than 1). At relative high risk values the difference in the contribution to risk pie-charts for the different curves applied is small (Table 12).

At intermediate risk values (risk around 5%) the total risk value is equal irrespective which curve is applied. This is caused by the fact that all curves cross at the 5% value. At intermediate risk values the difference in the contribution to risk pie-charts for the different curves applied is small (Table 13).

At relative low risk values (risk < 5%) the total risk value is the highest when the *old* curve is applied. This is caused by the fact that the *old* curve is some what steeper than the *average* curve and the *separate* curves for the produced water profile with this composition (lower risk values at PEC_PNEC ratios below 1). At relative low risk values the contribution of groups with a shallow PEC_PNEC-to-risk curve, like PAH 2-3 rings, is higher (Table 14).

In Annex 3 Table 25 (PEC_PNEC ratios) and Table 26 (risk values) present detailed results of the risk calculations for the different groups.

Table 12 Contribution to risk, cumulative risk and corresponding mixture PEC_PNEC ratio at a dilution of 1,000 of produced water profile 2, for the three different curves.

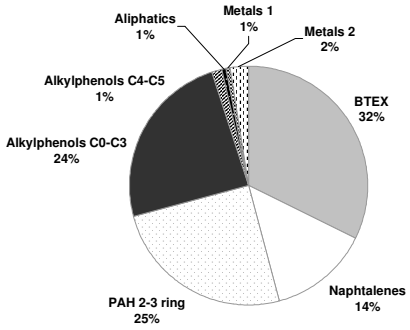
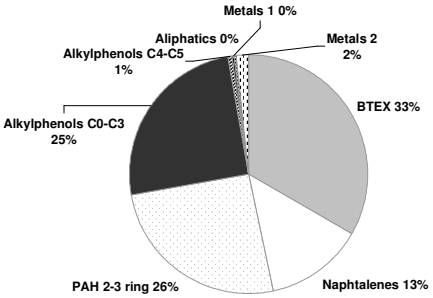
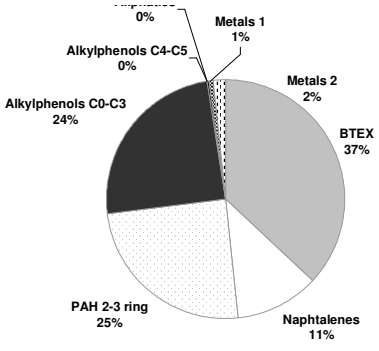
Produced water profile 2, dilution = 1,000 x	
	Contribution to the overall risk of the different groups using the *old* PEC_PNEC-to-risk curve. Risk = 74% Mixture PEC:PNEC = 54
	Contribution to the overall risk of the different groups using the *average* PEC_PNEC-to-risk curve. Risk = 85% Mixture PEC:PNEC = 42
	Contribution to the overall risk of the different groups using the *separate* PEC_PNEC-to-risk curves. Risk = 90% Mixture PEC:PNEC = 60

Table 13 Contribution to risk, cumulative risk and corresponding mixture PEC_PNEC ratio at a dilution of 10,000 of produced water profile 2, for the three different curves.

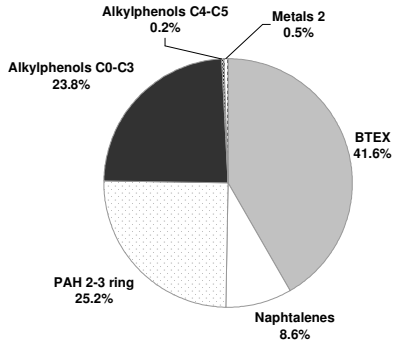
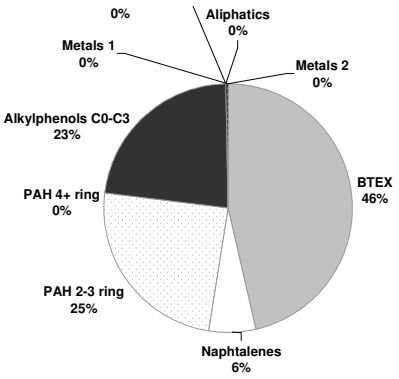
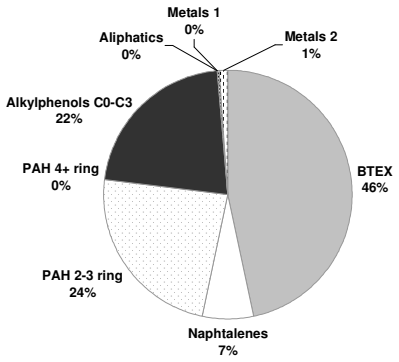
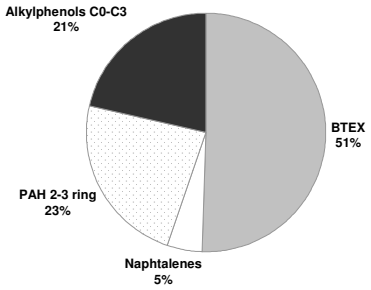
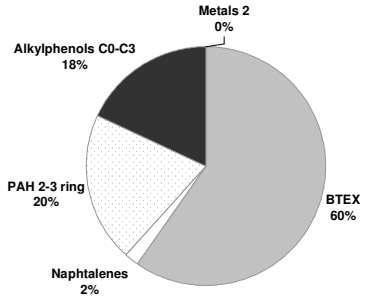
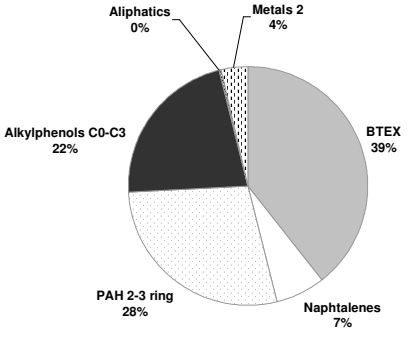
Produced water profile 2, dilution = 10,000 x	
	Contribution to the overall risk of the different groups using the *old* PEC_PNEC-to-risk curve. Risk = 11% Mixture PEC:PNEC = 2.1
	Contribution to the overall risk of the different groups using the *average* PEC_PNEC-to-risk curve. Risk = 10% Mixture PEC:PNEC = 1.7
	Contribution to the overall risk of the different groups using the *separate* PEC_PNEC-to-risk curves. Risk = 10% Mixture PEC:PNEC = 1.6

Table 14 Contribution to risk, cumulative risk and corresponding mixture PEC_PNEC ratio at a dilution of 100,000 of produced water profile 2, for the three different curves.

Produced water profile 2, dilution = 100,000 x	
	Contribution to the overall risk of the different groups using the *old* PEC_PNEC-to-risk curve. Risk = 0.29% Mixture PEC:PNEC = 0.14
	Contribution to the overall risk of the different groups using the *average* PEC_PNEC-to-risk curve. Risk = 0.07% Mixture PEC:PNEC = 0.12
	Contribution to the overall risk of the different groups using the *separate* PEC_PNEC-to-risk curves. Risk = 0.03% Mixture PEC:PNEC = 0.09

3.2.3 Profile 3

Profile 3 is characterized by a high level of PAH 4+ and alkylated phenols. Table 15, Table 16 and Table 17 present the results of the calculation procedure as described in 3.1 for produced water profile 3 for a dilution factor of 1,000, 10,000 and 100,000 respectively.

At relative high risk values (risk >>5%) the total risk value is the highest when the *separate* curves are applied. This is caused by the fact that the *separate* curves of dominant groups in profile 2 are steeper than the *average* curve (higher risk values at PEC_PNEC ratios higher than 1). At relative high risk values the difference in the contribution to risk pie-charts for the different curves applied is small (Table 15).

At intermediate risk values (risk around 5%) the total risk value is equal irrespective which curve is applied. This is caused by the fact that all curves cross at the 5% value. At intermediate risk values the difference in the contribution to risk pie-charts for the different curves applied is small (Table 16).

At relative low risk values (risk < 5%) the total risk value is the highest when the *old* curve is applied. This is caused by the fact that the *old* curve is some what shallower than the new *average* curve and the *separate* curves of the dominant groups of this profile (lower risk values at PEC_PNEC ratios below 1). At relative low risk values the contribution of groups with a shallow PEC_PNEC-to-risk curve, in this case the metals, is higher (Table 17).

In Annex 3 Table 27 (PEC_PNEC ratios) and Table 28 (risk values) present detailed results of the risk calculations for the different groups.

Table 15 Contribution to risk, cumulative risk and corresponding mixture PEC_PNEC ratio at a dilution of 1,000 of produced water profile 3, for the three different curves.

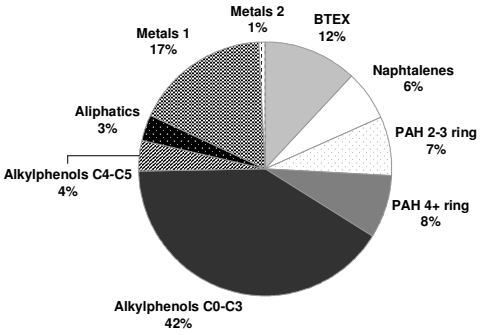
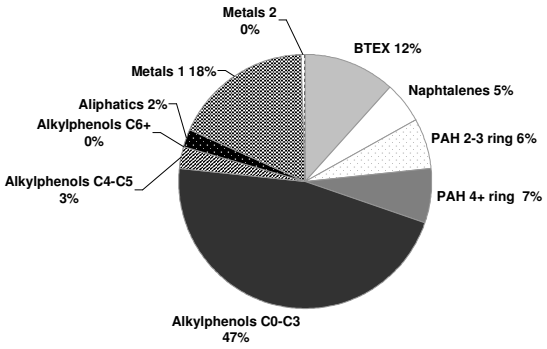
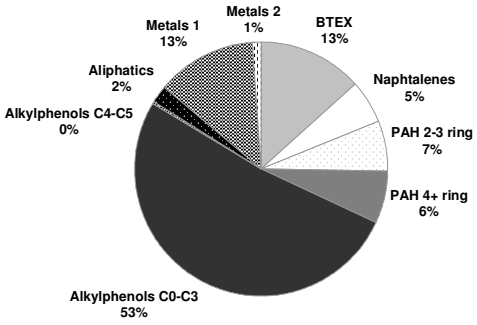
Produced water profile 3, dilution = 1,000 x	
	Contribution to the overall risk of the different groups using the *old* PEC_PNEC-to-risk curve. Risk = 58% Mixture PEC:PNEC = 25
	Contribution to the overall risk of the different groups using the *average* PEC_PNEC-to-risk curve. Risk = 67% Mixture PEC:PNEC = 18
	Contribution to the overall risk of the different groups using the *separate* PEC_PNEC-to-risk curves. Risk = 67% Mixture PEC:PNEC = 18

Table 16 Contribution to risk, cumulative risk and corresponding mixture PEC_PNEC ratio at a dilution of 10,000 of produced water profile 3, for the three different curves.

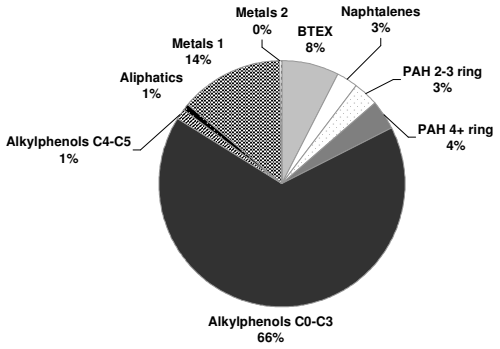
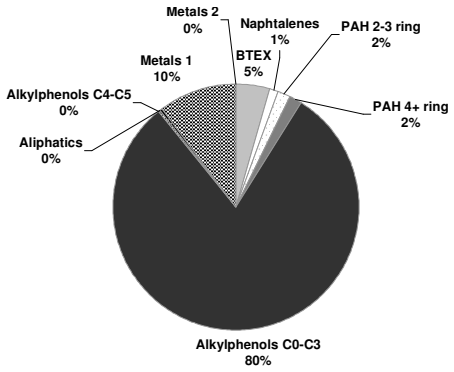
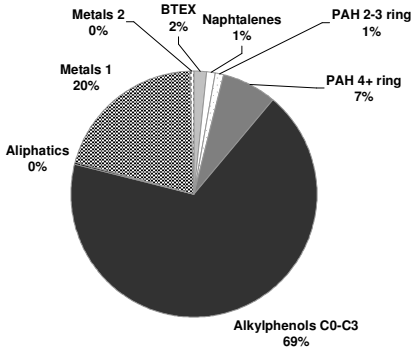
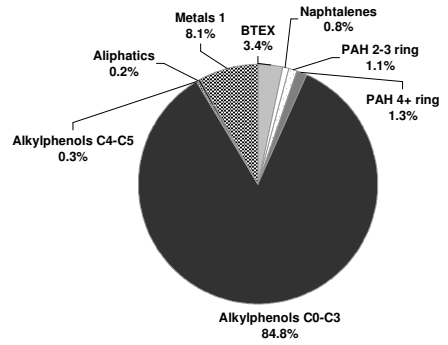
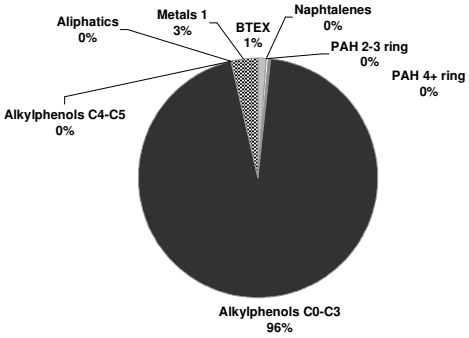
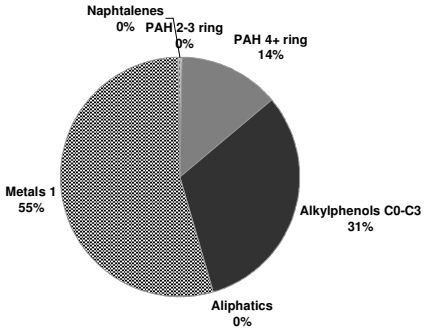
Produced water profile 3, dilution = 10,000 x	
	Contribution to the overall risk of the different groups using the *old* PEC_PNEC-to-risk curve. Risk = 5.5% Mixture PEC:PNEC = 1.1
	Contribution to the overall risk of the different groups using the *average* PEC_PNEC-to-risk curve. Risk = 4.2% Mixture PEC:PNEC = 0.89
	Contribution to the overall risk of the different groups using the *separate* PEC_PNEC-to-risk curves. Risk = 4.8% Mixture PEC:PNEC = 0.97

Table 17 Contribution to risk, cumulative risk and corresponding mixture PEC_PNEC ratio at a dilution of 100,000 of produced water profile 3, for the three different curves.

Produced water profile 3, dilution = 100,000 x	
	Contribution to the overall risk of the different groups using the *old* PEC_PNEC-to-risk curve. Risk = 0.11% Mixture PEC:PNEC = 0.08
	Contribution to the overall risk of the different groups using the *average* PEC_PNEC-to-risk curve. Risk = 0.03% Mixture PEC:PNEC = 0.08
	Contribution to the overall risk of the different groups using the *separate* PEC_PNEC-to-risk curves. Risk = 0.04% Mixture PEC:PNEC = 0.10

3.2.4 Profile 4

Table 18, Table 19 and Table 20 present the results of the calculation procedure as described in 3.1 for produced water profile 4 for a dilution factor of 100, 1,000 and 10,000 respectively.

At relative high risk values (risk >>5%) the total risk value is the highest when the *separate* curves are applied. This is caused by the fact that the *separate* curves of dominant groups in profile 2 are steeper than the *average* curve (higher risk values at PEC_PNEC ratios higher than 1). At relative high risk values the difference in the contribution to risk pie-charts for the different curves applied is small (Table 18).

At intermediate risk values (risk around 5%) the total risk value is equal irrespective which curve is applied. This is caused by the fact that all curves cross at the 5% value. At intermediate risk values the difference in the contribution to risk pie-charts for the different curves applied is small (Table 19).

At relative low risk values (risk < 5%) the total risk value is the highest when the *old* curve is applied. This is caused by the fact that the *old* curve is some what shallower than the *average* curve and the *separate* curves for the produced water profile with this composition (higher risk values at PEC_PNEC ratios below 1). At relative low risk values the contribution of groups with a shallow PEC_PNEC-to-risk curve, in this case metals, is higher (Table 20).

In Annex 3 Table 29 (PEC_PNEC ratios) and Table 30 (risk values) present detailed results of the risk calculations for the different groups.

Table 18 Contribution to risk, cumulative risk and corresponding mixture PEC_PNEC ratio at a dilution of 100 of produced water profile 4, for the three different curves.

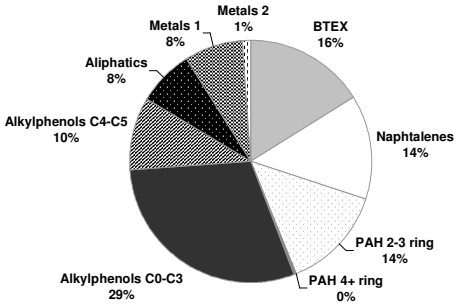
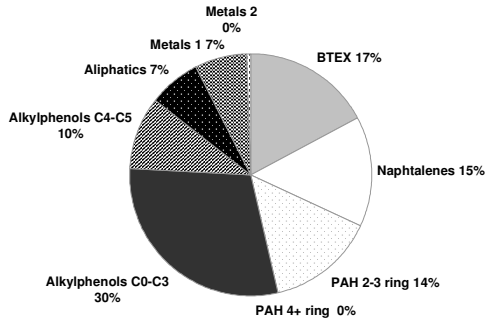
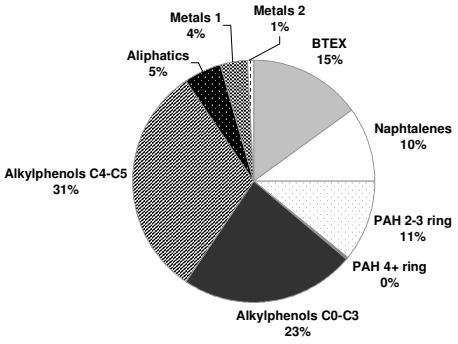
Produced water profile 4, dilution = 100 x	
	Contribution to the overall risk of the different groups using the *old* PEC_PNEC-to-risk curve. Risk = 88% Mixture PEC:PNEC = 134
	Contribution to the overall risk of the different groups using the *average* PEC_PNEC-to-risk curve. Risk = 98% Mixture PEC:PNEC = 194
	Contribution to the overall risk of the different groups using the *separate* PEC_PNEC-to-risk curves. Risk = 100% Mixture PEC:PNEC = 892

Table 19 Contribution to risk, cumulative risk and corresponding mixture PEC_PNEC ratio at a dilution of 1,000 of produced water profile 4, for the three different curves.

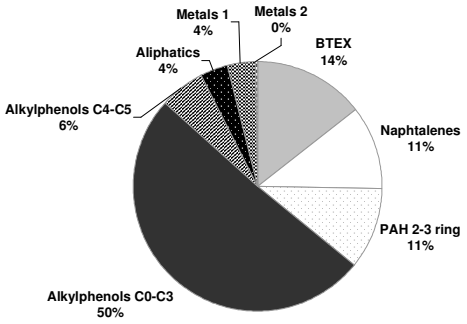
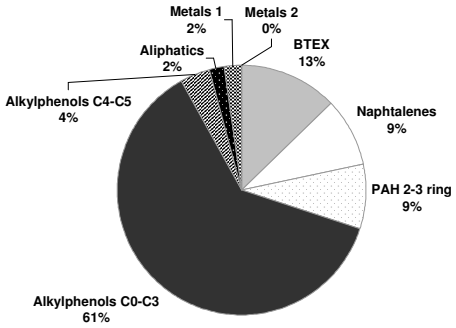
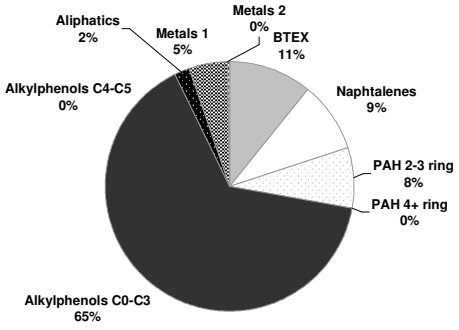
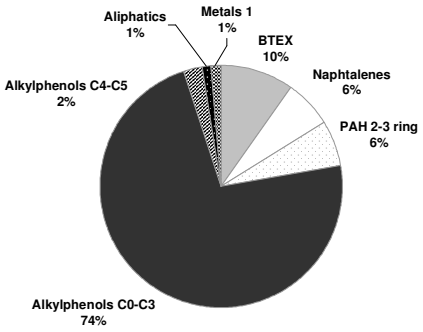
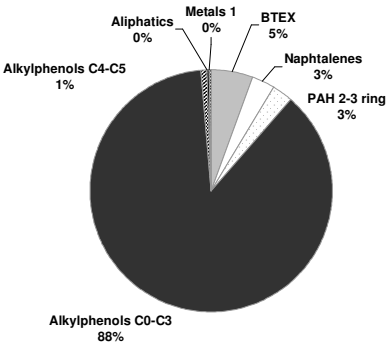
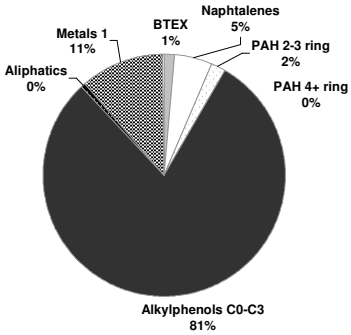
Produced water profile 4, dilution = 1,000 x	
	Contribution to the overall risk of the different groups using the *old* PEC_PNEC-to-risk curve. Risk = 19% Mixture PEC:PNEC = 3.7
	Contribution to the overall risk of the different groups using the *average* PEC_PNEC-to-risk curve. Risk = 18% Mixture PEC:PNEC = 2.8
	Contribution to the overall risk of the different groups using the *separate* PEC_PNEC-to-risk curves. Risk = 18% Mixture PEC:PNEC = 2.8

Table 20 Contribution to risk, cumulative risk and corresponding mixture PEC_PNEC ratio at a dilution of 10,000 of produced water profile 4, for the three different curves.

Produced water profile 4, dilution = 10,000 x	
	Contribution to the overall risk of the different groups using the *old* PEC_PNEC-to-risk curve. Risk = 0.66% Mixture PEC:PNEC = 0.23
	Contribution to the overall risk of the different groups using the *average* PEC_PNEC-to-risk curve. Risk = 0.26% Mixture PEC:PNEC = 0.20
	Contribution to the overall risk of the different groups using the *separate* PEC_PNEC-to-risk curves. Risk = 0.21% Mixture PEC:PNEC = 0.18

3.3 Results in general

From the results of the risk calculations as presented in 3.2 the following general observations can be made:

- There are no large differences in the total risk values when the new *average* PEC_PNEC-to-risk curve or the *separate* PEC_PNEC-to-risk curves are applied in stead of the *old* PEC_PNEC-to-risk curve from Karman & Reerink (1997). The (small) differences that do exist in the total risk value are present at high PEC_PNEC ratios and low PEC_PNEC ratios. Near PEC_PNEC ratios of 1 these differences are smallest.

- Only at risk levels below 5% the pie-charts showing the contribution to risk of the different component groups in the produced water profile based on *separate* PEC_PNEC-to-risk curves differ significantly from the pie-charts based on the old and the *average* PEC_PNEC-to-risk curve.

- In the calculation of the EIF only water volumes with a mixture risk higher than 5% are taken into account. Because all the PEC_PNEC-to-risk curves cross the point where PEC:PNEC = 1 equals a risk of 5%, the curves will be very similar around this point. Therefore, it is observed that the different pie-charts expressing contribution to risk based on the different curves applied do not change much at risk levels higher that 5%. This will mean that a change in the applied curve will also not result in a major change in the final contributions to risk in the result of the EIF calculation.

4. Discussion and conclusions of part II

4.1 Grouping of substances in 11 EIF groups

The data needed for a risk assessment as described in Part I of this document is available for 10 of the 11 groups of natural components as defined in the Environmental Impact factor (EIF). Chronic NOECs are hardly available, but EC_{50}s can be used to estimate the variation in species sensitivity. The grouping of components is based on chemical structure of the components. Analytical methods and mitigation measures can also be defined for these groups of components.

Statistical analysis of the data (EC_{50}s) has indicated that there is a variation in the mean toxicity of the components within one group (Xm). One PNEC is defined per component group. According to the precautionary principle, the most toxic component within this group will represent the toxicity of all components in the group. There is no significant difference in the variation in toxicity data for one component in a component group (Sm) compared to other components in the same group. Therefore grouping of these components and assuming one common value for the variation in sensitivity (i.e. the slope of the SSD (Sm)) for all these components in this group is defensible.

The variation in sensitivity of species to exposure of metals is the comparable for all metals (similar Sm value for the metals). The low PNEC value for Pb indicates that this is the most toxic metal component. For the non-metals the group of PAHs >C4 is the most toxic. However the group of > C6 alkylated phenols is likely to cause more effects at higher exposure concentrations because of the small variation in species sensitivity.

4.2 PEC_PNEC-to-risk curves

The separate PEC_PNEC-to-risk curves which are constructed based on the variation in species sensitivity obtained from the variation in EC50 values, show that there is a wide range of variation in species sensitivity which is component specific. This means that the likelihood of effects occurring at a certain PEC_PNEC ratio differs per component group. This is also the reason why PEC_PNEC ratios should not be added.

The *average* PEC_PNEC-to-risk curve (derived in this study) is steeper than the *old* PEC_PNEC-to-risk curve which was earlier derived from 17 components. These components are only a small selection of the components present in produced water discharges (Karman & Reerink, 1997). Risk calculations on four produced water profiles are carried out in order to identify effects of replacing this *old* PEC_PNEC-to-risk curve by this new average curve based on relevant components.

4.3 PEC_PNEC-to-risk calculations

The observed differences in the cumulative risk calculated with the different PEC_PNEC-to-risk curves for the total of the 11 groups of compounds for four realistic produced water profiles is dependent on the dilution of the produced water release. At a dilution where the PEC is close to the PNEC there is hardly any difference present. At higher and lower dilutions the observed differences in the cumulative risk calculated with the different PEC_PNEC-to-risk curves increase. However the difference in the calculated cumulative risk stays within the same range, well within the expected uncertainty limits.

The calculated separate contributions of the 11 substances to the overall risk calculated for the four produced water profiles with the different PEC_PNEC-to-risk curves indicates that at joint risk probabilities around 5% or higher the choice of the PEC_PNEC-to-risk curve applied, has only a limited influence on the contribution distribution of the separate components. At dilutions resulting in a joint risk probability <<5%, the contribution of components with a shallow PEC_PNEC-to-risk curve will always be dominant.

Replacing the old PEC_PNEC-to-risk curve by the separate curves for the different component groups is a refinement of the PEC_PNEC-to-risk calculation. For the added chemicals the *average* PEC_PNEC-to-risk curve can be applied. It is expected that these changes will not affect the present results of the EIF calculations nor the contributions to risk of separate components in a large extent. Only when the contribution of risk is calculated for cases with a joint risk probability below 5%, the result will be different.

5. References

Aldenberg T. & W. Slob (1993): Confidence limits for hazardous concentrations based on logistically distributed NOEC toxicity data. Ecotoxicol. Environ. Saf. 25:48-63.

Aldenberg T. & J.S. Jaworska (2000): Uncertainty of the hazardous concentration and fraction affected for normal species sensitivity distributions. Ecotoxicol. Environ. Saf. 46:1-18.

Calow P. & V.E. Forbes (2003): Does ecotoxicology inform ecological risk assessment? Environ. Sci. Technol. pp 146A - 151A.

EC (1998): Risk Assessment for contaminated sites in Europe, LQM press, Nottingham, UK.

EC (2003): Technical Guidance Document on Risk Assessment in support of Commission Directive 93/67/EEC on Risk Assessment for new notified substances Commission Regulation (EC) No 1488/94 on Risk Assessment for existing substances Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market. European Commission Joint Research Centre. EUR 20418 EN/2.

Forbes V.E. & P. Calow (2002a): Sensitivity distributions - Why species selection matters. SETAC Globe 3(5):22-23.

Forbes V.E. & P. Calow (2002b): Species Sensitivity Distributions Revisited: A Critical Appraisal Human and Ecological Risk Assessment, Vol. 8 No. 3, pp. 473-492.

Frost T.K. (2002): Environmental risk assessment, Technical Guidance Document (TGD), Predicted No Effect Concentration (PNEC), Acute and Chronic toxicity, Produced water components, Validation criteria. Statoil TEK FandT MST. C.TEK.FO. GB41.

Grini P.G., M. Hjelsvold & S.Johnsen (2002): Choosing Produced Water Treatment Technologies Based on Environmental Impact Reduction Statoil ASA, Trondheim, SPE paper 74002.

Hoeven van der N. (2001): Estimating the 5-percentile of the species sensitivity distributions without any assumptions about the distribution. Ecotoxicology 10(1):25-34.

ISO (2002): ISO 17776 Petroleum and natural gas industries - offshore production - Guidelines on tools and techniques for hazard identification and risk assessment.

Jager D.T. & C.J.M. Visser (eds.) (1994): Uniform System for the Evaluation of Substances (USES). RIVM VROM WVC.

Jager T., T.G. Vermeire, M.G.J. Rikken & P. van der Poel (2001): Opportunities for a probabilistic risk assessment of chemicals in the European Union. Chemosphere 43(2):257-264.

Johnson S. T.K. Frost, M. Hjelsvold & T. Røe Utvik (2000): The environmental imapct factor – a proposed tool for produced water impact reduction, management and regulation. SPE paper 61178.

Karman C.C., & H.G. Reerink (1997): Dynamic Assessment of the Ecological Risk of the Discharge of Produced Water from Oil and Gas Producing Platforms. Journal of Hazardous Materials 61 (1998): 43-51.

Kodell R.L. & Felton R.P. (1991): Two stage and Weibull models for carcinogenesis applied to the ED01 discontinued dosing data. Environ. Health Persp. 92:155-166.

Kooijman S.A.L.M. (1981): Parametric analysis of mortality rates in bioassays. Water Res. 15:107-109.

Kooijman S.A.L.M. (1987): A safety factor for LC50 values allowing for differences in sensitivity among species. Water Res. 21:269-276.

Newman M.C., D.R. Ownby, L.C.A. Mezin, D.C. Powell, T.R.L. Christensen, S.B. Lerberg & B.A. Anderson (2000): Applying species-sensitivity distributions in ecological risk assessment: Assumptions of distribution type and sufficient numbers of species. Environ. Toxicol. Chem. 19(2):508-515.

Okkerman P.C., E. v.d. Plassche, H.J.B. Emans & J.H. Canton (1993): Validation of some extrapolation methods with toxicity data derived from multiple species experiments. Ecotoxicol. Environ. Saf. 25:341-359.

OSPAR (2003): Agreements of OSPAR with respect to risk assessment for the marine environment agreement. OSPAR agreement 20-2003.

Posthuma L., G.W. Suter II & T.P. Traas (2002): Species sensitivity distributions in ecotoxicology. Lewis Publishers.

Scholten M.C.Th., C.C. Karman & S. Huwer (2000): Ecotoxicological risk assessment related to chemicals and pollutants in off-shore oil production. Toxicol. Lett. 112/113:283-288.

Smit M.G.D., A.J. Hendriks, J.H.M. Schobben, C.C. Karman & H.P.M. Schobben (2001): The variation in the slope of concentration-effect relationships. Ecotoxicol. Environ. Saf. 48:43-50.

Straalen N.M. van & C.A.J. Denneman (1989): Ecotoxicological evaluation of soil quality criteria. Ecotoxicol. Environ. Saf. 18:241-251.

Suter G.W. (1993): Ecological Risk Assessment, Lewis Publishers, Inc., Boca Raton, Florida.

Thatcher M., M. Robson, L.R. Henriquez & C.C. Karman (1999): CHARM: Chemical Hazard Assessment and Risk Management for the use and discharge of chemicals used offshore. User guide V1.0.

USEPA (1993): Risk assessment in the Federal Government: Managing the Process, National Academy Press, Washington DC.

USEPA (1998): Guidelines for Ecological Risk Assessment, Federal Register, Vol. 63, No. 93, May 14, pp. 26846-26924

Vermeire T.G., D.T. Jager, B. Bussian, J. Devillers, K. den Haan, B. Hansen, I. Lundberg, H. Niessen, S. Robertson, H. Tyle & P.T.J. van der Zandt (1997): European Union system for the evaluation of substances (EUSES). Principles and structure. Chemosphere 34(8):1823-1836.

Versteeg D.J., S.E. Belanger & G.J. Carr (1999): Understanding single-species and model ecosystem sensitivity: Data-based comparison. Environ. Toxicol. Chem. 18(6):1329-1346.

Wagner C. & H. Løkke (1991): Estimation of ecotoxicological protection levels from NOEC toxicity data. Water Res. 25:1237-1242.

Wheeler J.R., E.P.M. Grist, K.M.Y. Leung, D. Morritt & M. Crane (2002): Species sensitivity distributions: data and model choice. Mar. Pollut. Bull. 45:192-202.

6. Authentication

Name and address of the principal:
ERMS projectgroup

Names and functions of the cooperators:

M.G.D. Smit	Project leader
K.I.E. Holthaus	Research scientist
J.E. Tamis	Research scientist
C.C. Karman	Research scientist

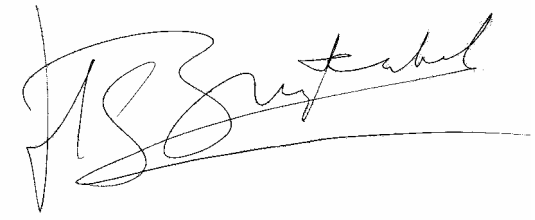
Names and establishments to which part of the research was put out to contract:
-

Date upon which, or period in which, the research took place:
June 2002 – June 2005

Signature:

M.G.D. Smit
Project leader
June 29, 2005

Approved by:



H.S. Buijtenhek
Team Leader a.i.
June 29, 2005

Annex 1 Overview of toxicity data for the different substances within each group

Table 21 Number of EC_{50}-species combinations per component for the 11 defined groups of substances in produced water.

Group no.	Main Group	Substances	Number of species
1	**BTEX**	Benzene	42
		Toluene	14
		Ethylbenzene	21
		m-Xylene	7
		o-Xylene	7
		p-Xylene	7
		Xylene	13
2	**Naphthalenes**	1-Methylnaphthalene	5
		2,3,5-Trimethylnaphthalene	1
		2,6-Dimethylnaphthalene	1
		2-Methylnaphthalene	4
		Naphthalene	24
3	**PAH 2-3 ring**	Acenaphtene	2
		Anthracene	3
		Fluoranthene	1
		Fluorene	5
		Phenanthrene	8
4	**PAH 4-ring+**	Benzo(a)pyrene	9
		Benzo(a)anthracene	3
5	**Alkylphenols C0-C3**	2,3-dimethylphenol	1
		2,4-dimethylphenol	3
		2,5-dimethylphenol	1
		2,6-dimethylphenol	2
		2-methylphenol	1
		3,4-dimethylphenol	2
		3,5-dimethylphenol	1
		3-methylphenol	1
		4-methylphenol	1
		4-ethylphenol	1
		4-propylphenol	1
		cresol	16
		o-cresol	1
		phenol	12
6	**Alkylphenols C4-C5**	2-tert-butylphenol	1
		3-tert-butylphenol	1
		4-tert-butylphenol	1
		2,6-di-tert-butylphenol	5
		2-sec-butylphenol	1
		4-sec-butylphenol	2
		4-pentylphenol	2
		4-tert-pentylphenol	3

Table 21 (continued)

Group no.	Main Group	Substances	Number of species
7	**Alkylphenols C6+**	4-heptylphenol	2
		4-hexylphenol	2
		4-nonylphenol	3
		4-octylphenol	1
		4-tert-octylphenol	8
		nonylphenol	6
8	**Aliphatic hydrocarbons**	Decane	3
		Pentane	4
		Hexane	3
		Heptane	1
		Tetradecane	2
9	**Metals 1**	Cu	100
		Ni	16
		Zn	151
10	**Metals 2**	Cd	68
		Hg	49
		Pb	26
11	**Organic acids**	Acetic acid	4
		Butyric acid	2
		Valeric acid	4

Annex 2 Statistical analysis of the used EC50 values for the components in the different groups.

Table 22 Statistical analysis of EC_{50} values with a 1-way ANOVA or t-test for the variables substance, trophic group, exposure duration, type of endpoint and salinity.

Group of substances	Number of data analysed	Type of statistical analysis	Variable	Differences between means significant	Significance level	Differences between variances significant	Significance level
Sum	709	ANOVA	Substance	**yes**	***	**yes**	***
Sum	645	ANOVA	Trophic group	**yes**	**	no	-
Sum	653	ANOVA	Exposure duration	**yes**	*	**yes**	**
Sum	671	ANOVA	Type of endpoint	no	-	**yes**	**
Sum	508	t-test	Salinity	no	-	**yes**	***
1	110	ANOVA	Substance	**yes**	***	no	-
1	96	ANOVA	Trophic group	no	-	**yes**	**
1	110	ANOVA	Exposure duration	no	-	no	-
1	109	ANOVA	Type of endpoint	**yes**	***	n.a.	n.a.
1	110	t-test	Salinity	**yes**	***	**yes**	**
2	31	ANOVA	Substance	**yes**	*	n.a.	n.a.
2	29	t-test	Trophic group	no	-	no	-
2	34	ANOVA	Exposure duration	no	-	no	-
2	33	t-test	Type of endpoint	no	-	no	-
2	34	t-test	Salinity	no	-	no	-
3	19	ANOVA	Substance	**yes**	***	n.a.	n.a.
3	15	t-test	Trophic group	no	-	no	-
3	19	ANOVA	Exposure duration	no	-	n.a.	n.a.
3	19	t-test	Salinity	no	-	no	-
4	12	t-test	Substance	**yes**	*	no	-
4	10	t-test	Trophic group	**yes**	*	no	-
5	50	ANOVA	Substance	no	-	n.a.	n.a.
5	43	t-test	Trophic group	no	-	**yes**	*
5	54	ANOVA	Exposure duration	no	-	n.a.	n.a.
5	52	t-test	Type of endpoint	no	-	**yes**	*
5	54	t-test	Salinity	no	-	no	-

Table 22 (continued)

Group of substances	Number of data analysed	Type of statistical analysis	Variable	Differences between means significant	Significance level	Differences between variances significant	Significance level
6	10	ANOVA	Substance	**yes**	*	n.a.	n.a.
6	16	ANOVA	Trophic group	no	-	n.a.	n.a.
6	16	t-test	Exposure duration	no	-	no	-
6	15	t-test	Type of endpoint	no	-	no	-
6	16	t-test	Salinity	no	-	no	-
7	22	t-test	Substance	no	-	n.a.	n.a.
7	23	ANOVA	Trophic group	no	-	n.a.	n.a.
7	22	t-test	Exposure duration	no	-	**yes**	**
7	23	ANOVA	Type of endpoint	no	-	n.a.	n.a.
7	23	t-test	Salinity	no	-	no	-
8	12	ANOVA	Substance	no	-	n.a.	n.a.
8	13	ANOVA	Trophic group	**yes**	*	n.a.	n.a.
8	11	t-test	Exposure duration	no	-	no	-
9	267	ANOVA	Substance	**yes**	***	no	-
9	162	ANOVA	Trophic group	no	-	no	-
9	267	ANOVA	Exposure duration	**yes**	***	**yes**	**
9	251	ANOVA	Type of endpoint	no	-	n.a.	n.a.
9	224	t-test	Salinity	**no**	-	no	-
10	143	ANOVA	Substance	**yes**	***	no	-
10	88	ANOVA	Tax.group	no	-	**yes**	**
10	143	ANOVA	Exposure duration	no	-	no	-
10	135	ANOVA	Type of endpoint	no	-	n.a.	n.a.
10	143	t-test	Salinity	**yes**	***	no	-
11	10	ANOVA	Substance	no	-	n.a.	n.a.
11	9	t-test	Trophic group	no	-	**yes**	*
11	9	ANOVA	Exposure duration	**yes**	**	n.a.	n.a.

n.a. not applicable

Annex 3 Detailed results of the risk calculations of the different dilutions of the four selected profiles.

Table 23 Overview of the PEC_PNEC ratios of the different component groups at different dilutions of profile 1

dilution	0 x PEC/PNEC	1,000 x PEC/PNEC	10,000 x PEC/PNEC	100,000 x PEC/PNEC
Group 1	682	0.682	0.068	0.007
Group 2	848	0.848	0.085	0.008
Group 3	10667	10.667	1.067	0.107
Group 4	60	0.060	0.006	0.001
Group 5	2900	2.900	0.290	0.029
Group 6	611	0.611	0.061	0.006
Group 7	25	0.025	0.003	0.000
Group 8	990	0.990	0.099	0.010
Group 9	7000	7.000	0.700	0.070
Group 10	50	0.050	0.005	0.001
*sum PEC:PNEC**	*23833*	*23.8*	*2.38*	*0.238*

* Sum PEC:PNEC is the sum of the PEC:PNEC values of the different groups. This value has no ecological relevance and is only included for reasons of comparison.

Table 24 Risk values per component group at different dilutions of produced water profile 1, with the application of the different PEC_PNEC-to-risk curves

dilution	1,000 x			10,000 x			100,000 x		
	old curve	average	separate	old curve	average	separate	old curve	average	separate
Group 1	3.2%	2.7%	2.4%	0.1%	0.0%	0.0%	0.0%	0.0%	0.0%
Group 2	4.2%	3.9%	3.9%	0.1%	0.0%	0.0%	0.0%	0.0%	0.0%
Group 3	39%	53%	57%	5.5%	5.5%	5.5%	0.2%	0.1%	0.0%
Group 4	0.1%	0.0%	0.1%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Group 5	15%	19%	21%	0.9%	0.6%	0.5%	0.0%	0.0%	0.0%
Group 6	2.7%	2.3%	0.1%	0.1%	0.0%	0.0%	0.0%	0.0%	0.0%
Group 7	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Group 8	5.0%	4.9%	4.9%	0.2%	0.0%	0.0%	0.0%	0.0%	0.0%
Group 9	30%	40%	25%	3.3%	2.9%	3.4%	0.1%	0.0%	0.1%
Group 10	0.0%	0.0%	0.1%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
cumulative risk	**69%**	**80%**	**77%**	**10%**	**9%**	**9%**	**0.26%**	**0.08%**	**0.18%**
mixture PEC:PNEC	**41**	**32**	**28**	**1.8**	**1.5**	**1.6**	**0.13**	**0.12**	**0.17**

Table 25 Overview of the PEC_PNEC ratios of the different component groups at different dilutions of profile 2

dilution	0 x PEC/PNEC	1,000 x PEC/PNEC	10,000 x PEC/PNEC	100,000 x PEC/PNEC
Group 1	9765	9.765	0.976	0.098
Group 2	3062	3.062	0.306	0.031
Group 3	6533	6.533	0.653	0.065
Group 4	4	0.004	0.000	0.000
Group 5	6250	6.250	0.625	0.063
Group 6	389	0.389	0.039	0.004
Group 7	5	0.005	0.001	0.000
Group 8	248	0.248	0.025	0.002
Group 9	250	0.250	0.025	0.003
Group 10	625	0.625	0.063	0.006
sum PEC:PNEC*	**27130**	**27.1**	**2.71**	**0.271**

* Sum PEC:PNEC is the sum of the PEC:PNEC values of the different groups. This value has no ecological relevance and is only included for reasons of comparison.

Table 26 Risk values per component group at different dilutions of produced water profile 2, with the application of the different PEC_PNEC-to-risk curves

dilution	1,000 x			10,000 x			100,000 x		
	old curve	average	separate	old curve	average	separate	old curve	average	separate
Group 1	37%	50%	63%	4.9%	4.8%	4.8%	0.1%	0.0%	0.0%
Group 2	16%	20%	19%	1.0%	0.6%	0.7%	0.0%	0.0%	0.0%
Group 3	29%	39%	42%	3.0%	2.5%	2.4%	0.1%	0.0%	0.0%
Group 4	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Group 5	28%	37%	41%	2.8%	2.4%	2.2%	0.1%	0.0%	0.0%
Group 6	1.5%	1.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Group 7	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Group 8	0.7%	0.4%	0.4%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Group 9	0.7%	0.4%	1.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Group 10	2.8%	2.4%	3.0%	0.1%	0.0%	0.1%	0.0%	0.0%	0.0%
cumulative risk	**74%**	**85%**	**90%**	**11%**	**10%**	**10%**	**0.29%**	**0.07%**	**0.03%**
mixture PEC:PNEC	**54**	**42**	**59**	**2.1**	**1.7**	**1.6**	**0.14**	**0.12**	**0.09**

Table 27 Overview of the PEC_PNEC ratios of the different component groups at different dilutions of profile 3

dilution	0 x PEC/PNEC	1,000 x PEC/PNEC	10,000 x PEC/PNEC	100,000 x PEC/PNEC
Group 1	1765	1.765	0.176	0.018
Group 2	1000	1.000	0.100	0.010
Group 3	1133	1.133	0.113	0.011
Group 4	1200	1.200	0.120	0.012
Group 5	7750	7.750	0.775	0.078
Group 6	667	0.667	0.067	0.007
Group 7	75	0.075	0.008	0.001
Group 8	577	0.577	0.058	0.006
Group 9	2550	2.550	0.255	0.026
Group 10	250	0.250	0.025	0.003
sum PEC:PNEC*	**16966**	**17.0**	**1.70**	**0.170**

* Sum PEC:PNEC is the sum of the PEC:PNEC values of the different groups. This value has no ecological relevance and is only included for reasons of comparison.

Table 28 Risk values per component group at different dilutions of produced water profile 3, with the application of the different PEC_PNEC-to-risk curves

dilution	1,000 x			10,000 x			100,000 x		
	old curve	average	separate	old curve	average	separate	old curve	average	separate
Group 1	9.5%	11%	12%	0.4%	0.2%	0.1%	0.0%	0.0%	0.0%
Group 2	5.1%	5.0%	5.0%	0.2%	0.0%	0.1%	0.0%	0.0%	0.0%
Group 3	5.9%	6.0%	6.1%	0.2%	0.1%	0.0%	0.0%	0.0%	0.0%
Group 4	6.3%	6.5%	6.0%	0.2%	0.1%	0.3%	0.0%	0.0%	0.0%
Group 5	32%	43%	48%	3.7%	3.4%	3.3%	0.1%	0.0%	0.0%
Group 6	3.1%	2.6%	0.2%	0.1%	0.0%	0.0%	0.0%	0.0%	0.0%
Group 7	0.1%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Group 8	2.5%	2.1%	2.0%	0.1%	0.0%	0.0%	0.0%	0.0%	0.0%
Group 9	14%	17%	12%	0.8%	0.4%	1.0%	0.0%	0.0%	0.0%
Group 10	0.7%	0.4%	0.9%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
cumulative risk	**58%**	**67%**	**67%**	**5.5%**	**4.2%**	**4.8%**	**0.11%**	**0.03%**	**0.04%**
mixture PEC:PNEC	**25**	**18**	**18**	**1.1**	**0.89**	**0.97**	**0.08**	**0.08**	**0.10**

Table 29 Overview of the PEC_PNEC ratios of the different component groups at different dilutions of profile 4

dilution	0 x PEC/PNEC	100 x PEC/PNEC	1,000 x PEC/PNEC	10,000 x PEC/PNEC
Group 1	635	6.353	0.635	0.064
Group 2	519	5.190	0.519	0.052
Group 3	507	5.067	0.507	0.051
Group 4	20	0.200	0.020	0.002
Group 5	1900	19.000	1.900	0.190
Group 6	333	3.333	0.333	0.033
Group 7	8	0.075	0.008	0.001
Group 8	248	2.475	0.248	0.025
Group 9	250	2.500	0.250	0.025
Group 10	50	0.500	0.050	0.005
sum PEC:PNEC*	**4469**	**44.7**	**4.47**	**0.447**

* Sum PEC:PNEC is the sum of the PEC:PNEC values of the different groups. This value has no ecological relevance and is only included for reasons of comparison.

Table 30 Risk values per component group at different dilutions of produced water profile 4, with the application of the different PEC_PNEC-to-risk curves

dilution	1,000 x			10,000 x			100,000 x		
	old curve	average	separate	old curve	average	separate	old curve	average	separate
Group 1	28%	48%	48%	2.9%	2.4%	2.1%	0.1%	0.0%	0.0%
Group 2	24%	41%	31%	2.2%	1.7%	1.8%	0.0%	0.0%	0.0%
Group 3	24%	40%	35%	2.1%	1.6%	1.5%	0.0%	0.0%	0.0%
Group 4	1%	0%	1%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Group 5	52%	82%	74%	10%	12%	13%	0.5%	0.2%	0.2%
Group 6	17%	27%	99%	1.2%	0.7%	0.0%	0.0%	0.0%	0.0%
Group 7	0%	0%	0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Group 8	13%	19%	16%	0.7%	0.4%	0.4%	0.0%	0.0%	0.0%
Group 9	13%	20%	12%	0.7%	0.4%	1.0%	0.0%	0.0%	0.0%
Group 10	2%	1%	2%	0.0%	0.0%	0.1%	0.0%	0.0%	0.0%
cumulative risk	**88%**	**98%**	**100%**	**19%**	**18%**	**18%**	**0.66%**	**0.26%**	**0.21%**
mixture PEC:PNEC	**134**	**194**	**893**	**3.7**	**2.8**	**2.8**	**0.23**	**0.20**	**0.18**