

# **Manual to proposed Dutch implementation of OSPAR's risk-based approach to the management of produced water discharges**

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## **Preface**

IMARES was contracted by Rijkswaterstaat Sea and Delta and State Supervision of Mines to draft a laymen's manual for the Dutch implementation of OSPAR's risk-based approach to the management of produced water. The report at hand provides this manual, which is based on the guidelines imposed by OSPAR and input from the client. It is at the clients discretion whether or not they integrally or partly enrol the implementation as proposed here.

It should be noted that the first platforms to apply the RBA in the Netherlands will serve as a trail. Based on the results of this trail, the Dutch implementation - and therewith this manual - may be adjusted.

## Abbreviations / glossary of terms

BAT	Best Available Techniques; see OSPAR Convention, Appendix 1
BEP	Best Environmental Practice, see OSPAR Convention, Appendix. 1
BTEX	Benzene, Toluene, Ethyl Benzene and Xylene; Collection of the aforementioned substances
CHARM	Chemical Hazard Assessment and Risk Management
DCS	Dutch Continental Shelf
DECC	UK Department of Energy and Climate Change ( <a href="http://www.decc.gov.uk/">http://www.decc.gov.uk/</a> )
EC50	Median effect concentration; The toxicity data are typically reported as the concentrations at which x % (e.g. 50%) mortality or inhibition of a function (e.g. growth) is observed and are expressed as the lethal concentration (LCx) or the effect concentration (ECx), e.g. LC50 or EC50. L/EC50-values are usually obtained from short term tests (duration in the range of hours to a few days, depending on the test organism)
ECHA	European Chemicals Agency ( <a href="http://echa.europa.eu/">http://echa.europa.eu/</a> )
EPA	US Environmental Protection Agency ( <a href="http://www.epa.gov/">http://www.epa.gov/</a> )
EPA PAH	List of 16 PAHs with high priority assigned by the EPA
GC/FID	Gas Chromatography with Flame Ionization Detection; Analytical device for separation and detection of chemicals
GC/MS	Gas Chromatography with Mass Spectrometry; Analytical device for separation and detection of chemicals
HOCNF	Harmonised Offshore Chemical Notification Format, see OSPAR Guidelines 2010-5
OIC	Offshore Industry Committee ( <a href="http://www.ospar.org/html_documents/ospar/html/01-04e_terms_of_reference.pdf#nameddest=OIC">http://www.ospar.org/html_documents/ospar/html/01-04e_terms_of_reference.pdf#nameddest=OIC</a> )
OSPAR	OSlo-PARis Convention ( <a href="http://www.ospar.org">http://www.ospar.org</a> )
PAH	Polycyclic Aromatic Hydrocarbons; A chemical class of substances that are present in produced water, some of which are carcinogenic
PEC	Predicted Environmental Concentration; the concentration of a chemical or an effluent in the environment based on model calculations. PEC is expressed as concentration for individual substances or as dilution for the whole effluent
PLONOR	Pose Little Or NO Risk; OSPAR list of substances / preparations used and discharged offshore which are considered to pose little or no risk to the environment
PNEC	Predicted No Effect Concentration; the concentration of a chemical or effluent below which adverse effects on the aquatic ecosystem and its organisms will most likely not occur during long-term or short term exposure
Produced Water	By-product of oil and gas extraction
RA	Risk Assessment
RBA	Risk-based approach; Approach for the management of produced water discharges as proposed by the OIC (08/13/1-E) <ul style="list-style-type: none"><li>- based on a characterization of the risk to the environment of a produced water discharge by examining both the exposure resulting from discharge of the produced water effluent and the sensitivity of the receiving environment to this exposure,</li><li>- by taking appropriate measures to avoid or minimise exposure levels above the PNEC</li></ul>
REACH	Registration, Evaluation, Authorisation and Restriction of Chemical substances;

Risk	EC regulation for chemicals (EC 1907/2006) means the likelihood that adverse effects may occur, expressed as the PEC: PNEC ratio or the fraction of species potentially affected
Substances	Substances in the context of managing produced water discharges means naturally occurring substances(including heavy metals, PAHs etc) and components of added chemicals present in the produced water
TIE	Toxicity Identification and Evaluation; a cycle of procedures relying on combinations of physical/chemical manipulations and toxicity tests to characterize, identify, and confirm the causes of measured toxicity in a sample (for instance an effluent)
US-EPA	See EPA
WEA	Whole Effluent Assessment; the characterisation of the persistence, bio-accumulative potential and toxicity of the entire effluent using a variety of physical, chemical and biological methods
WET	Whole Effluent Toxicity; the characterisation of the toxicity of the entire effluent using biological methods

## Summary

The Risk-based approach (RBA) is a method of prioritising mitigation actions on those produced water discharges and substances that pose the greatest risk to the environment. By adopting the RBA Recommendation<sup>1</sup> and its associated Guidelines, OSPAR moves forward towards a more holistic approach rather than focusing solely on oil in produced water discharges (i.e., OSPAR Recommendation 2001/1). The RBA will determine the magnitude of the total risk based on all substances present in the produced water and, where appropriate, which substance or group of substances contributes most to the total risk. Furthermore, it will determine whether exposure levels in the receiving environment relating to the discharge, or specific components of the discharge, indicate that the risk is adequately controlled, so that Contracting Parties can take the most effective risk reduction management measures. OSPAR requires that the risk will be characterised on the basis of Whole Effluent Toxicity (WET) studies and/or an assessment of the individual substances or groups of substances, identified in the produced water, taking account of the exposure relating to the discharge and the sensitivity of the receiving marine environment. The Contracting Parties can decide which assessments will be required for national implementation<sup>2</sup>. If the risk is not considered to be acceptable, appropriate measures will be required to be implemented by industry to avoid or minimise the risk. The RBA will be implemented for all offshore installations with produced water discharges in the OSPAR maritime area with the aim of achieving full implementation by 31 December 2018.

This manual is intended to assist operators on the Dutch Continental Shelf in the application of the Dutch implementation of the RBA. It describes all steps required to follow the complete risk management cycle. The first platforms applying the RBA in the Netherlands will serve as a trail for the Dutch implementation. Based on the results of this trail, the Dutch implementation, and therewith this manual, may be adjusted.

The steps required to follow the Dutch implementation of the RBA are:

0. Start  
The onset of the cycle is determined by the authorities, based on either the pre-screening of platforms, significant changes in the discharge of produced water causing a potential increase of risk to the environment, new platforms discharging produced water, or 5 years after the previous cycle.
1. Sampling  
The first task in the cycle is sampling. This needs to be well prepared and adjusted to the next steps in the cycle as the various biological and chemical tests require different conditions regarding volume, sampling, transport, preservation and pre-treatment of samples. The number and volumes of samples needed for both the bioassays and the chemical analyses should be communicated with the contract laboratories.
2. Whole Effluent Toxicity Risk Assessment (WET RA)  
WET RA is required within the Dutch implementation of the RBA. It involves a battery of biological toxicity tests applied to the entire effluent sample instead of to the individual substances allowing also measuring the effects of possibly unknown substances in produced

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<sup>1</sup> OSPAR Recommendation 2012/5: Recommendation for a Risk-based Approach to the Management of Produced Water Discharges from Offshore Installations

<sup>2</sup> The Netherlands presented the plan to achieve full implementation by the 31st of December 2018 of the OSPAR Recommendation 2012/5 to the Offshore Industry Committee (OIC) in March 2013, as described in "The implementation by the Netherlands of the OSPAR Recommendation 2012/5 for a risk-based approach to the Management of Produced Water from Offshore Installations, Draft 5th of February 2013 version 1.2".



water and mixture effects. If the WET RA based on acute toxicity tests results in an acceptable risk (i.e. effects are unlikely at a distance within 500 m from the discharge point), an RBA report is submitted. Five years after the submission the cycle needs to be repeated. Additional measures are required when WET RA indicates unacceptable risk.

### 3. Substance based RA

Chemical analyses, which is part of the substance based RA is required in the first cycle for each platform, to determine the concentration of the substances in the produced water. The results of the chemical analyses in the first cycle will be collected by the authorities with the purpose of building up the platform dossier. After completing the first cycle, chemical analyses will be optional but is recommended. Substance based RA compares the concentration of the substances in the produced water to the sensitivity of the receiving environment in order to determine whether a substance poses a risk (i.e. PEC:PNEC ratio  $\geq 1$ ). The substance based RA could be used to identify the substances that are potentially responsible for exceeding the risk limit based on WET tests. The results are hence useful in defining appropriate measures to reduce the risk.

### 4. Measures

If the WET RA results in an unacceptable risk, the results will be evaluated and, in a dialogue with the authorities, measures are applied to reduce the risk and a RBA report is submitted (see next step). At a time indicated by the authorities, the cycle needs to be repeated (Start) in order to evaluate the effectiveness of the measures and to ensure that the produced water poses an acceptable risk.

### 5. Reporting

The operator reports to the competent authorities

- the outcome of the chemical analysis (required in first cycle, following cycles recommended);
- the outcome of the substance-based risk characterisation (recommended);
- the outcome of the WET tests (required);
- the outcome of the WET-based risk characterisation (required);
- the measures intended to implement to reduce the risk, and the rationale behind them (required in case of unacceptable risk);
- evaluation of measures taken in the previous management cycle (required if applicable);
- deviations from this manual (required if applicable);

The reporting format provided in this manual can be used as a template for the report (at least all elements in this format should be included).

A report needs to be submitted after the risk characterisation is completed and measures are specified when required. The report needs to be submitted to the competent authorities no later than one year after the start of the risk management cycle.

## **Acknowledgements**

We gratefully acknowledge constructive feedback on early drafts of this document by Erwin Roex (Deltares) which helped improve the quality of the work.

## **1. Introduction**

### **Background**

OSPAR is committed to taking all possible steps to prevent and eliminate pollution from offshore sources and in particular to achieve a reduction in discharges of hazardous substances via produced water, by making every endeavour to move towards the target of cessation of discharges of hazardous substances by the year 2020, with the ultimate aim of achieving concentrations in the marine environment near background values for naturally occurring substances and close to zero for man-made synthetic substances (OSPAR, 2013a).

OSPAR Recommendation 2001/1 focuses on oil in produced water and the with oil associated application of Best Available Technique (BAT) and Best Environmental Practice (BEP). But discharges of produced water also contain other substances, such as heavy metals, aromatic hydrocarbons, and alkylphenols which are present in the hydrocarbon reservoir, and added chemicals that are used during the production and produced water treatment processes. Therefore, there was a need to move forward towards a more holistic approach rather than focusing solely on oil in produced water discharges. At the 2008 meeting of the Offshore Industry Committee (OIC) it was decided that a Risk Based Approach (RBA) should be developed for the management of produced water (OSPAR, 2008).

### **Risk Based Approach**

The RBA is a method of prioritising mitigation actions on those discharges and substances that pose the greatest risk to the environment (OSPAR, 2013a). In the RBA all substances present in the produced water contribute to the total risk. The RBA will determine the magnitude of the total risk and, where appropriate, which substance or group of substances contributes most to the total risk. Furthermore, it will determine whether exposure levels in the receiving environment relating to the discharge, or specific components of the discharge, indicate that the risk is adequately controlled, so that Contracting Parties can take the most effective risk reduction management measures. The OSPAR guidelines (OSPAR, 2012b) prescribe that the risk will be characterised on the basis of Whole Effluent Toxicity (WET) studies and/or an assessment of the individual substances or groups of substances, identified in the produced water, taking account of the exposure relating to the discharge and the sensitivity of the receiving marine environment. If the risk is not considered to be acceptable, appropriate measures based on BAT and BEP will be required to be implemented by industry to avoid or minimise the risk. This approach will be implemented for all offshore installations with produced water discharges in the OSPAR maritime area (OSPAR, 2013a).

### **Implementation process of the RBA**

The RBA Recommendation (Recommendation for a Risk-based Approach to the Management of Produced Water Discharges from Offshore Installations (OSPAR, 2012a)) and its associated Guidelines (OSPAR, 2012b) were adopted at the OSPAR Commission meeting in 2012. All Contracting Parties have finalised their implementation plans<sup>3</sup> in 2013, with the aim of achieving full implementation by 31 December

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<sup>3</sup> The Netherlands presented the plan to achieve full implementation by the 31st of December 2018 of the OSPAR Recommendation 2012/5 to the Offshore Industry Committee (OIC) in March 2013, as described in "The implementation by the Netherlands of the OSPAR Recommendation 2012/5 for a risk-based approach to the Management of Produced Water from Offshore Installations, Draft 5th of February 2013 version 1.2".

2018. Starting in 2014, Contracting Parties will report annually on progress during the implementation period, through the OSPAR Offshore Industry Committee, and the Committee will undertake an evaluation of the effectiveness of the risk-based approach every five years after 2018 (OSPAR, 2012a). The objective is that by 2020 all offshore installations with produced water discharges in the OSPAR maritime area will have been assessed to determine the level of the risk and that, where appropriate, measures will have been taken to reduce the risk posed by the most hazardous substances (OSPAR, 2013a).

## **Reading guide**

This manual is intended to assist operators in the application of the RBA. It contains a list of abbreviations and glossary to explain the terms used in the manual. The next chapter (chapter 2) describes the risk management cycle. This cycle follows all steps required for the RBA, which are all individually addressed in the following chapters: chapter 3 (sampling); chapter 4 (whole effluent toxicity risk assessment, including ecotoxicological testing of the effluent and risk characterisation); chapter 5 (substance-based risk assessment, including chemical analysis and risk characterisation); chapter 6 (measures) and chapter 7 (reporting). All chapters follow the same structure:

1. why it is necessary (why?);
2. what exactly is required (what?);
3. how should this be achieved (how?);
4. when it should be executed (when?);
5. who is responsible and/or could (help to) perform the tasks (who?).

This manual describes the general instructions for application of the RBA. When more detailed and/or specific instructions apply, these are provided in text boxes or appendixes. In some cases the reader is referred to specific guidelines that are not part of this document.

## 2. Outline of the risk management cycle

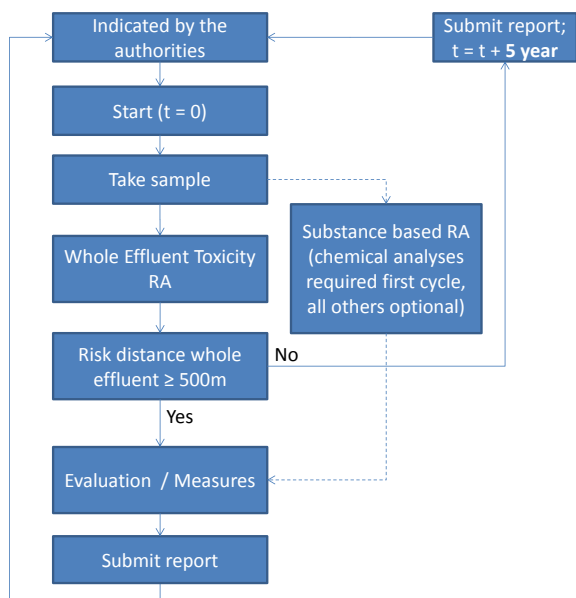
### Risk

The term 'risk' in this document refers to the environmental risk as the result of produced water discharges. More specifically, risk means the likelihood that adverse effects may occur, expressed as the PEC: PNEC ratio (the ratio between the Predicted Environmental Concentration (PEC) and the Predicted No Effect Concentration (PNEC)). The risk can be calculated as either the risk of undiluted produced water or as the risk of diluted produced water in the receiving environment, at a certain distance from the discharge point. More details on the underlying principles and calculation rules for determining the risk are given in Chapters 4 and 5.

### The cycle

The risk management cycle is the cycle in which the risk is first characterised; actions are identified and executed in order to reduce the risk (when required); after implementation of the measures the cycle starts over to determine whether the actions taken were effective and the remaining risk is now acceptable.

The risk management cycle (*Figure 1*) schematically presents the proposed Dutch implementation of OSPAR's risk-based approach to the management of produced water discharges. It should be noted that the first platforms to apply the RBA in the Netherlands will serve as a trail. Based on the results of this trail, the Dutch implementation - and therewith this manual - may be adjusted.



*Figure 1 Risk management cycle of produced water discharges on the Dutch Continental Shelf, following OSPARs Risk Based Approach (RA = Risk Assessment).*

The onset ("Start (t=0)") of the cycle is determined by the authorities, based on either the pre-screening of platforms, significant changes in the discharge of produced water causing a potential increase of risk to the environment, new platforms discharging produced water, or 5 years after the previous cycle. All triggers are described in more detail in the following sections.

The first task in the cycle is sampling ("Take sample", see Chapter 3). This needs to be well prepared and adjusted to the next steps in the cycle as the various biological and chemical tests require different conditions regarding volume, sampling, transport, preservation and pre-treatment of samples.

After sampling the Risk Assessment (RA) process begins. The OSPAR Recommendation on the RBA (OSPAR, 2012) allows Contracting Parties to use a substance based approach (i.e. substance based RA) or a whole effluent approach (i.e. Whole Effluent Toxicity (WET) RA), or a combination of these approaches. The Dutch implementation requires the Risk Characterisation on the basis of the WET approach i.e., additional measures are only required when WET RA indicates unacceptable risk.

"WET RA" (Chapter 4) involves a battery of biological toxicity tests applied to the entire effluent sample instead of to the individual substances allowing also measuring the effects of possible unknown substances in produced water and mixture effects. If the WET RA based on acute toxicity tests results in an acceptable risk (i.e. effects are unlikely at a distance within 500 m from the discharge point), an RBA report is submitted (Chapter 7) and five year after the submission ("Submit report; t=t+5 year"), the cycle needs to be repeated ("Start (t=0)").

"Substance based RA" (Chapter 5) compares the concentration of the substances in the produced water to the sensitivity of the receiving environment in order to determine whether a substance poses a risk (i.e. PEC:PNEC ratio  $\geq 1$ ). The substance based RA could be used to identify the substances that are potentially responsible for exceeding the risk limit based on WET tests. The results are hence useful in defining appropriate measures to reduce the risk (see Chapter 6). The substance based RA is optional with the exception of chemical analyses in the first cycle for each platform (Chapter 5), which is required to determine the concentration of the substances in the produced water. The results of the chemical analyses in the first cycle will be collected by the authorities with the purpose of building up the platform dossier. After completing the first cycle, chemical analyses will be optional but is recommended.

If the WET RA results in an unacceptable risk, the results will be evaluated and, in a dialogue with the authorities, measures are applied to reduce the risk ("Measures", see Chapter 6) and a RBA report is submitted (Chapter 7). At a time indicated by the authorities, the cycle needs to be repeated ("Start (t=0)") in order to evaluate the effectiveness of the measures and to ensure that the produced water poses an acceptable risk.

## **Indications of the authorities to start the cycle for a platform**

### **Pre-screening and prioritisation of platforms**

In essence all oil and gas platforms on the Dutch Continental Shelf (DCS) have to go through the risk management cycle at least once, where the pre-screening determines in which order the platforms enter the cycle. All platforms are divided into three groups, each group entering the cycle in subsequent years, starting in 2015. First a trial will start with platforms in sensitive areas. The results will be analysed and discussed before further implementation will continue. Platforms with the highest expected risk or those in/near sensitive areas (i.e. Natura 2000 areas) are to be assessed first, followed in the subsequent

years by the platforms with lower expected risk. The first risk management cycle serves as a baseline to which future reduction of risk is compared.

In order to prioritise the platforms for this purpose, the competent authorities will use the estimated discharged produced water volumes from the Environmental Annual Reports (Milieujaarrapportages) of the operators, as this volume is strongly related to the risk as determined according to OSPAR guidelines (OSPAR, 2012b).

The competent authorities will generate a list, in consolidation with the operators, indicating which platforms are expected to enter the risk management cycle in which year. Operators may deviate from this list, in concert with the competent authorities, for logistic or operational planning reasons. However, moving platforms backward on the list will mean that others should be put forward, such that each year roughly a third of the platforms on the DCS enter the cycle.

### **Significant change or new platforms**

For the purpose of this RBA, significant changes in the discharge of produced water are only those changes that potentially increase the risk to the environment. A significant change is specified in OSPAR guidelines (item 43 of OSPAR Agreement: 2012-7) as follows:

*"Typically, a review and update takes place when there is a significant change in the produced water discharge (characteristics) due to implementation of risk reduction measures or other modifications, such as:*

- *Implementation of new end-of-pipe technique;*
- *Substitution of added chemicals or new chemicals taken into use;*
- *Significant change in the discharge of added chemicals; and*
- *Tie-in of new produced water streams (satellites) and/or new wells."*

In context of the Dutch implementation, "a review and update" indicates repeating the risk management cycle as presented above. More specifically, a change is only considered in this context when it is anticipated to increase the risk to the environment. Platforms with such a change should enter the cycle within a year of the change.

Because all oil and gas platforms on the Dutch Continental Shelf (DCS) have to go through the risk management cycle at least once, new platforms should also enter the cycle within the first year after they start of producing and discharging produced water.

### **3. Sampling**

#### **Why?**

A sample of produced water representative of its discharge is required to assess the risk of the substances in the produced water. Both the substance-based RA (chemical analyses, Chapter 5) as the WET tests (bioassays, Chapter 4) are performed on a set of samples which are taken at the same time (or in parallel).

#### **What?**

Produced water samples for bioassays and for chemical analysis should be collected in parallel. The number and volumes of samples needed for both the bioassays and the chemical analyses should be communicated with the contract laboratories (Roex, 2012). Typically, 11 separate samples are taken, 4 for the bioassays and 7 for the chemical analysis:

- **Samples for bioassays (WET tests)**  
Each acute bioassay could require a one litre sample of produced water, or just a few millilitres (for the bacteria and algae tests). The contracted laboratory determines if separate samples should be taken for the latter tests or that one sample could be used for two tests, for example. Thus the number and volumes of samples needed is variable and should be communicated with the laboratory. There are different acute bioassays available: microtox®, MARA, LUMIMARA, algal test, crustacean test and oyster larvae test. Samples are required for at least three bioassays representing three different trophic levels (see Chapter 4 and Appendix A). One sample may be required as reserve.
- **Samples for chemical analysis (substance-based risk assessment)**  
A total of 7 separate samples are required for chemical analysis; one for each group of chemicals. Table 1 shows the groups of chemicals with corresponding sample volumes, including instructions, according to the Dutch practical program and the DECC (Department of Energy and Climate Change) Guidance Notes. Deviations from this table are possible.



Table 1 Sampling and transport procedure for chemicals (Roex, 2012; DECC, 2010) deviations from this table are possible. NL: the Netherlands/ Dutch procedure; UK: United Kingdom / UK procedure. The sampling and transport procedure needed for chemical analyses should always be communicated with the contract laboratories

Chemical group	Sample volume	Bottle specifications	Filling instructions	Transport
PAHs	1-litre	Acid washed amber glass sample bottle (containing 1ml of 3% sodium thiosulphate solution (UK))	Fill bottle leaving no air gap (100% fill up). Add 5ml of 50% HCl for acidification (UK), secure lid and check for leaks. Invert six times to ensure thorough mixing	Cooled and unpreserved
NPD* (Naphthalene, Phenanthrene and Dibenzothiophene)	1-litre	Glass bottle	Fill bottle leaving no air gap (100% fill up).	Cooled and unpreserved
BTEX	250 ml (NL); 1-litre (UK)	Acid washed glass sample bottles	Fill bottle leaving no air gap (100% fill up). Acidify with H <sub>2</sub> SO <sub>4</sub> to pH=2 (NL). Secure lid and check for leaks.	Cooled
Metal(other than Mercury)	1-litre	Acid washed polyethylene bottle	Fill bottle to the mark. Add acid (5ml of 50% HCl (UK) or HNO <sub>3</sub> to pH=2 (NL)), secure lid and check for leaks. Invert six times to ensure thorough mixing	Cooled
Mercury	100 ml (NL); 0.5 litre (UK)	Glass sample bottle (containing 10 ml of 0.1M potassium dichromate oxidising agent (UK))	100% fill up of bottle (Roex, 2012). Fill bottle to the mark. Add acid (10-ml aliquots of sulphuric acid (UK) or HNO <sub>3</sub> /K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> to pH=2 (NL)), secure lid and check for leaks. Invert six times to ensure thorough mixing	Cooled
Dispersed oil	1-litre	Solvent washed glass bottle, containing 5ml of 50% HCl (UK)	Fill bottle to the 1-litre mark (UK) / 80% fill up and add acid (HCl to pH=2, NL). Secure lid and check for leaks. Invert six times to ensure thorough mixing	Cooled and unpreserved
Alkyl phenols	500 ml (NL); 1-litre (UK)	Acid solvent washed amber glass bottle	100% fill up of bottle (NL) / fill bottle to the 900ml mark (UK). Secure lid and check for leaks.	Cooled and unpreserved

\* The Dutch practical program includes the PAHs Naphthalene, Phenanthrene and Dibenzothiophene (NPD) as a separate group (Roex, 2012), whereas the UK includes these compounds in the PAH analysis (DECC, 2010).

## How?

General sampling procedures are described in Box 1. Specific instructions for bio-assays and for chemical analysis are provided in Box 2 and Box 3, respectively.

### Box 1 General sampling procedures

These aspects need to be considered when taking samples for the RBA. Note that additional sampling procedures are required for bioassays (see Box 2) and for chemical analyses (see Box 3).

- The sampling and transport procedure needed for analyses should always be communicated with the contract laboratories.
- Specific guidelines for sampling of produced water are available, i.e. Guidelines on sample taking and sample handling from OSPAR Agreement 2006-06 . It describes the location, design, flow rate and condition of the sample point, and the sample bottle requirements. Ensure that the sample point and bottles meet these requirements. Further guidance is available in the Guidance Notes for The Sampling and Analysis of Produced Water and Other Hydrocarbon Discharges (DECC, 2010).
- Make sure that appropriate labels are used on the sample containers, mostly in collaboration with the contract laboratory: type of sample (i.e. bio-assay (see Table 2) or chemical group (see Table 1)) date, time, sampling point/location and name of installation.
- If the temperature of the produced water sample is hot, heat protective gloves should be worn when collecting the samples.
- If the bottle is overfilled the sample must be discarded and the process repeated using a fresh, clean sample bottle.
- Cap the bottle. The lid should be secured and the bottle should be checked for leaks.
- Sample temperature can typically be determined using an IR or laser thermometer, or another method which avoids immersing a thermometer into the sample. The accuracy of the selected method should be checked on a 6 monthly basis. This can be carried out, for example, by a cross check against an alcohol thermometer with a certificate of conformity. Taking a temperature measurement of a liquid, both thermometers should read within  $\pm 3^{\circ}\text{C}$  of each other. If the IR thermometer does not pass this check it should be replaced or recalibrated. The results of cross checks should be recorded in the oil in water logbook.

## Box 2 Sampling for bioassays (WET tests)

The sampling procedure for bioassays needs a different approach than sampling done for chemical analyses (see Box 3) with respect to the following aspects (Roex, 2012; OSPAR, 2012b):

- The most important aspect to take into account is that adding chemicals to the sample in order to conserve the samples should **always** be avoided, as these chemicals will influence the results of the bioassays;
- Make sure that the bottles or containers which are shipped offshore are rinsed with demineralised water as a last step, to remove remains of detergents, which may be still present even if new glassware is used;
- The materials of containers used for sampling or storage should be chemically inert, easy to clean and resistant to heating and freezing. Glassware is recommended;
- The bottles should be rinsed 2-3 times with produced water before taking the actual sample;
- Containers should be filled completely to avoid degradation by air;
- In general, try to keep the time between sampling, transport and testing as short as possible. Precipitation of substances like iron, strontium and calcium may take place during transport and storage. This may have an impact on the test results. To shorten the time period between sampling and arrival in the laboratory, agreements have to be made with both operators of the installations and the laboratory, at which the bio assays will be performed.
- As soon as practicable after sampling, samples should be cooled, preferably until they reach the laboratory. In the Dutch practical program, cooling boxes were used to store the samples during transport. Samples should be cooled to between 0°C and 5°C and stored in the dark. When cooled in this way, most samples are normally stable for up to 24 hours.
- Freezing of samples should be avoided as much as possible. Deep freezing below – 18°C in general increases the stability in preservation (preservation duration preferable less than two weeks, maximum two months according to ISO 5667-16). However, it is known that freezing and thawing of samples may result in loss of toxicity. When the thawing process is not controlled, volatile components may be lost. Particle size and distribution may also change, thereby influencing other tests. In addition, allowing particles to settle over a short period can result in a significant reduction in toxicity;
- Immediate measurements of selected physical-chemical parameters (pH, ammonium, salinity, etc.), is recommended upon arrival of the bioassay samples in the laboratory. This is to allow for adjustment of the samples if considered necessary for performance of the bioassays.

### Box 3 Sampling for chemical analysis (substance-based risk assessment)

- Follow the specific instructions for sampling, transport and preservation for each of the produced water compound groups, as provided in Table 1. General instructions are provided below:
- Sample bottles must not be rinsed out prior to sampling as some of the sample bottles may already contain small amounts of preservation reagents (see instructions Table 1).
- If acidification with HCl is required, acidify the sample with a 1:1 hydrochloric acid-water mixture to a pH <2, noting the volume of acid used. After mixing the sample, check the pH by touching pH-sensitive paper to the cap to ensure that the pH is 2 or lower. Do not use immersion type pH probes to measure the pH of samples.

**Warning:**

Produced water may contain sulphide compounds that when acidified may release hydrogen sulphide, which is extremely toxic, into the atmosphere. Acidification of the produced water sample must be carried out in an operational fume cupboard.

Appropriate safety precautions should be taken when adding the acid, see the Material Safety Data Sheet (MSDS) of the chemical. Always add acid to water, never water to acid.

- Cool the sample to lab ambient temperature (approx. 15°-20°C, but no more than 20°C) prior to the analysis being carried out. Other temperatures may be selected but only if they are specified in either a recognised analysis method or are recommended by the instrument manufacturer. The cap should be loosened during the cooling process and once cool, tightened securely.
- Sample sparging using nitrogen (or any other gas), is no longer permitted and should not be used under any circumstances unless it has been discussed and agreed with the authorities.
- Samples should be stored in a refrigerator (4°C to 8°C) if they are not going to be analysed within twelve hours. Prior to any analysis being carried out they must be warmed to laboratory ambient temperature or another specified temperature (see above).
- For a variety of reasons it may not be possible to analyse the sample immediately (e.g. waiting on a replacement analyser, samples to be sent onshore for analysis), in which case samples must be acidified with a 1:1 hydrochloric acid-water mixture to a pH <2 and stored in a refrigerator (4°C to 8°C) until analysed. Samples sent onshore for analysis should be stored at or below in a refrigerator (4°C to 8°C), once received, until analysed. Preserved samples must be analysed within seven days of collection. Where analysis within seven days is not possible, an explanation must be provided to the appropriate authorities. For installations where samples are returned to shore for analysis on the same day as sampling, and where acid is unavailable, samples should be acidified on arrival at the onshore laboratory.
- When taking duplicate produced water samples mark duplicate sample bottles at 1/3, 2/3 and 3/3 volume measurement and then fill the sample bottles 1/3 at a time in turn until all bottles are full.

## When?

Sampling needs to be well prepared and adjusted to the next steps in the cycle, involving the various chemical and biological tests. These tests require different conditions regarding volume, sampling, transport, preservation and pre-treatment of samples. In general, try to keep the time between sampling, transport and testing as short as possible. To shorten the time period between sampling and arrival in the laboratory, agreements have to be made with both operators of the installations and the laboratory, at which the analyses will be performed.

When entering the RBA management cycle, sampling is the first task (see *Figure 1* in Chapter 2). The onset of the cycle is determined by the authorities, triggered by:

- Pre-screening of platforms  
The competent authorities will generate a list, in consolidation with the operators, indicating which platforms are expected to enter the risk management cycle in which year. Operators may deviate from this list, in concert with the competent authorities, for logistic or operational planning reasons. Note that each year, starting from 2015, roughly a third of the platforms on the DCS should enter the cycle.
- Significant changes in the discharge (characteristics) of produced water causing a potential increased risk to the environment  
Platforms with significant changes causing a potential **increased risk** to the environment due to substitution of added chemicals or new chemicals taken into use, significant change in the discharge of added chemicals and tie-in of new produced water streams (satellites) and/or new wells, should enter the cycle within a year of the change. Significant changes due to implementation of **risk reduction** measures or other modifications, such as implementation of new end-of-pipe technique do not trigger a new cycle.
- New platforms  
New platforms should also enter the cycle within the first year after they start of producing and discharging produced water.
- Five years after initializing the first risk management cycle (as the according to OSPAR guidelines, the cycle has to be repeated periodically).

## Who?

Sampling can be done by the contracting laboratory or by operators on the platform. If the sampling is done by operators on the installation, make sure that they are fully aware of all the above aspects.

## 4. Whole effluent toxicity risk assessment

### Effect based testing of the effluent

#### Why?

The effect concentrations of the whole effluent for a selection of biota (i.e., covering three trophic levels) is required for the derivation of a Predicted No Effect Concentration (PNEC). This PNEC value is required for the Whole Effluent Toxicity risk assessment, which is one of the two approaches according to the OSPAR guideline to determine the total risk of produced water to the receiving environment. The Netherlands have chosen to use WET as a leading methodology in the RBA.

The WET approach must be used to assess the toxicity of produced water by effect based testing of the effluent by using a battery of bioassays. This approach assesses the combined toxicity from all substances in the produced water, including possible unknown substances. In the Dutch implementation of the RBA, WET is undertaken in conjunction with chemical characterisation. However, WET is always required within the RBA cycle and determines whether the total risk of the produced water is acceptable. Chemical characterisation is only required within the first cycle for each platform. In following cycles of the RBA chemical analyses are recommended but optionally applied. The bioassays provides the necessary data for derivation of a PNEC for the whole produced water effluent, which is required for the risk characterisation, as described in the next paragraph.

#### What?

According to the OSPAR Guidelines on RBA (OSPAR, 2012b), at least a minimum of three in vivo bioassays in line with standardised protocols (ECHA Guidance on information requirements and chemical safety assessment, R10.3.2) should be performed, representing three different trophic levels e.g. bacteria, algae and crustacean. Fish tests, or other tests with vertebrates, should be avoided, because of ethical reasons (Roex, 2012). The fish toxicity test will therefore not be carried out in the Netherlands and a proposal to apply the oyster larvae (*Crassostrea gigas*) or Sea-urchin (*Echinocardium cordatum*) testing is currently being discussed (OSPAR, 2013b). It should be noted that the latter tests are currently not an alternative to fish tests, i.e. they are not representing the same trophic level.

To minimise economic and time constraints, the focus should primarily be on acute toxicity tests, although chronic toxicity tests give more realistic information (Roex, 2012). Chronic toxicity tests are therefore only considered when the substance based RA results in an unacceptable risk (see *Figure 1* in Chapter 2). Whether to use chronic toxicity test in aid to determine the cause of the risk, and therewith possible measures to reduce the risk, will be evaluated (see Chapter 6 'Measures'). *Table 2* gives an overview of the most common acute tests that have been used in the past on produced water samples. More information about some of the most relevant bioassays is described in "A practical program for Whole Effluent Assessment for discharges from the offshore industry" (Roex, 2012). Chronic toxicity tests are shown in *Table 3*.

A number of physical/chemical parameters are very relevant in the final interpretation of the bioassay results. It is recommended that the following parameters are measured upon arrival in the lab: pH, ammonium, nitrite, conductivity, salinity, oxygen and particles. Some parameters like sulphite are only relevant for specific bioassays (Roex, 2012).

Table 2 Acute tests for whole effluent testing

<b>Trophic level / taxonomic group / Species</b>	<b>Test description</b>	<b>Protocol</b>	<b>Reference</b>
<b>Microbial community</b>			
<b>Bacteria</b>			
<i>Vibrio fischeri</i>	Luminescence inhibition, 0.5h	ISO 11348-2	Roex (2012)
<i>Vibrio fischeri</i>	Acute inhibition light emission, 0.5h	11348-1, 11348-2, 11348-3 DIN 38412 T34/T341; AFNOR T90.320	OSPAR (2000)
LUMIMARA (11 different bacterial species)	Luminescence inhibition, 0.25h	NCIMB Ltd internal work instruction	Roex (2012), NCIMB website
MARA (10 different bacterial species and 1 yeast species)	Growth inhibition, 18h	NCIMB Ltd internal work instruction	Roex (2012), NCIMB website
<b>Primary producers</b>			
<b>Algae</b>			
<i>Phaeodactylum tricornutum</i>	Chronic growth inhibition, 72h	ISO 10253	Roex (2012), OSPAR (2000)
<i>Skeletonema costatum</i>	Chronic growth inhibition, 72h	ISO 10253	Roex (2012), OSPAR (2000)
<b>Primary consumers</b>			
<b>Crustaceae</b>			
<i>Acartia tonsa</i>	Acute mortality test, 48h	ISO 14669	Roex (2012), OSPAR (2000)
<i>Tisbe battagliai</i>	Acute mortality test, 48h	ISO 14669	Roex (2012), OSPAR (2000)
<i>Nitocra spinipes</i>	Acute mortality test, 48h	ISO 14669	OSPAR (2000)
<b>Mollusks (bivalves)</b>			
<i>Crassostrea gigas</i> (Oyster larvae)	Abnormal development, 48h (embryo/larval)	ICES Techniques in Marine Environmental Sciences No. 54	Roex (2012), Leverett & Thain (2013)
<i>Crassostrea gigas</i> , <i>Crassostrea virginica</i> , <i>Mercenaria mercenaria</i> , <i>Mytilus edulis</i>	Acute survival and abnormal development, 48h (embryo/larval)	EPA/OPPTS 850.1055 draft ASTM E 724-98	OSPAR (2000)
<i>Crassostrea virginica</i>	Acute shell growth, 72h	EPA/OPPTS 850.1025 draft	OSPAR (2000)
<b>Echinoderms</b>			
<i>Psammechinus miliaris</i> (Green sea urchin embryo)	16-day echinoid early life stage (ELS) bioassay	<a href="http://www.sciencedirect.com/science/article/pii/S0147651311002429">http://www.sciencedirect.com/science/article/pii/S0147651311002429</a>	

Table 3 Chronic tests for whole effluent testing

Trophic level / taxonomic group	Species	Protocol	Reference
Primary producers			
Algae	<i>Phaedactylum tricorutum</i>	ISO 10523	Roex (2012)
	<i>Skelatonema costatum</i>	ISO 10523	Roex (2012)
Primary consumers			
Crustaceae	<i>Americanyasis bahia</i> (former <i>Mysidopsis bahia</i> )	EPA, 2007	Roex (2012)
Mollusks	<i>Mytilus edilus</i>	ASTM, 1993	Roex (2012)
	<i>Psammechinus miliaris</i>	semi-chronic, internal SOP based on USEPA	Foekema (pers. comm.)
	<i>Psammechinus miliaris</i>	Dinnel, 1993	Roex (2012)
	<i>Crassostrea gigas</i>	semi-chronic, USEPA 203 & SCA	Foekema (pers. comm.)

## How?

In general, the WET tests require the following steps:

- Samples of the produced water effluent are required for the bio-assays. Chapter 3 (sampling) describes the sampling and transport procedure for bio-assays.
- Pre-treatment of samples may be required to modify the sample only as far as the bio-assay test requirements demand. Box 4 describes the pre-treatment for the most used bio-assays.
- When carrying out WET testing the OSPAR Guidelines on the RBA (OSPAR, 2012b) recommend to follow the Practical Guidance Document on Whole Effluent Assessment for offshore Discharges (Roex, 2010) or similar guidance. An overview of bio-assays is provided in *Table 2* and the most relevant tests are described by Roex (2010). Detailed information about the execution of the bioassays can be found in the protocols, mentioned in *Table 2*. Operators have to make sure that the contracting laboratories that will eventually perform the bioassays will have enough experience to carry out the bioassays according to the protocols (Roex, 2012).
- Effect levels should be determined in a dilution range. More information on the dilution range is provided in Box 4.



## Box 4 WET tests

### Physical-chemical parameters

The parameters as shown in the table below should be measured upon arrival in the lab. When the parameters measured in the test exceed the ranges reported, effects caused by these parameters cannot be excluded. In those cases, it is recommended to adjust these parameters in order to comply with the ranges reported in the table. An approximate measure of some parameters (pH, ammonium, nitrite, sulphite) can be done initially by using test strips. If there is an indication that parameters exceed the criteria more sophisticated equipment, like specific electrodes, are needed. In general, when parameters exceed the upper range, the best way forward is dilution of the sample, except for the parameter pH. In that case, neutralization is the best way forward.

*Overview of the ranges of the physical-chemical parameters for the most used bio-assays (Roex, 2012)*

Species	pH	O <sub>2</sub>	NO <sub>2</sub> <sup>-</sup>	Ammonium	Sulphide	Chloride	Conductivity	Salinity
<i>Vibrio fisheri</i>	6-8.5	>30	<70	<1000	<3.3	<20	<4600	18-35
<i>Phaeodactylum tricorutum</i>	7.7-8.3	n.r	<150	<60	-	5-20	1150-4600	9-36
<i>Brachionus plicatilis</i>	5-9	>15	<1660	<1000	-	0.6-18	140-4150	1-32
<i>Acartia tonsa</i>	7-9	>25	<10	<30	-	5.5-22	1300-5100	10-40
<i>Artemia salina</i>	4-9	>30	<200	<600	-	0.7-18	200-4150	1-32
<i>Poecilia reticulata</i>	5-9	>60	-	<70	-	<23	<5500	<41
<i>Crassostrea gigas</i>	7.5-8.5	40-110	<32	<3	<0.1	11-18	2500-4200	20-32
<i>Psammechinus miliaris</i>	7.5-8.5	>70	<15	<10-<32*	-	-	-	28-36
<i>Echinocardium cordatum</i>	7.5-8.5	>60	<50-<200*	<5-<25*	<5	>16	>3500	>28
<i>Corophium volutator</i>	7-9	>50	<30-<200*	<10-<100*	<2	2-22	500-5100	4-40

### Dilution range

The dilution range to determine the effect levels should preferably start with undiluted produced water, and diluting in a suitable logarithmic series of at least 4 concentrations, e.g. 1, 0.32, 0.18, 0.10 and 0.056 (a concentration of 0.1 indicates that the whole effluent is diluted 1/0.1 = 10 times). All these dilutions originate from the same subsample (1 litre bottle). However, there may be legitimate reasons to start with a dilution, because of earlier results of the bioassays with the same sample, or because of confounding factors (e.g. salinity). The dilution should be made on the day of testing by mixing the produced water with artificial seawater or natural sea water from a controlled clean location.

### Caution:

While performing the bioassays, lab employees should be notified that produced water contains so-called Naturally Occurring Radioactive Materials (NORM), most abundant are Radium-226 and Radium 228 and relative high levels of BTEX. These substances may impose health risks to workers.

## When?

WET testing needs to be well prepared and adjusted to the previous step in the cycle, sampling, and the parallel step, chemical analyses. Important aspects for preparation are:

- Specific requirements for sampling, preservation and transportation apply for the different analyses (see sampling instructions in Chapter 3);
- Keep the time between sampling, transport and testing as short as possible;
- Samples for WET en chemical analyses should be taken on the same time;
- Immediate measurements of selected physical-chemical parameters (pH, ammonium, salinity, etc.), is recommended upon arrival of the bioassay samples in the laboratory. This is to allow for adjustment of the samples if considered necessary for performance of the bioassays.

After entering the RBA management cycle and taking the samples (first task, see *Figure 1* in Chapter 2), WET testing is the second task. WET testing is part of the WET RA, as described in this Chapter (Chapter 4). The WET RA needs to be performed together with the chemical characterisation when the latter is required (i.e., in the first risk management cycle) (Chapter 5), however, the WET RA is leading, i.e. the outcome determines if the risk is unacceptable and if additional measures are required (see Chapter 2).

## Who?

Select a laboratory that is acceptable to the competent authority. The authorities require that laboratories carrying out WET tests be accredited. When accredited laboratories are not available, the competent authorities should be consolidated. Laboratories should use (preferably internationally) accepted protocols (i.e., those specified in *Table 2*). Furthermore, operators who should all have an Environmental Management System in place, must assure themselves of the quality of work being carried out by contract laboratories on their behalf. Laboratories in the Netherlands that conduct marine WET tests are e.g. IMARES and Grontmij|Aquasense.

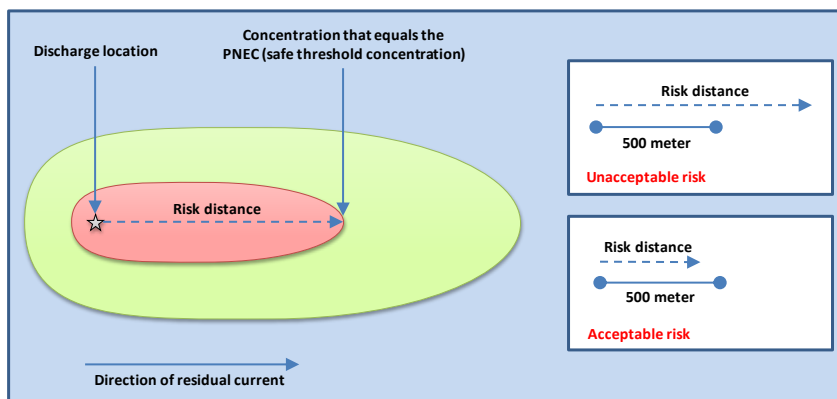
## Risk characterisation

### Why?

The goal of the risk based approach is to reduce the environmental risk resulting from produced water discharges. In order to reduce this risk, it first needs to be characterised.

### What?

In this risk characterisation step, the risk distance is determined. The risk distance is the distance within which a safe threshold concentration is exceeded and effects can therefore not be excluded (*Figure 1*). Risk is considered unacceptable when the risk distance is greater than 500 m, in which case it needs to be managed by taking measures (Chapter 6).



*Figure 2 Schematic representation of a discharge plume and illustration of the risk distance. When the risk distance exceeds the safety distance of 500m, the risk is considered acceptable. If it's greater, the risk needs to be managed.*

For the risk characterisation WET test results (as specified in the section 'Effect based testing of the effluent') are required to derive the 'safe' threshold concentration.

Discharge and environmental characteristics are required to determine the dilution of the effluent in space.

### How?

In principle the acute toxicity of the effluent is determined for at least three trophic levels as described in the section 'Effect based testing of the effluent'. Exposure levels in those tests were expressed as volume fraction of the whole effluent. From the WET tests a predicted no effect concentration (PNEC) is derived (Box 5). A PNEC is a threshold concentration below which effects are not anticipated.

The risk distance is the maximum distance within which discharged concentration exceeds this PNEC. Hence, a model is required that calculates the dilution of the effluent as a function of the distance from the discharge location. Box 6 shows an example of a relatively simple model that is recommended for this purpose. Operators are allowed to use more realistic (but more complicated) models for this purpose (e.g., three dimensional particle tracking models such as DREAM or DELF3D). **However, once a model is used for a platform it should be used consistently for each management cycle: i.e., risk reduction cannot be achieved by applying different models.** This does not mean that operators cannot select a different model at a certain point in time. However if an operator desires to choose a

different model, risk calculations from previous cycles have to be repeated with this new model. This is required to have consistent results for each year. Also, such models need to be validated with relevant data. Relevant information with respect to the validation needs to be included in the report.

Once the risk distance is calculated and is greater than or equal to 500 m, the risk is considered unacceptable and needs to be managed by taking appropriate measures (Chapter 6). The substance-based risk assessment (Chapter 5) can be used to identify the substances posing the highest risk and therewith help to determine the most suitable measures. Regardless of whether there is a (un)acceptable risk, the findings have to be reported to the competent authorities (Chapter 7). If the risk is unacceptable, the cycle has to be repeated within a period that will be specified by the competent authorities; when the risk is considered acceptable, the cycle has to be repeated after five years after the initialisation of the current cycle.

#### Box 5 Deriving a PNEC value from the WET tests

End points in the bioassays (e.g. 50% effect concentration for acute tests, or no observed effect concentration for chronic tests) are expressed as volume fractions of the entire effluent; where a low fraction indicates high toxicity as only a small fraction of effluent still has an effect and vice versa.

##### **Example of volume fraction:**

A concentration of 0.1 indicates that the whole effluent is diluted  $1/0.1 = 10$  times.

The PNEC is in this case also expressed as a volume fraction of the effluent and is calculated from the (no) effect concentration (also expressed as volume fraction) of the worst WET test. This (no) effect concentration is divided by a safety factor.

Conform OSPAR guidelines (2012-7), an assessment factor of 1000 should be applied when three taxonomically distinct species have been tested. This assessment factor can be lowered by performing more acute tests on different trophic levels or by performing chronic tests.

##### **Example of deriving a PNEC:**

The following hypothetical results were obtained from the WET tests:

Species	EC50 (as fraction of the effluent)	The factor by which the effluent had to be diluted to achieve 50% effect in the bioassay
Algae	0.1	$1/0.1 = 10$
Crustacean	0.5	$1/0.5 = 2$
Oyster larvae	0.2	$1/0.2 = 5$

The algae were most sensitive with an EC50 of 0.1. Hence,  $PNEC = 0.1/1000 = 1 \times 10^{-4}$  in this example.

## Box 6 Calculating the risk distance

For the purpose of calculating the risk distance, the one dimensional dilution model by Rye et al. (1996), as also implemented with CHARM (Karman and Vik, 1996), can be used:

$$D = \frac{V}{F_w/86400} \left( \frac{96 \cdot K \cdot X^3}{U} \right)^{0.5}$$

in which:

$D$  = dilution factor (the number of times the discharged concentration is diluted at distance  $X$ )

$K$  = vertical diffusion coefficient (CHARM default :  $1.4 \cdot 10^{-3} \text{ m}^2 \cdot \text{s}^{-1}$ )

$V$  = horizontal diffusion coefficient (CHARM default :  $0.18 \text{ m} \cdot \text{s}^{-1}$ )

$U$  = residual current speed / the net water current (CHARM default :  $0.2 \text{ m} \cdot \text{s}^{-1}$ )<sup>4</sup>

$X$  = distance (m) for which the dilution is calculated

$F_w$  = discharge rate of produced water ( $\text{m}^3 \cdot \text{d}^{-1}$ )

86400 = number of seconds in one day ( $\text{s} \cdot \text{d}^{-1}$ )

From this equation we want to solve the distance from the discharge ( $X$ ) where the dilution factor equals the inverse of the PNEC (as derived in Box 5), or formulated as an equation:  $D = \frac{1}{\text{PNEC}}$

The risk distance is therefore formulated as:

$$X = \left( \frac{U}{96 \cdot K} \left( \frac{F_w}{86400 \cdot V \cdot \text{PNEC}} \right)^2 \right)^{\frac{1}{3}}$$

### Example of calculating risk distance:

Let's say that the PNEC equals  $1 \times 10^{-4}$  as determined in the example in Box 5 and the discharge rate is  $1000 \text{ m}^3/\text{day}$ . Using the formula above we get:

$$\begin{aligned} X &= \left( \frac{0.2}{96 \cdot 1.4 \cdot 10^{-3}} \left( \frac{1000}{86400 \cdot 0.18 \cdot 1 \cdot 10^{-4}} \right)^2 \right)^{\frac{1}{3}} \\ &= (1.49 \cdot 6430^2)^{1/3} \\ &= 85 \text{ m} \end{aligned}$$

Meaning that the diluted effluent no longer exceed the PNEC at distances greater than 85 meter.

Note that this model ignores certain processes (e.g., evaporation, (bio)degradation) but is generally considered conservative.

<sup>4</sup> The default value in CHARM represents a worst case residual currents. Operators can use more realistic currents (e.g. based on data from [www.myocean.eu](http://www.myocean.eu)). However, the value selected value for a platform should be used **consistently** for that platform in each risk management cycle. I.e., risk reduction should **not** be the result of changing values of the residual currents parameter!

**When?**

Each risk management cycle needs to be reported within a year from the start of the cycle. Preparation for this step can start at any time, but can only be completed when the required data (WET tests and discharge/environmental characteristics) are available.

**Who?**

In principle, operators are responsible for the risk characterisation and its reporting. Optionally, operators can outsource this task to consultants, which may be necessary when operators wish to use more complex dilution models.

## 5. Substance-based risk assessment

### Chemical analysis

#### Why?

The RBA does not focus solely on oil in produced water discharges, but on all substances present in the produced water, as they all contribute to the total risk. One of the two approaches to determine the total risk of produced water to the receiving environment is substance based risk assessment. The other approach, WET RA (see Chapter 4), is always required within the RBA cycle and determines whether the total risk of the produced water is acceptable. Substance based risk assessment is only applied additionally to the WET RA. Substance based risk assessment is based on the exposure relating to the discharge (Predicted Environmental Concentration: PEC) and the sensitivity of the receiving marine environment (Predicted No Effect Concentration: PNEC). In order to determine the PEC for naturally occurring substances in produced water, the concentrations of these substances needs to be known. Chemical analysis is necessary to determine these concentrations and is required for the first cycle of each platform. It is optional but recommended for subsequent risk management cycles.

#### What?

The produced water substances that should at least be analysed within the first RBA cycle for each platform are shown in *Table 4*.

*Table 4 Substances for chemical analyses (OSPAR, 2012b; Roex, 2012; DECC, 2010; and OSPAR in prep./2014)*

Substance group	Substance
Metals	Arsenic, cadmium, chromium, copper, mercury, lead, nickel and zinc
BTEX	Benzene, toluene, ethylbenzene and o,m,p xylene
Dispersed oil	Dispersed oil (oil in water), C7-C40
PAHs (with the <b>16 EPA PAH in bold</b> )	<b>Naphthalene</b> and alkyl homologues (1-methylnaphthalene, 2-methylnaphthalene, 9-methylnaphthalene, 2,6 dimethyl naphthalene, 2-isopropylnaphthalene), dibenzothiophene and alkyl homologues (4-methyldibenzothiophene, 4-ethyl dibenzothiophene), <b>acenaphtylene, acenaphtene, fluorene, phenanthrene</b> and alkyl homologues (9-ethylphenanthrene, trimethylphenanthrene, 1,2,6-trimethylphenanthrene), <b>anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a)anthracene, benzo (g,h,i)perylene, indeno(1,2,3,-cd)pyrene</b>
Alkylphenols	Phenol (and C1-C3 alkyl phenols), Butylphenol (and other C4 alkyl phenols), Pentylphenol (and other C5 alkyl phenols), Octylphenol (and C6-C8 alkyl phenols), Nonylphenol (and other C9 alkyl phenols)

## How?

The recommended analysis, methods and limits of quantification for produced water substances (naturally occurring) is shown in *Table 5*.

Examples of procedures for the sampling and analysis of substances in produced water are provided in the following documents (note: Available chemical analysis protocols for produced water in general do not include analysis of added chemicals):

- OSPAR Agreement 2006-06. Oil in produced water analysis. Guideline on criteria for alternative method acceptance and general guidelines on sample taking and handling;
- the 'Produced Water Sampling and Analysis Guidance Notes' from the Department of Energy and Climate Change (DECC, 2010) in the United Kingdom;
- the Norwegian oil and gas guidelines for sampling and analysis of produced water (Norwegian Oil and Gas, 2012).



Table 5 Overview of recommended analysis, methods and limits of quantification for produced water substances (naturally occurring). No: Norwegian analysis, as described in Appendix 4 of the OSPAR Guidelines (OSPAR, 2012b); UK: UK analyses (DECC, 2010).

Substances	Methods	Standards of analysis	Detection limits
<b>Metals</b>			
Arsenic	AAS/ICP-MS /DRC-ICP-MS /HR-ICP-MS (No); ICP-AES, AAS, DRC-ICP-MS, HR-ICP-MS, HG-AAS, or ICP-MS (UK)	EPA 200.7/200.8	1 – 5 (No); 1 (UK)
Cadmium	Idem	Idem	0.05 – 6 (No); 0.5 (UK)
Chromium	Idem	Idem	0.1 – 1,5 (No); 1.5 (UK)
Copper	Idem	Idem	0.5 – 6 (No); 10 (UK)
Lead	Idem	Idem	0,3 – 1,5 (No); 1 (UK)
Nickel	Idem	Idem	0,5 – 9 (No); 9 (UK)
Zinc	Idem	Idem	2 – 15 (No); 5 (UK)
Mercury.	CV-AAS/ICP-MS/DRC-ICP-MS (No); ICP-AES, or CV-AAS. Standard addition should be used. Voltammetry may be suitable (UK)	Idem	0.002 – 0.1 (No); 0.5 (UK)
(Iron)	AAS/ICP-MS/DRC-ICP-MS/ICP-AES	Idem	1 – 4 (No)
(Barium)	Idem	Idem	0.1 – 10 (No)
<b>Mono Aromatic Hydrocarbons (BTEX)</b>			
Benzene	GC-MS or GC-FID Headspace or purge-and-trap (No); headspace method based on GC/MS (UK)	Internal method M-036 (No); ISO method 11423-1 <sup>5</sup> (UK)	1 – 10 (No); 1.0 (UK)
Ethylbenzene	Idem	Idem	1 – 50 (No); 1.0 (UK)
Xylene (p, m, o)	Idem	Idem	1 – 30 (No); 1.0 (UK)
Toluene	Idem	Internal method M-047 (No); ISO method 11423-1 (UK)	1 – 20 (No); 1.0 (UK)
<b>Dispersed oil</b>			
C7-C40	GC/FID (No); DECC Triple Peak method (UK)	Mod. NS-EN ISO 9377-2/OSPAR 2005-15	0.2 (No)
<b>Polycyclic Aromatic Hydrocarbons (PAHs)</b>			
16 EPA and other PAHs (see Table 4)	GC/MS	Internal method M-036 (No); ISO WD 14653-2:1997 <sup>6</sup> or US EPA 610 (UK)	0.01 – 0.1 (No); 0.1 (UK)
<b>Alkylphenols</b>			
Sum C1-C3, C4-C5 and C6-C9 alkylphenols	GC-MS 2285 (No); GC-MS (UK)	Method established by Battelle, US (No)	0,01 – 0,1 (No); 0.1 (UK)

<sup>5</sup> ISO method 11423-1- "Water-quality Determination of benzene and some derivatives. Part 1: Head-space gas chromatographic method"

## **When?**

Chemical analyses needs to be well prepared and adjusted to the previous step in the cycle, sampling, and the parallel step, biological tests. Important aspects for preparation are:

- Specific requirements for sampling, preservation and transportation apply for the different analyses (see sampling instructions in Chapter 3);
- Keep the time between sampling, transport and testing as short as possible;
- Chemical analyses should be performed on the same set of samples as for the bio-assays.

After entering the RBA management cycle and taking the samples (first task, see *Figure 1* in Chapter 2), chemical analyses is the second task. Chemical analyses is part of the substance based RA, as described in this Chapter (Chapter 5) and is required for each platform only within the first RBA cycle. After completing the first cycle, chemical analyses (and substance based RA) are recommended but not required. In order to be able to use the substance based RA results in defining appropriate measures to reduce the risk if necessary (see Chapter 6), the substance based RA needs to be performed based on information gathered, sampled together with the information on which the WET RA is based upon (Chapter 4).

## **Who?**

Select a laboratory that is acceptable to the competent authority and where the OSPAR Reference Method can be carried out (OSPAR, 2006). The authorities require that laboratories carrying out chemical analysis be accredited. Furthermore, operators who should all have an Environmental Management System in place, must assure themselves of the quality of work being carried out by contract laboratories on their behalf. Laboratories should use (preferably internationally) accepted protocols and detection limits should be below the PNECs. When accredit laboratories are not available or cannot achieve a limit of detection below the PNECs, the competent authorities should be consolidated.

## **Risk characterisation**

### **Why?**

The goal of the risk based approach is to help reduce the environmental risk resulting from produced water discharges. In order to reduce this risk, it first needs to be characterised. As, initially the Whole Effluent Toxicity is only determined with acute tests, the substance-based risk assessment will provide information on risks resulting from chronic exposure.

Also when measures are necessary, the substance-based risk can be used provide a focus on (a) specific chemical(s).

### **What?**

The risk is determined for individual chemicals. It is defined for each substance as the ratio between Predicted Environmental Concentration (PEC) and the concentration above which effects cannot be excluded (or more formally: the Predicted No Effect Concentration; PNEC). When this ratio is below 1 it is unlikely that ecological effects will occur. When this ratio is equal or greater than 1, ecological effects cannot be excluded.

The following substances should be included in the substance-based risk characterisation:

- the analysed substances (see Section 'Chemical analysis');
- individual non-PLONOR chemicals in applied products and;
- individual PLONOR<sup>7</sup> chemicals that are applied in large quantities and will be specified by the competent authorities.

For all individual chemicals Predicted Environmental Concentrations (PEC) are required, which is assumed to be equal to the discharged concentration in this case.

### **How?**

There are 3 basic steps that need to be followed:

- determine the discharge concentration for each substance (PEC);
- obtain or derive threshold concentrations (PNEC), see the "Background document for establishment of a list of Predicted No Effect Concentrations (PNECs) for naturally occurring substances in produced water. PNECs list for use in the Risk Based Approach to the management of produced water discharged from offshore installations" (OSPAR, in prep/2014);
- calculate the PEC:PNEC ratio.

Each step is described in more (technical) detail in Box 7. Substances with the highest PEC:PNEC ratios pose the highest risk to the receiving environment.

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<sup>7</sup> PLONORs are included in the risk-based approach, as they can contribute to the overall risk, especially when they are discharged in large quantities.

Box 7 Technical calculation rules for determining the substance-based risk.

#### **Discharged concentration**

The concentrations for the 'naturally occurring' substances are determined with the chemical analyses. When a concentration is below the limit of detection, the limit of detection divided by two is taken as the discharge concentration.

The discharge concentrations for chemical additives are based on chemical components (and not on the entire product). These discharge concentrations should be derived conform the Chemical Hazard Assessment and Risk Management (CHARM) model (Karman & Vik 1996), based on the HOCNF registration of the products. Basically this means that the discharge concentration is obtained by dividing the permitted amount by the discharged volume produced water.

As the substance based RA is only applied to determine the relative risk of individual components in the produced water (i.e. prioritising), dilution in the receiving environment does not need to be addressed and the discharged concentration is used as PEC.

#### **Predicted No Effect Concentrations (PNECs)**

PNECs for 'naturally occurring' should be based on the standardised list of PNECs in the OSPAR background document (OSPAR, in prep./2014). Deviation from this list should be explicitly reported and underpinned with an explanation.

PNECs for non-PLONOR additives based on HOCNF registered toxicity information. The derivation should be conform OSPAR Agreement 2012-7. In essence, if three trophic levels of species have been tested (as is usually the case), the worst (lowest) effect concentration should be divided by a safety factor of 1000.

As toxicity data for PLONORs are not available from the HOCNF, it should be based on data from literature. PNECs for PLONOR additives should also be derived conform OSPAR guidelines (Agreement 2012-7).

#### **Calculating the PEC:PNEC ratio**

This ratio is calculated for each substance based on the PEC and PNEC as described in the previous steps.

#### **When?**

Each risk management cycle needs to be reported within a year from the start of the cycle. Preparation for this step can start at any time, but can only be completed when the required data (chemical analyses and discharge/environmental characteristics, in the first cycle) are available.

#### **Who?**

In principle, operators are responsible for the risk characterisation and its reporting. Optionally, operators can outsource this task to consultants.

## 6. Measures

### Why?

The goal of the risk based approach is to determine the environmental risk resulting from produced water discharges and to effectively reduce unacceptable risks. When risk characterisation in the risk management cycle indicates that the current risk is unacceptable, as determined with the WET RA (Chapter 4), measures need to be considered aiming at the reduction of the risk. Based on evaluation of the results, suitable measures are proposed and implemented in discussion with the authorities. Hence, the risk-based approach should assist the discussion between the operator and competent authorities on the measures required to reduce the environmental risk.

### What?

Measures are clearly defined in OSPAR Agreement 2012-7:

"39. Risk reduction measures (OSPAR Commission publication on the Background Document concerning Techniques for the Management of Produced Water from Offshore Installations) may comprise some or all of the following:

- technical measures, such as abatement at the source by redesign of the applied processes (water shut off in the well);
- substitution of chemicals;
- application of closed systems (e.g. injection of produced water);
- end-of-pipe techniques such as separation or clarification techniques to treat produced water prior to discharge, and;
- organisational measures such as management systems in place (training, instructions, procedures and reporting)."

Measures are proposed, reported (Chapter 7) and implemented and evaluated in a new management cycle. At indication of the competent authorities, chronic WET test may be required in a following risk management cycle.

### How?

Measures should be aimed at reducing risk in case the WET RA (Chapter 4) resulted in an unacceptable risk (risk distance whole effluent  $\geq 500$  m). The substance-based risk characterisation (Chapter 5) gives an indication of the relative contribution of the chemical components in the discharge to the risk. Measures should be targeted at those substances that have a high contribution to the risk.

For instance, when the substance that contributes most to the risk is an additive, measures may be aimed at substitution of the additive. When that substance is a 'naturally occurring' substance in produced water, measures should be aimed at for instance end-of-pipe techniques.

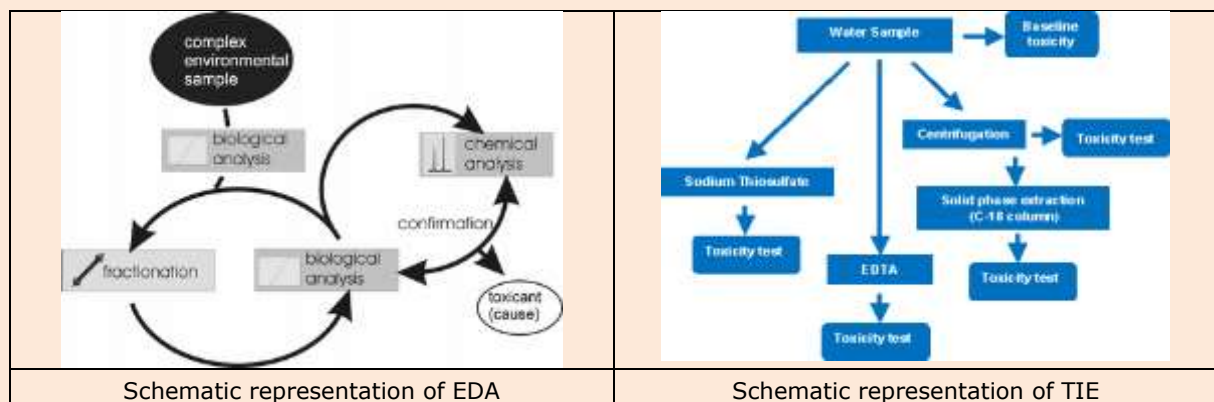
When measures were taken in a previous risk management cycle, those measure need to be evaluated. This evaluation should be included in the process of providing a rationale for new measures; i.e., we should learn from the (lack of) previous successes.

Operators are encouraged to use so-called 'effect-directed analyses' or 'toxicity identification and evaluation' techniques in combination with WET tests (see Box 8). These techniques are used to assign

effects observed in WET tests to specific chemical groups with specific physicochemical properties. This can be particularly useful when end-of-pipe techniques are considered. Note that such additional analysis may require additional sampling and hence planning in advance.

Box 8 'Effect-directed analyses' (EDA) / 'toxicity identification and evaluation' (TIE) explained

Both TIE and EDA use chemical properties of the substances in a mixture to separate these chemicals from each other, or to deactivate them. For instance, with EDTA (Ethylenediaminetetraacetic acid), metals can be bound, making them much less available for toxic activity. If a mixture still show toxic activity after adding EDTA, it's not likely caused by metals. By using such fractionating or deactivation of specific chemical groups cleverly, insight is gained on the most likely suspects in a mixture. Not only that, it also provides technical hints on how to eliminate those suspects from the mixture.



Measures should not deliberately shift risks to other environmental compartments or locations.

From OSPAR Agreement 2012-7 we also stress that:

- "40. The application of BAT and BEP should be demonstrated as described in Appendix 1 of the OSPAR Convention.
- 41. When setting priorities and in assessing the nature and extent of the measures and their time scales, Contracting Parties should use the criteria as mentioned in Appendix 2 of the OSPAR Convention.
- 42. Further explanation on the evaluation and implementation of Risk Management Measures is provided by ECHA (Chapter R13: Risk management measures and operational conditions)"

Competent authorities may also require chronic (rather than acute) WET tests in a following risk management cycle. Although such tests are more demanding, they provide a better insight in chronic effects of the effluent and lower safety factors can be applied (conform OSPAR guidelines 2012-7).

**When?**

Measures need to be considered and implemented in discussion with the authorities when in the risk characterisation step a risk distance greater than 500 meters was determined (WET RA, Chapter 4). Intended measures and its rationale need to be formulated and reported within a year after the start of the management cycle. The measures need to be implemented as discussed with- and agreed by the authorities, after which the management cycle is started again, within a time-frame agreed upon with the competent authorities, to assess the effectiveness of the implemented measures.

**Who?**

Operators are responsible for proposing possible risk reduction measures to the authorities. In discussion with the authorities, suitable measures will be implemented.

## **7. Reporting**

### **Why?**

The competent authorities have to report the achieved reduction in risk to OSPAR OIC. The authorities have to base this report on the information provided by each operator per platform. Also, the authorities require the information as an audit trail of the assessment.

### **What?**

The operator reports the outcome of the chemical analysis, the substance-based risk characterisation, the WET tests and the WET-based risk characterisation to the competent authorities.

When risk characterisation indicates unacceptable risk (i.e., the risk distance is greater than 500 meters), the operator also reports the measures they intend to implement to reduce the risk, and the rationale behind them.

If measures were taken in the previous management cycle, operators must also evaluate those measures. Were they successful at reducing the risk? The (lack of) success of previous measures should be included in the rationale for new measures.

Deviations from this manual must be explicitly reported and explained.

### **How?**

An example of the reporting format as given in Appendix B which can be used as a template for the report. When different formats are used, at least all elements in the reporting format as given in Appendix B should be included.

### **When?**

A report needs to be submitted after the risk characterisation is completed and measures are specified when required. The report needs to be submitted to the competent authorities no later than one year after the start of the risk management cycle.

When measures were required, the management cycle has to be repeated within a time-frame agreed upon with the competent authorities.

When measures were not required (i.e., the risk was determined to be acceptable), the management cycle only has to be repeated within five years after the start of the current cycle or earlier when significant changes to the produced water discharge apply (see section 'Significant change or new platforms'). In the latter case, the new risk management cycle starts at the moment of the significant change.

### **Who?**

The operator is responsible for providing a signed report within the specified time-frame for each risk management cycle.



## **8. Quality Assurance**

IMARES utilises an ISO 9001:2008 certified quality management system (certificate number: 124296-2012-AQ-NLD-RvA). This certificate is valid until 15 December 2015. The organisation has been certified since 27 February 2001. The certification was issued by DNV Certification B.V. Furthermore, the chemical laboratory of the Fish Division has NEN-EN-ISO/IEC 17025:2005 accreditation for test laboratories with number L097. This accreditation is valid until 1th of April 2017 and was first issued on 27 March 1997. Accreditation was granted by the Council for Accreditation.

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OSPAR (2012b): OSPAR Guidelines in support of Recommendation 2012/5 for a Risk-based Approach to the Management of Produced Water Discharges from Offshore Installations, (OSPAR Agreement: 2012-7): [http://www.ospar.org/documents/dbase/decrecs/agreements/12-07e\\_rba%20guidelines.doc](http://www.ospar.org/documents/dbase/decrecs/agreements/12-07e_rba%20guidelines.doc)

OSPAR (2013a): Risk-Based Approach to the Management of Produced Water Discharges from Offshore Installations: [http://www.ospar.org/html\\_documents/ospar/html/data/assessment\\_fact\\_sheets/ospar\\_factsheet\\_rba\\_2013.pdf](http://www.ospar.org/html_documents/ospar/html/data/assessment_fact_sheets/ospar_factsheet_rba_2013.pdf)

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## Justification

Report number : C057.14

Project number : 430.52043.01

The scientific quality of this report has been peer reviewed by the a colleague scientist and the head of the department of IMARES.

Approved: Sander Glorius  
Research Scientist



Signature:

Date: 31 March 2014

Approved: Floris Groenendijk  
Department Head

Signature:

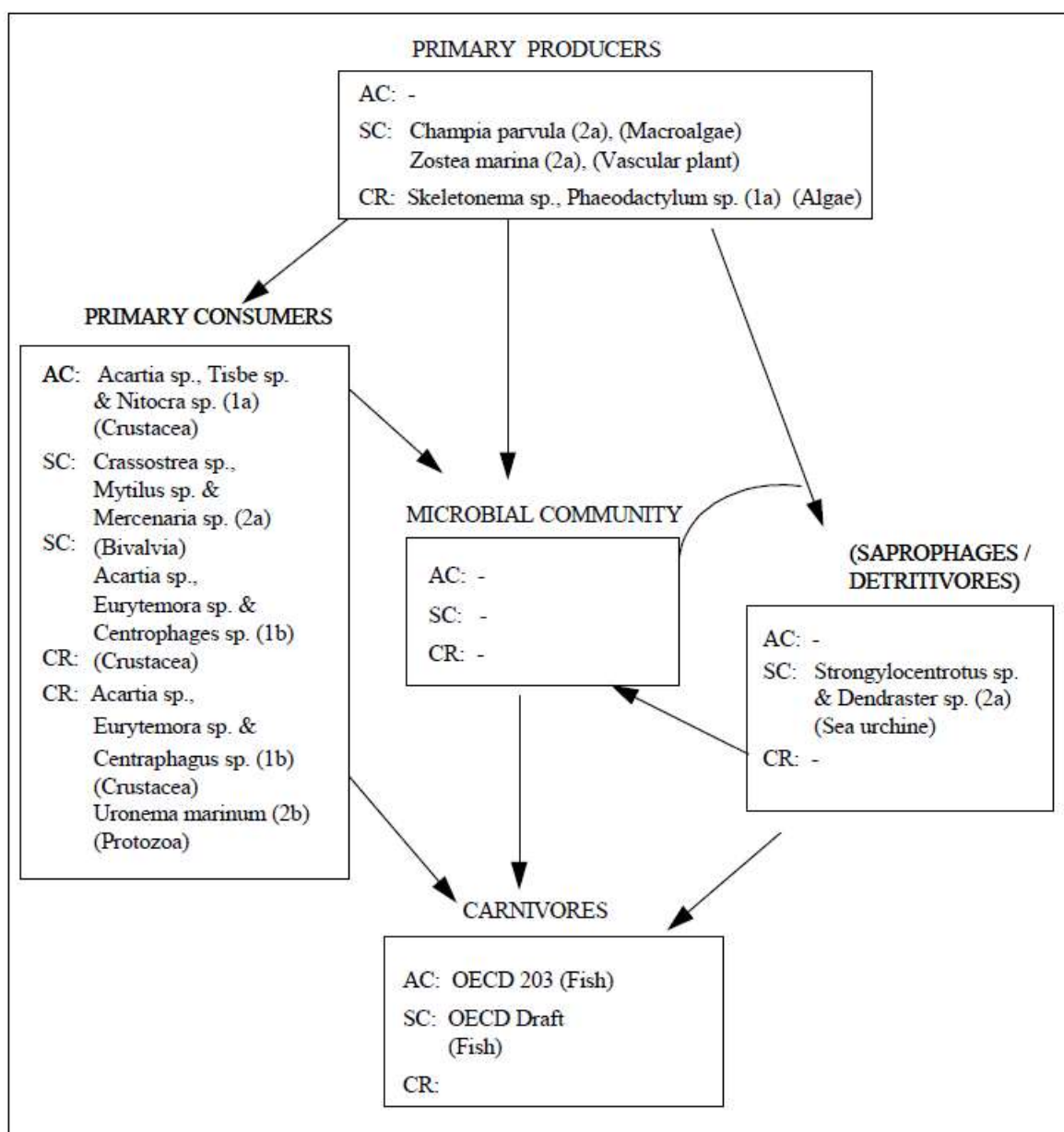


Date: 31 March 2014

## Appendix A. Test methods shown in a food web frame

Source: OECD (1998): OECD series on testing and assessment, Number 1, Detailed Review Paper on Aquatic Testing Methods for Pesticides and Industrial Chemicals, Part 1: Report, ENV/MC/CHEM(98)19/PART1. Available at : [http://search.oecd.org/officialdocuments/displaydocumentpdf/?cote=env/mc/chem\(98\)19/part1&doclang=eng](http://search.oecd.org/officialdocuments/displaydocumentpdf/?cote=env/mc/chem(98)19/part1&doclang=eng)

Primary (1a and 1b) and secondary (2a and 2b) recommendations  
(AC: acute, C: subchronic, CR: chronic)



## Appendix B. Example of the reporting format

The tables below give an **example** of the reporting format.

Please fill out the blank cells in the tables and answer all questions

Start date for the management cycle (DD-MM-YYYY)		When is the management cycle started (as indicated by the authorities)
--	--	--

### Previous risk management cycle

Was the platform assessed previously, in this context?	<input type="checkbox"/> yes <input type="checkbox"/> No	If no, go to the sampling table If yes, continue with this table
Were there risk reducing measures implemented as the result of the previous assessment?	<input type="checkbox"/> yes <input type="checkbox"/> No	If no, go to the sampling table If yes, continue with this table
Were the measures successful at reducing the risk?	<input type="checkbox"/> yes <input type="checkbox"/> No	If no, please explain the absence of success if possible.

### Sampling

Sampling date (DD-MM-YYYY)		
Sampling conform the manual?	<input type="checkbox"/> yes <input type="checkbox"/> No	If no, which deviations were made and why?

### WET analyses

WET analysis date(s) (DD-MM-YYYY)		
Were at least 3 trophic levels tested as specified in the manual?	<input type="checkbox"/> yes <input type="checkbox"/> No	If no, why were less levels tested?
Are WET tested organisms listed in the manual?	<input type="checkbox"/> yes <input type="checkbox"/> No	If no, which organisms are tested and why do they deviated from the recommended species?
Are WET protocols as listed in the manual used?	<input type="checkbox"/> yes <input type="checkbox"/> No	If no, which protocols are used and why do they deviate from the recommended protocols?
Please list WET test results (add more rows to the table when necessary)		
Organism tested	Concentration (fraction of whole effluent volume)	Reference to original report

**WET-based risk characterisation**

Please provide the calculation of the PNEC and the resulting value (in a fraction of the whole effluent volume)		
Is the risk distance calculated conform the manual?	<input type="checkbox"/> yes <input type="checkbox"/> No	If no, provide details on the calculations used
Please provide the calculated risk distance in meters		
Is the risk distance greater than 500 meters?	<input type="checkbox"/> yes <input type="checkbox"/> No	If yes, continue filling out the remainder of the tables If no, fill out the chemical analysis when require and continue to signing the reporting form

**Substance-based risk assessment**

Chemical analyses date(s) (DD-MM-YYYY)		
Chemical analyses conform the manual?	<input type="checkbox"/> yes <input type="checkbox"/> No	If no, which deviations were made and why?
Were chemicals listed in the manual excluded from the analyses?	<input type="checkbox"/> yes <input type="checkbox"/> No	If no, which chemicals were excluded and why?
For the naturally occurring substances: were the PNEC values as provided in the background document (OSPAR, in prep. 2014) used?	<input type="checkbox"/> yes <input type="checkbox"/> No	If no, which PNECs were used and why?

Please list all chemicals, both analysed 'natural' substances and chemical additives (add more rows to the tables when necessary)

Substance name and CAS number <sup>8</sup>	Discharge concentration (PEC) (value)	Discharge concentration (unit)	Report number <sup>9</sup> or HOCNF	PNEC	PEC:PNEC ratio

**Measures**

Which measures are proposed to be implemented	Please provide a rationale for selecting these measures. Indicate why it is expected the measures will reduce the risk and support this (e.g., with the substance-based risk characterisation or additional effect-directed analyses/toxicity identification and evaluation in the WET tests). Also include the (lack of) success of measures in previous cycles when available. Also indicate when BAT / BEP applies.

Signature

\_\_\_\_\_

<sup>8</sup> Additives may be anonymised when necessary  
<sup>9</sup> The report of the chemical analyses should be made available to the competent authorities on request.