Potentially affected fraction of species from dynamic marine exposure

Life cycle impact assessment of marine ecotoxic impacts from offshore discontinuous discharges

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Diplomoppgave våren 2003 ved
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Project description

Project summary

This document is a result of my master thesis at the Norwegian University of Science and Technology (NTNU) during the spring semester of 2003.

A big part of the project time has been spent on investigation of the existing life cycle impact assessment methods for quantification of ecotoxical impacts, especially the concept of potentially affected fraction of species (PAF) used in the Eco-indicator 99 method. It also required some time to understand the works of the Dose-related risk and effects assessment model (DREAM) software simulation tool. The PAF concept had to be adapted for discontinuous discharges before any simulations could be done for the dynamic marine exposure PAF of glutaraldehyde. Different discharge scenarios were tested to check the sensitivity in the method proposed for dynamic marine exposure.

Guidance

Mark Reed (Sintef) and Henrik Rye (Statoil Research Center) have kindly guided me in the principles of the DREAM model. John Eirik Paulsen (Statoil TFM-Group) has provided information on the processes of offshore drilling. He has also helped me keep motivated through the period of the project. Feedback on the PAF adaptation for discontinuous discharges has been received from Edgar Hertwick (NTNU). This document is otherwise a result of my own independent work.

I would like to thank Statoil for giving me this opportunity to work with life cycle assessment methodology. I am thankful also to Prof. Kjetill Østgaard for letting me do this master thesis even though life cycle assessment is a field not normally considered part of environmental biotechnology.

Report summary

For any substance that is used and discharged offshore the contractor has to choose the best alternative in relation to the effects of the substance upon discharge. Any environmental impact that the choice might have in other localities related to either processes before the product is used (e.g. raw material extraction and refining), or in the following treatment of byproducts (offshore or on shore) are neglected. Basing the selection of products solely on the potential marine toxicological impact of the substances will systematically prioritize small local improvements to greater improvement potentials in production or internal and external recycling.

Life cycle impact assessment (LCA) is a tool developed for environmental evaluation of entire product systems; that is all processes for from raw material production to the end-of-life treatment of the product. Material input and output streams to the processes are converted to environmental impacts in the life cycle impact assessment (LCIA) stage of LCA. Characterization factors are used to quantify the impact within impact groups.

Eco-indicator 99 and the CLM problem oriented approach (CML-POA) are two LCIA methods that include characterization factors for eco-toxic impacts. Both methods use adapted versions of the EUSES/SimpleBox model to simulate the fate of substances, but the methods do not apply the same definition of eco-toxic damage to quantify the relative impact of different substances. Eco-indicator 99 uses the Potentially affected fraction of species (PAF), while CML-POA uses the Risk Characterization Ratio. EUSES/SimpleBox is a multi media steady-state fate model, and concentrations in different environmental media are calculated from annual continuous emissions.

Offshore discharges are distributed in time and space. The resulting concentrations are high compared to the concentration in the total marine volume, and the affected volume is limited. Given the discontinuous properties of exposure from offshore discharges the EUSES/SimpleBox model is not suited to model such emissions.

A method to calculate characterization factors for discontinuous offshore discharges is proposed in this study. The method is based on the PAF as defined in the Eco-indicator 99 method. Changes from the Eco-indicator 99 method are:

- Replacement of the static hazard unit increase with a time integrated function to better describe the time dependant exposure from offshore discharges.
- Replacement of the static total marine volume with the time integrated volume.

The resulting dynamic marine exposure PAF (dme-PAF) is compatible with the ecotoxicity characterization factors in Eco-indicator 99. It is proposed to omit the acute period in the time integrals and only assess the chronic exposure period beginning from day four.

The Dose-related risk and effect assessment model (DREAM) is used to simulate the time variation of offshore discharges. DREAM is used today by Statoil in environmental risk assessments of such discharges. The model is not a multi-media fate model although it includes most of the processes that are part of the EUSES/SimpleBox model. DREAM produces time dependant profiles of discharges. These are used to calculate the time integrals in the dme-PAF method.

Simulations were performed to calculate ecotoxicity characterization factors for glutaraldehyde with the dme-PAF method. The simulations performed show that one of the settings in DREAM will have great influence on the resulting characterization factors, namely the lower concentration limit (LCL). DREAM calculates concentration in cells, and this data is stored and can be extracted in text format. Cells with concentrations below LCL will not be stored and the volume of these cells will be neglected. In order to be able to calculate dme-PAF properly LCL should be set at zero. This will maximize the number of recorded cells. Given the limitations of MS Office Excel other software must be sought to accommodate calculation of dme-PAF.

Dme-PAF will be affected by changes of the mass, concentration or period of the discharge. Ecotoxicity factors therefore should be calculated for different scenarios regarding the location, concentration, mass and period of the discharge.

Johan Pettersen
Trondheim, June 18. 2003

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Table of contents

1 Problem and scope definitions

1.1 Background to the study

In recent years, environmental benchmarking has become equally important for companies as benchmarking on economical performances. The industry has learned that improvement in environmental performance often result in economical benefits as well, either as a direct consequence of improved resource management or through improvements in image. Environmental management systems, such as ISO [1996] and the European Union Eco-Management and Audit Scheme (EMAS) [EU, 2001], are applied systematically to improve environmental reporting and revision. In most industries companies have to work within a regulatory system that continually tightens the demands for emissions' control. This is the situation for the petroleum industry, and in particular for their offshore activities.

Important environmental impacts from offshore petroleum activities include impacts caused by airborne emissions from transport and energy generating processes, and marine and terrestrial impacts from drilling and production byproducts. The products of the activities are oil and gas, both vital parts of the society's energy sources.

Environmental regulation concerning drilling byproduct streams has been, and still is, focused on marine toxicological impacts from an eventual offshore discharge. Parameters that have been assessed are:

- toxicological effects on specified organisms in laboratory testing programs;
- persistency in the marine environment;
- intrinsic bio-accumulating properties estimated from the water-octanol partitioning coefficient; and
- potential endocrine effects.

For any substance that is used and discharged offshore the contractor has to choose the best alternative in relation to these four parameters. Any environmental impact that the choice might have in other localities related to either processes before the product is used (e.g. raw material extraction and refining), or in the following treatment of byproducts (offshore or on shore) are neglected. It should be obvious that such a regulatory scheme is not made to improve the total environmental performance of the activity, but that it rather will systematically prioritize small local improvements to greater improvement potentials in production or internal and external recycling.

1

1 Problem and scope definitions

Life cycle assessment (LCA) is a tool that allows for the evaluation of a product's total environmental impacts. LCA is "*... a method to account for the environmental impacts associated with a product or service. The term life cycle indicates that all stages in a product's life, from resource extraction to ultimate disposal, are taken into account."* [Udo de Haes, 2002]. In short, in a LCA all inputs and outputs throughout the product's life stages are quantified and summed; inputs in this regard being emissions/byproducts and outputs being resources consumed or utilized. The input/output streams are converted to quantified environmental impacts in the process called life cycle impact assessment.

Characterization factors are the key factors in the calculation of the environmental load caused during the product life cycle. They are the knots that tie the material flows to environmental effects. Depending on the accuracy of the characterization factors one is able to locate processes that have the greatest environmental impact, and see how to best improve the environmental performance of the product system.

Life cycle assessments of chemical products used offshore must include eventual toxicological impacts of emissions and discharges of substances given that this is the spotlight of the regulating authorities. For such authorities to accept LCA studies, these effects have to be included in a proper fashion [EU, 1996].

Eco-indicator 99 [Goedkoop & Spriensma, 2001] and the CML problem oriented approach (CML-POA) [Guineè *et al*, 2002] are life cycle impact assessment methods that include characterization factors for toxicological effects on eco-systems, but their approach for quantification of the toxicological damage in not the same. Eco-indicator 99 uses the *Potentially affected fraction of species* (PAF), while CML-POA uses the *Risk characterization ratio* (RCR) defined by the European Union System for the Evaluation of Substances (EUSES). Even though their damage definition is not the same both datasets rely on similar fate simulation models. Both Goedkoop & Spriensma and Guineè *et al* use adapted versions of the EUSES/SimpleBox multi-media fate model in their simulation of fate of emissions.

In the context of assessing offshore petroleum activities, both Eco-indicator 99 and the CML-POA have weaknesses. The Eco-indicator 99 dataset has only calculated the potentials for a few chemicals, mostly either metals or pesticides. In addition to this, the method does not include the marine environment as an initial recipient option. The CML-POA dataset contains more substances, and it has emissions to the sea as an option. On the other hand, because CML-POA uses the SimpleBox fate model, emissions will not be simulated in a way that accounts for the properties of offshore discharges. Discharges from offshore drilling activities are located to a few sites with a small number of discharges

per year and discharge periods of hours. Offshore discharges will give small marine zones of relatively high concentrations compared to the total marine volume. The SimpleBox model is tailor-made for simulating continuous discharges, and calculates the steady-state concentrations in different environmental media from annual continuous emissions. Compartments, or phases, that are included in SimpleBox are: the air, terrestrial phases, marine and fresh water phases, marine and fresh water sediment phases and biological (organic) phases. Because of the discontinuous properties of offshore discharges, the SimpleBox model is not suited for modeling their exposure profiles.

The Norwegian Pollution Agency (SFT) requires risk assessments of all petroleum related activities Norwegian Continental Shelf prior to granting any permit application. Statoil, and a few other operators, use the *Dose-related risk and effect assessment model* (DREAM) [MEMV, 2003] to simulate the distribution of substances discharged offshore. DREAM includes all physical, chemical and biological processes found in SimpleBox, and given a discharge location and rate it will calculate the resulting concentrations in the water column using data on currents, depths and winds. While DREAM is not a multi media model like SimpleBox it allows the user to find real-time concentrations and affected volumes caused by discontinuous discharges.

1.2 Scope of the study

The two existing life cycle assessment impact assessment (LCIA) methods Eco-indicator 99 and CML problem oriented approach both use the EUSES/SimpleBox model to simulate the fate (distribution) of substances. EUSES/SimpleBox models with continuous discgarges and a steady-state situation. Resulting concentrations from the model are therefore not applicable for offshore discharges, given that such discharges are distributed discontinuously both in time and space.

DREAM offers a possibility to simulate the fate of discontinuous marine discharges. This study explores the possibilities of development of LCIA characterization factors for marine ecotoxicity for discontinuous discharges with the DREAM model. In order to make such factors a methodology adapted to the limitations of the DREAM model will be outlined and used to calculate ecotoxicity potentials for a test substance.

The Potentially affected fraction of species (PAF), introduced to the LCIA methodology in the Eco-indicator 99 method, will be the basis for the calculation of ecotoxicity potentials.

1.3 Report outline

The first part of this report is dedicated to description of relevant theory and procedure concerning offshore processes (Chapter 2), ecotoxicity in general and as part of environmental risk assessment (Chapter 3), and life cycle assessment (Chapter 4). The methodology applied in the existing LCIA characterization factors for ecotoxicity is elaborated in greater detail in Chapter 5, while Chapter 6 offers a description of the DREAM model.

Methodology of the proposed new dynamic marine exposure PAF is outlined in detail in Chapter 7. Settings in the calculation of PAF for glutaraldehyde are given in Chapter 8. Results of simulations of dynamic marine exposure PAF, along with results from a brief model sensitivity check, is given in Chapter 9.

 Results are discussed in Chapter 10 with conclusions listed in Chapter 11.

2 Offshore processes

2.1 Outline

The description of offshore activities given in this chapter relies on the document by Thatcher *et al* [2001].

Figure 2.1: Byproduct streams from offshore installations.
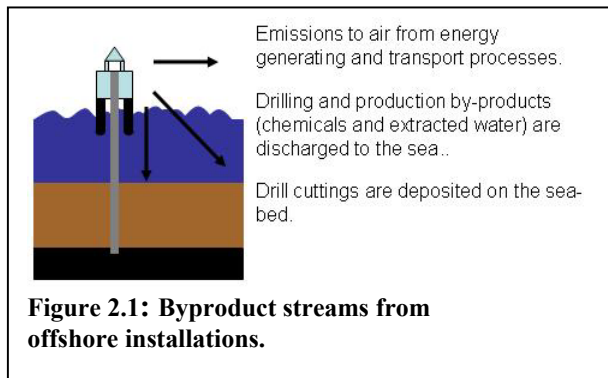
By-product outputs from offshore petroleum installations are substances of various kinds that are released into different media. Figure 3.1 offers an overview of the emissions and discharges from offshore installations. This study focuses on the drilling process, leaving airborne emissions and any other by-product streams outside.

The discharges of drilling chemicals and drill cuttings (see Figure 2.1) are interconnected both in that they appear in the same processes but also in that they often are physically bound in the same phase when resurfacing from the well.

Figure 2.2: Processes in the lifetime of oil and gas wells.
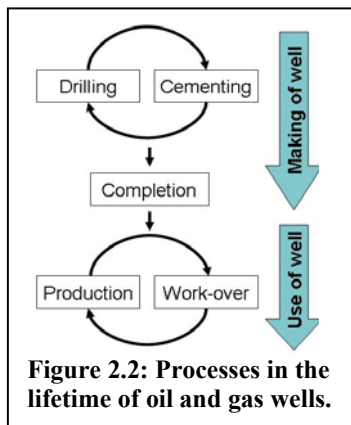
The lifetime of an oil or gas well can be divided into separate stages. Before a new production well can be drilled, (usually) several exploration wells are drilled. The exploration stage is the first stage in the lifetime of a well. Given the experimental nature of this stage it is the least standardized life stage. Other main stages in the lifetime of an average well are outlined in Figure 2.2. The main life stages are drilling, cementing, completion, work-over and production. Only the stages part of the making of the well are within the scope of this study, so only discharges from drilling, cementing and completion processes are included in the following parts of this report.

Periodically during the drilling, casings are lowered into the well on the completion of each drilling sequence. The casings are metal columns fit into the well. They are cemented into the well to stabilize the outer walls. During the first sequences, the columns run the entire length of the well. This effectively decreases the well diameter as new casings are inserted. Liners are used in the lower

sequences. They work in the same way as the casings, but in contrast to the casings they are hung on the lower part of the previous insert. Casings and liners are illustrated in Figure 2.3.

Figure 2.3: Casings and liners are cemented into the well.
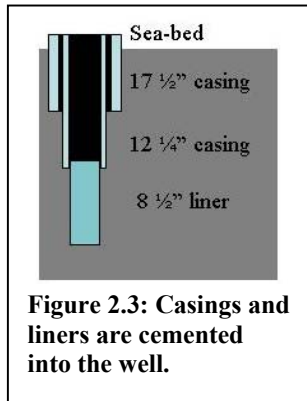
Once the drilling process is completed and the reservoir is reached, the well is cleaned and made ready for production in the completion stage. The completion process is in many ways similar to the work-over process that is periodically done during the production stage.

Chemicals used in the different life-stages will be released into the sea or brought up from the well depending on what process they have been part of. Chemicals used in specific life stages often have physical and chemical properties in common, and it is therefore usual to divide them into classes on the basis of the process they are used in.

The following sections describe the processes involved in the different life-stages.

Figure 2.4: Illustration of the drill-bit, drill-string and annulus.
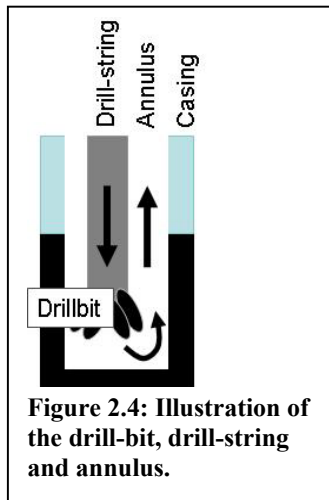
2.2 Drilling

The rock material that is drilled out in the drilling process is called cuttings. Drilling fluid is used to transport cuttings up from the well. The fluid also works as a cooling agent for the drill-bit and it brings pressure down-hole in order to stabilize the walls of the well. Drilling fluid circulates down the center of the drill-string, through the drill-bit and up to the surface through the annulus of the well (along the sides of the drill-string), as illustrated in Figure 2.4. Resurfacing, cuttings are embedded in the viscosified fluid. The drilling fluid is also referred to as drilling mud, while mud often means the mix of cuttings and fluid.

Figure 2.5: The mud cycling process.
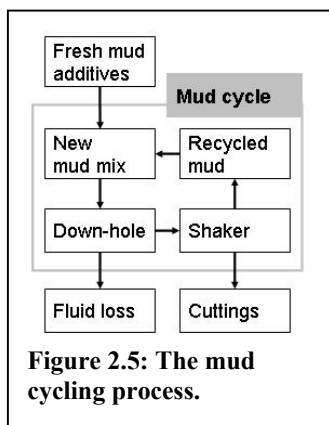
The cuttings are separated from the drilling fluid by 'shakers' before the remaining fluid is re-circulated through the drill-string. Re-composition of the fluid is usually necessary before further use. Mud cycling is illustrated in Figure 2.5

Drilling fluids are classified according to the base-fluid used. The fluids can be water-based (WBM; water-based mud), oil-based (OBM) or synthetically based (SBM). Synthetic based drilling fluids use non-oil organic components for the base-

fluid, such as esters or organic acids. In addition to the base-fluid the drilling mud contains a number of other substances that are meant to provide the fluid with specific properties. Additives used vary with the base fluid and well characteristics. Normal additives are viscose enhancing substances such as bentonite clay and organic polymers, weight materials that increase the density of the mud (most often $CaCO_3$ or barite, with the main component $BaSO_4$), biocides that inhibit sulphate reducing bacteria, grease, corrosion inhibitors, detergents, alkalic chemicals (NaOH, $Ca(OH)_2$) to increase pH and reduce corrosion, and salts to balance drilling fluid salinity with the well geology (NaCl, $CaCl_2$ and KCl).

Existing regulations for drilling mud allow discharges of cuttings and mud so long as the content of oil in the material is less than 1 % (wt) SFT [undated]. Because of the technical difficulties of reaching such values this is in fact a prohibition of discharge of oil-based mud and cuttings drilled with OBM. Because of the restrictions on discharge of OBM, of the total drilling fluid used in 2000, WBM and SBM represented 70 (WBM) and 6 (SBM) weight-% of the drilling mud used on the Norwegian continental shelf [SFT, 2002]. OBM is still used to some extent because it is the only option in technically demanding drilling operations.

For petroleum activities, drilling chemicals represent 85 % (wt) of the chemicals used, and 90 % (wt) of the chemicals discharged offshore [SFT, 2002]. The discharges of SBM and WBM occur during the drilling of the top sequences of the well. In these sections the cuttings and drilling fluid is deposited directly on the seabed. Because of the technical demanding procedure of drilling at great depths, the last sequences are normally drilled with OBM. Cuttings and fluid from these sections is returned to shore for treatment or re-injected to formations below the seabed.

2.3 Cementing

On the completion of the top sequences, casings are fitted into the well. Casings are attached to the well with cement. In order to make sure that sufficient cement is present, a part of the cement will end up on the seabed. The cement will release some of its chemical components in the period prior to solidification. Remaining chemicals in the cement will be locked inside the cement matrix.

Also the lower sequences of the well are fitted with steel columns. These are called liners, and are different from the casings in that they do not stretch the entire depth of the well. Instead they are hung on the casings previously put into the well. The liners are cemented into the well in the same manner as with the casings; by pumping the cement through the drill-string. A spacer fluid is pumped into the string in order to make sure that the cement does not mix with drilling mud still left in the well. If

WBM or SBM is used, the spacer, remaining cement and any remaining drilling mud will be deposited on the seabed. If OBM is used all of this has to be returned to the rig for treatment.

Chemicals added to the cement include accelerators and retardants that control the cementing process, extenders and weight materials added to control the density of the cement, viscose-controlling agents and chemicals added to minimize loss of cement and cement additives to the surrounding formations or water or gas phase.

2.4 Completion

The completion and work-over processes use many of the same chemicals, and are in many cases treated as one group.

Operations that are part of the completion process are the following: cleaning of liners and surface equipment, cleaning of casings and pipes, the removal of cleaning agents in the well and the initiation of production. The production is initiated by pumping low-density fluids into the well to lower the pressure down-hole. Given that the walls of the well do not cave in, the low pressure will create a pumping effect that boosts the well.

Chemicals used in the completion processes are among others pH-controlling agents, cleaning chemicals, viscose-controlling chemicals, defoaming agents that reduce the formation of gases, sea water, corrosion inhibitors, surface reactants, biocides and deoxydants that bind any O_2 present.

2.5 Discharge restrictions and regulatory classification of chemicals

Even though the main contribution to the discharges from offshore petroleum activities are water and rock material (drill cuttings), annual discharges of chemicals are 205 151 tonnes[1] on the Norwegian continental shelf [SFT, 2002]. The chemicals released have highly varying properties regarding toxicological potentials, biological accumulation and biological and chemical degradation. Based on these properties, chemicals are listed on the OSPAR List of substances of possible concern [OSPAR, 2003].

The Norwegian Pollution Agency (SFT) operates with three classifications of substances: green, red or black. Chemicals listed as black are restricted for any use. If red listed chemicals are used, the operator has to look for alternative, viable options for this particular chemical. Green listed chemicals can be

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[1] This includes water in the original products used.

used and discharged. Substances listed as green by the SFT are on the OSPAR list of substances/preparations used and discharged offshore which are considered to Pose Little Or NO Risk to the environment (the PLONOR list) [OSPAR 2003] when used and discharged offshore.

3 Ecotoxicology

3.1 *General principles of toxicology*

Chemicals that cause environmental problems when released by industrial activity may exist naturally in the environment. Problems arise when human made concentrations exceed what the eco-system is able to handle.

Toxicological responses depend on the dose and exposure time. The dose threshold for observable effects will vary with exposure time. Normally one differs between thresholds for short exposure time and prolonged exposure, quantifying them as the acute and chronic effects. Standardized procedures are applied to find toxicity thresholds on species level in laboratory experiments. Acute effects on species are usually quantified with the lethal concentration (LC), with LC_{50} as the denominator for a 50 % mortality rate for the population tested. Alternatively the EC_{50} (effect concentration) can be used if sub-lethal effects are assessed. Chronic effects will normally be quantified with the lowest observable effect concentration (LOEC) or the no observable effect concentration (NOEC). Chronic effects can include both lethal and sub-lethal effects from the exposure.

Because of the shorter test required, and therefore the lower cost involved, acute tests represent the larger part of toxicological studies performed. A number of studies have been performed in order to find ways to extrapolate results from acute tests to chronic effect concentrations. Elmegaard & Akkerhuis [2000], Pennington [2003] and Länge *et al* [1998] evaluate both the use of assessment factors and statistical methods as ways to extrapolate acute data to chronic effects (acute to chronic ratio, ARC).

In toxicological testing the organisms are tested in laboratory environments, with focus on reproducibility of the test results. This might influence the relevance of the test results if the main toxicological mode of the substance in the eco-system is different from the one deployed in the laboratory. Interactions between species in the eco-system can also influence the effects of the substance [Chapman, 2002].

The toxicological mechanisms vary greatly between different substances, and responses can be found on different levels. Effects might occur on single organisms, species or eco-system level. Small decreases in survival or reproductive capabilities for single organisms may have little or no effect on

the species' ability to survive. In other cases it might be vital. Eco-system redundancy may also work to reduce the impact of loss of a species [Chapman, 2002; Lam & Gray, 2001].

The concentration levels for adverse effects vary between species in the eco-system. The threshold concentration level will also differ from one type of environment to the next. This was pointed out by Leung *et al* [2001] for the relation between marine and freshwater effects concentrations. Physical factors, e.g. the existence of a sediment phase or change of temperature, will also influence the final impact of the substance.

In addition to the toxicological responses of species to substances, the assessment of the substances bio-accumulating properties and degradation rates are also part of most toxicological test guidelines [OSPAR, 2002a; European Commission 1996].

3.2 Species sensitivity distribution (SSD)

Single species toxicity tests were explained in the previous section. Results from single species tests can be combined with statistical analysis tools to quantify the stress related to environmental concentrations in the eco-system as a whole. The result of such analyses is the species sensitivity distribution (SSD).

Figure 3.1: The log normal distribution of effect concentration for species [Wright & Welbourn, 2002].
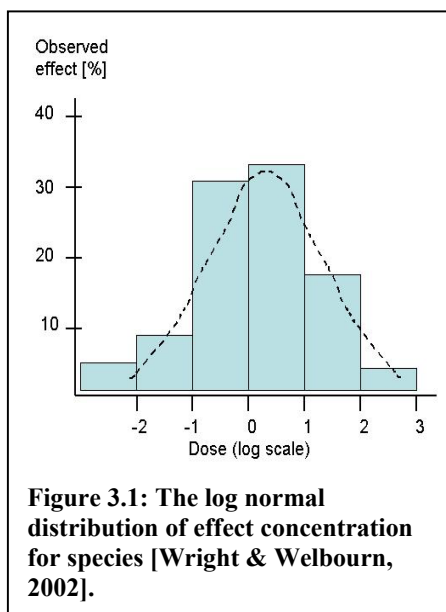
The SSD is a function fitted to match the plot of sensitivity results from toxicological tests on single species. SSD functions are based on the assumption that statistical distribution can be used to represent the distribution of sensitivity of the species in the eco-system. Figure 3.1 exemplifies a bell-shaped (Gaussian) distribution of sensitivities.

The potentially affected fraction (PAF) of species is a SSD that uses a logarithmic Gaussian curve (log-logistic curve) to represent the cumulative distribution of NOEC data [Brandes *et al*, 1996; Klepper & van de Meent, 1997; Bakker & van de Meent, 1997; Klepper *et al*, 1998]. PAF is the cumulative fraction, i.e. the percentage of species that are exposed to concentrations above their NOEC. It can be used to represent the stress to the eco-system caused by a single chemical, or to map the total stress on the eco-system as a result of the concentration of several chemicals or chemical groups. The curve of

PAF for a single substance is shown in Figure 3.2, with the equation for the PAF function given in Equation 3.1.

Figure 3.2: The Potentially Affected Fraction (PAF) of species is the cumulative fraction of species exposed to concentrations above their NOEC. It is a log-logarithmic function of the dose (concentration). [Mapper & van de Meent, 1997].
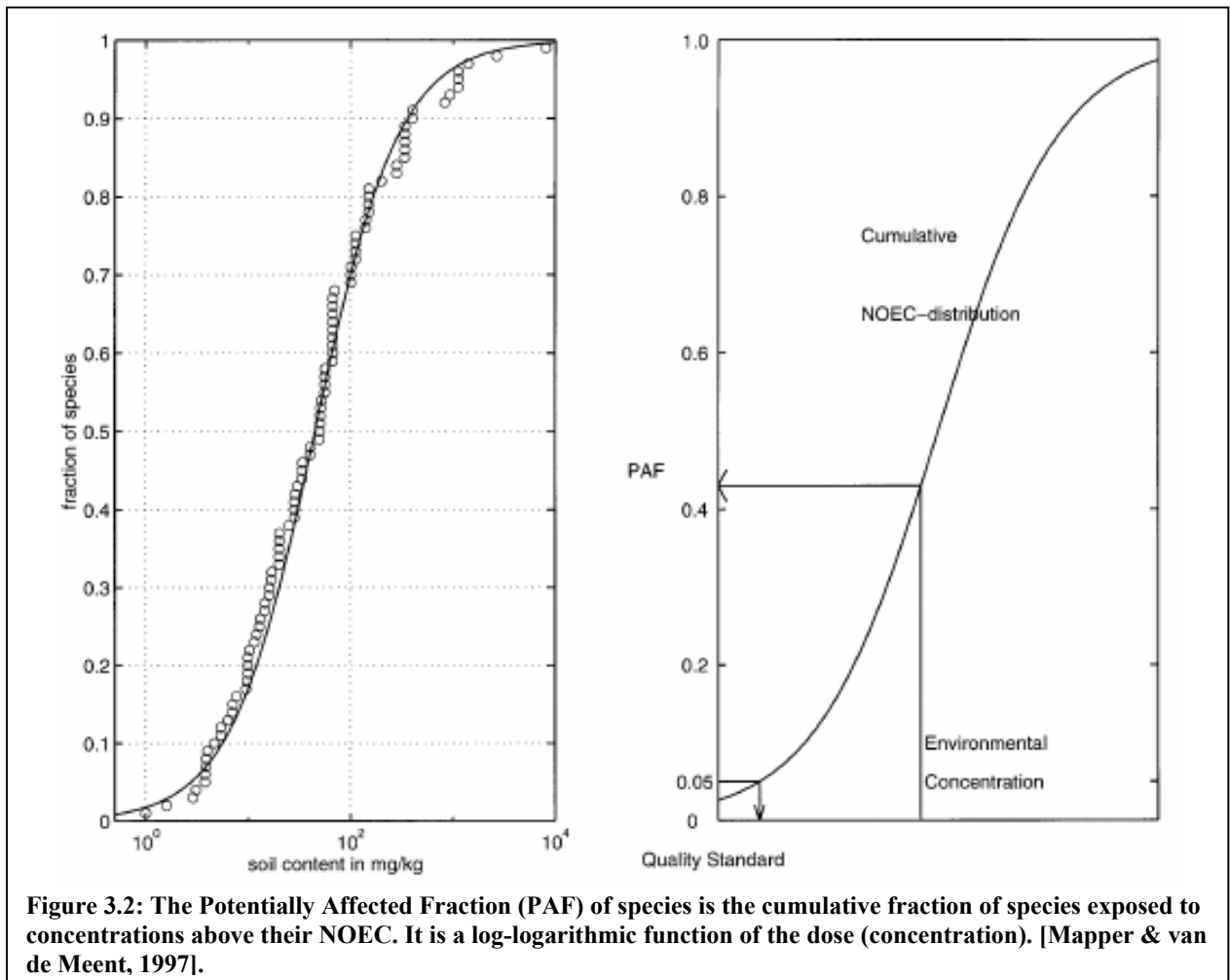
$$PAF = \frac{1}{1 + \dfrac{-(\log(C) - \alpha)}{\beta}}$$

Eq. 3.1

In Equation 3.1, C is the concentration of the substance while α and β are calculated from the toxicity data for the substance. The parameter α is the geometric mean of NOEC-values, calculated with Equation 3.2. β is calculated from the standard deviation of NOECs using Equation 3.3.

$$\alpha = \frac{\sum_n \log(NOEC_i)}{n}$$

Eq. 3.2

$$\beta = \sigma_{\log(NOEC)} \cdot \frac{\sqrt{3}}{\pi}$$

Eq. 3.3

The parameters α and β are important in studies of SSD. The former decides the location of the curve, while the latter gives the spread of the curve.

If PAF is used to map the stress of several chemicals, the combined stress (multiple substance PAF; msPAF) can be found with Equation 4.4.

$$msPAF = 1 - \prod_N \left(1 - PAF_n\right)$$ **Eq. 3.4**

There are developed several approaches for SSD functions. All have in common that the more sensitivity data available, the better the distribution of species sensitivity can be predicted. Wheeler *et al* [2002] suggest 10 data points as a minimum requirement to generate reliable estimates for regulatory purposes. The PAF function has shown to fit well for sensitivity distribution in aquatic eco-systems [Roman *et al*, 1999; Wheeler *et al,* 2002].

Table 3.1 lists strong and weak points of SSD [EUPRA, 2001].

Table 3.1: Strengths and weaknesses with SSD [EUPRA, 2001].

Strengths	Weaknesses
Can quantify variability and uncertainty	More complex
Can produce outputs with more ecological meaning	Some methods require more data
Make better use of the available data	May be difficult to communicate
May provide an alternative to field testing	Validation is difficult

3.3 Environmental risk assessment

The normal procedure of environmental risk assessment (ERA) of substances is a combination of two parameters [Wright & Welbourn, 2002]:

1. degree of toxicity; and
2. magnitude of exposure, for instance the environmental concentration.

The first parameter is the focus-point of toxicological testing and empirical studies of effects on eco-systems caused by emissions, while the latter can be quantified with estimates, simulations or by measurement.

The traditional paradigm of risk assessment consists of the following four steps [Wright & Welbourn, 2002; European Commission, 1996]:

- Hazard identification is a qualitative step, either based on former knowledge of the substance or hazard, or on the fact that no knowledge exists (i.e. by application of the pre-cautionary principle).
- Dose-response evaluation, which is quantified in toxicological testing or similar procedures (empirical studies, structure analysis etc.).
- Exposure assessment is the quantification of the dose.
- Risk characterization; the combination of the previous steps.

Figure 3.3: Structure of ecological risk assessment [Wright & Welbourn,
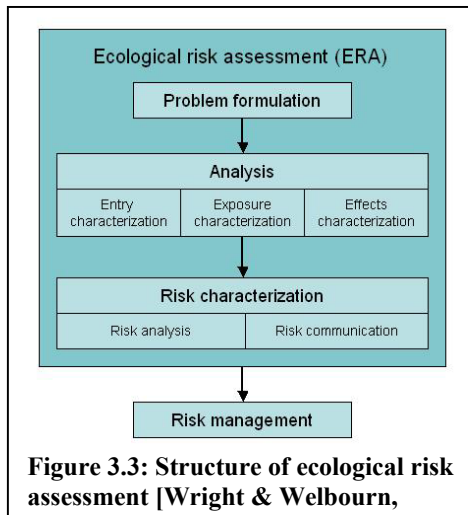
The basic procedure of risk assessment is outlined in Figure 3.3. This procedure forms the backbone of the risk assessment program of OSPAR.

The effects characterization is part of the Risk characterization step of ERA. The method most commonly used in effects assessment involves the use of predicted environmental concentrations (PEC) and predicted no-effect concentrations (PNEC).

PECs are found by exposure assessment; estimating the environmental concentration (or other definitions of dose) from emissions data or by direct measurement of the concentration.

The PNEC is the predicted threshold for adverse effects to species or eco-system. If it is predicted from single-species laboratory test results (described in Section 3.1) it will be the lowest species NOEC divided by an assessment factor (safety factor). Oftentimes only acute data is available, or only a few tests are performed for chronic exposure, in which case the assessment factor is scaled accordingly. Safety factors are used to make up for the eventual possibility that there are species in the eco-system more sensitive to the substance than the species tested in the laboratory. The ERA assessment factors in the guidelines for aquatic eco-systems range from 10 to 1000 for PNEC based on single-species test results, depending on the selection of species tested and the time scale of the test (i.e. chronic or acute) [European Commission, 1996].

When using single species toxicity data to derive PNECs it is important to remember that toxicity test protocols developed may not be directly applicable to systems in other parts of the world. This especially applies to the selection of test organisms [Lam & Gray, 2001; Chapman, 2002].

The PEC/PNEC ratio is an indicator of existence of risk of adverse effects. A PEC/PNEC>1 indicates that there is a possibility of species being affected by the concentrations of the substance. If one wants to quantify the damage caused by emissions other approaches have to be used. SSDs are based on toxicity data, but instead of using the data to form a static yes/no indicator the data can be used to quantify risk on eco-system level.

The Potentially Affected Fraction (PAF) of species, as described by Bakker & van de Meent [1997] and Klepper & van de Meent [1997], is an example of SSD used to quantify the fraction of species in the eco-system exposed to concentrations above their NOEC. Studies concluding that an estimated 5%

of the species are exposed to concentrations above their threshold give more information than just saying there is a risk of adverse effects (PEC/PNEC>1). This point was also stated in Table 3.1.

PNECs predicted from PAF, as an example of SSD derived PNECs, have two strong points:

a) The curve of PAF, outlined in Figure 3.2, shows that the marginal environmental risk (or environmental impact) of an emission depends on the marginal increase of concentration and the slope of the PAF curve. Static PEC/PNEC assessments will not include this effect.

b) Based on SSDs like the PAF, PNEC values for ERA can be found for chemicals with only few tests performed. A shift from lowest NOEC to the distribution of NOEC as basis for PNEC in risk assessments is also suggested by EUPRA [2001].

The pros and cons of SSDs in ERA are well discussed by EUPRA [2001], which also lists different SSD options. See also Isnard *et al* [2001] for discussions on use of and methods of regression for SSDs for ERA purposes.

4 Life cycle assessment

4.1 Shifting focus from process to product level

Environmental protection has for a long time been a part of Norwegian politics. As a result of this, a number of restrictions and regulations have been established concerning how industries are allowed to act concerning their own waste products. Regulations for localities and activities are continually revised, and the environmental demands towards the industry are increasingly tightened. In such a regulatory environment all actors will react mainly to reduce *their own* environmental loads, opening the possibilities for sub-system optimizations. The negative impacts on system level can be avoided by shifting the regulating focus; from processes to products.

Products can be said to have lifetimes divided into separate life stages; such as shown in figure 4.1.

Figure 4.1: Standardized illustration of a product's lifetime.
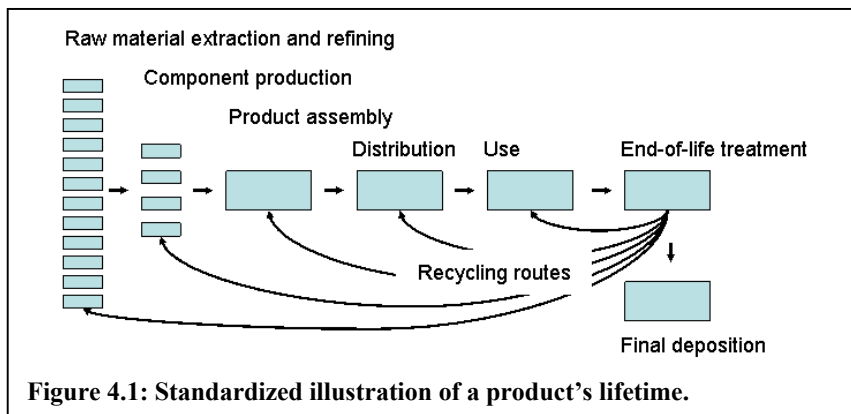
Over the lifetime of the product several actors are involved. All actors will have an influence on the product's total environmental performance. What is important is that the total environmental performance of the product system is maximized. Changes in processes in the product system must help reduce the environmental load of the *total product system*, as illustrated in Figure 4.2.

Life cycle assessment (LCA) is a systematic approach where the entire lifetime of the product is investigated and evaluated. Input and output streams are first quantified and then used to estimate the environmental impact of the product.

LCA can be used to compare two different product options that offer similar functions. In such cases it is important that all influential life phases are included in the study, i.e. all important life phases are within the borders of the evaluated system.

Figure 4.2: Environmental impacts as result of contributions throughout the product system.
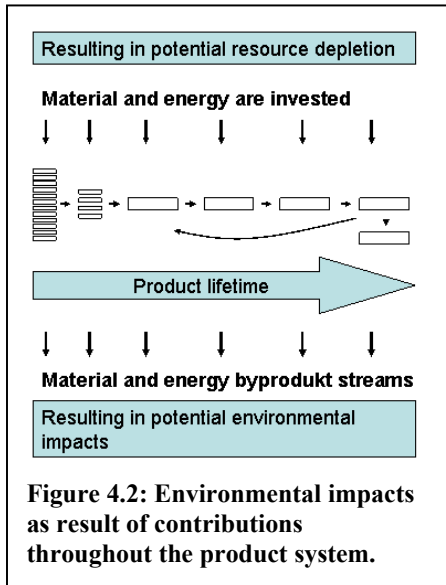
4.2 Steps in life cycle assessment

The International Organization for Standardization (ISO) has published several documents about LCA in the ISO 14040-series. According to ISO [1997] a LCA consists of four steps; Goal and scope definition, Life cycle inventory analysis, Life cycle impact assessment and Life cycle interpretation. The steps in LCA will now be explained according to the ISO documents.

4.2.1 Goal and scope

The first step in any study is to clearly state the purpose of the study, so also in LCA studies. An important part of this step is to define a functional unit. The functional unit is a quantified function that the product (or service) is meant to offer the user; e.g. transportation of a volume over a specified distance. Limitations in the study, for instance with regards to the environmental aspects included in the study, must be discussed in an early stage of the study. This is of great importance in reducing the time spent on finding the resource inputs and emissions data. The goal and scope must also define the physical boundaries that are to be used in the study; that is what processes will be part of the investigation. The goal and scope stage of a LCA is described in [ISO, 1998].

4.2.2 Life cycle inventory analysis (LCI)

The second stage of a LCA is the inventory stage where one collects data on emissions and resource use. The purpose is to quantify the inputs and outputs related to the functional unit in the different life stages of the product. Ideally the system boundaries should be set so that all that is counted as input in one process is found as output in either the same process or in a later one, although this is hardly ever accomplished. The principle of material balance can anyhow be applied to indicate insufficiencies in the inventory data. LCI is described in [ISO, 1998].

4.2.3 Life cycle impact assessment (LCIA)

ISO [2000a] divides the life cycle impact assessment stage into three separate steps:

i. **Categorization**: In the first part of LCIA the material flows are classified according to the impacts they have; e.g. CO_2, N_2O and CH_4 are among the gases that cause green house effect and will then be classified in the global warming category. If a substance has more than one environmental effect it will be categorized in all relevant impact groups.

ii. **Characterization**: Once the substances are categorized into impact categories, total impact within the categories are aggregated using the relative contributions from the substances relevant in the category. This is called the characterization step of LCIA. Technically, the input/output vector found in the LCI stage is multiplied with the characterization factors matrix.

iii. **Weigthing**: The final part of the LCIA is weighting of the contribution of the different impact categories. Because of the biased nature of the weighting process (who is to say that one impact is more important than the other) the weighting is oftentimes omitted in LCA studies. Even though the weighting process is a vulnerable part of the LCA methodology it can be the very part of LCA that is most interesting for decision management in companies; for instance if the purpose of the assessment is to support in choice of options.

4.2.4 Life cycle interpretation

Hopefully one is able to draw some conclusions on the results from the LCI and LCIA. Whether this is the case or not, the interpretation stage of the LCA is the concluding part of the technical work. Depending on what the goal and scope of the study are, the interpretation of the results usually is the last stage of the LCA. The life cycle interpretation is described in [ISO, 2000b].

4.2.5 The iterative nature of life cycle assessments
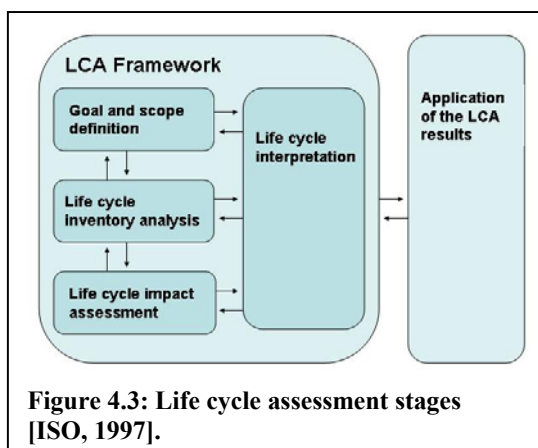
Figure 4.3: Life cycle assessment stages [ISO, 1997].

The process of LCA is iterative, as illustrated in Figure 4.3. In many cases it is necessary to go through the LCA stages several times in order to be able to define an applicable goal and scope for the study. Reliable conclusions concerning both the validity of the inventory data and the quantification of the environmental impacts are often not found in the first round of assessment. In cases where LCA is part of product development, the relevance of the inventory data relies on continual

updating. This could be achieved through combination with environmental management systems.

The result of the life cycle inventory is a vector describing the in- and outputs from the product system, i.e. the quantified sizes of the material streams in Figure 4.2. Preferably the material streams should be tied to their respective sub-processes so that the relative load of the individual processes can be calculated. This is valuable knowledge when improving the environmental performance of the product system later on.

Life cycle assessments are assessments of the *environmental impacts* associated with the lifetime of the product. This brings us to the life cycle impact assessment stage.

4.3 Life cycle impact assessment: connecting material flows to environmental impacts

According to Hertwich og Hammitt [2000]:

"Impact assessment needs to evaluate the relative importance of different environmental stressors (emissions, resource and land use) related to a life-cycle. This requires the definition of a common metric either for all impacts (e.g., eco-points, $) or for groups of impacts (e.g., CO_2-equivalents, DALYs[2])."

Useful metric definitions will vary depending on what information one wants to find. Two of the most commonly used LCIA systems available today have very different approaches to damage modeling of emissions. Eco-indicator 99, as describedby Goedkoop & Spriensma [2000], is a damage oriented impact assessment model, dividing the impacts caused by product systems into three end-point damage categories:

- Damage to mineral and fossil resources (in units of *MJ surplus energy*).
- Damage to eco-system quality (in units of *% vascular plant species·km^2·yr*).
- Damage to human health (in units of *disability adjusted life years, DALYs*).

The three main impact groups in the Eco-indicator 99 method are divided into different sub-level impacts. The ecosystem quality impact category includes for example eutrophication, acidification, eco-toxic impacts and effects of land occupation. Relative effects within each of the sub-level impact categories are quantified with damage modelling, using multi-media fate simulation soft-ware or empirical data. Either way, the model must show the quantified connection between the substance emitted, or action taken, and the measured (or modelled) effect. The sub-level impacts are then

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[2] DALYs (Disability Adjusted Life Years) is used to quantify impacts on human health.

combined into the main impact category through a second damage modelling stage, or by the fact that they share the same impact category metric.

Because of the many argument levels of end-point indicators, the final characterization factors might be subject to criticism. This effect can be decreased by applying a problem oriented approach. In the problem oriented approach several mid-point indicators are used instead of only a few end-point indicators. Typical examples of mid-point indicators are *kg antimony* as the unit for resource depletion; *CO_2-equivalents* as the indicator for green house gases; and *kg 1,4-dichlorobenzene* as the indicator for toxic effects. In these three cases, the impact of each substance within the impact category is calculated by relating the impact to that of a chosen reference substance. This approach is used in the CML problem oriented approach (CML-POA) by Guineè *et al* [2002].

The Eco-indicator method has one important feature. As a result of the end-point approach applied weighting of impact categories within the main damage categories can be omitted. The only weighting procedure necessary is between the main categories. The end-point model thereby includes much of the weighting process.

The result of the damage modeling is a set of characterization factors that describes the substances relative effects within the impact category. The dataset can be organized into characterization factor vectors for the individual impact categories or a characterization factor matrix for all the impact categories.

5 Characterization factors for eco-toxicological impacts

It was previously stated that there are two definitions of environmental damage used in previous LCA characterization factors developed for eco-toxicological impacts. The potentially affected fraction (PAF) of species is one of them, used in Eco-indicator 99 [Goedkoop & Spriensma, 2000]. The other is the Risk Characterization Ratio (RCR) employed by Huijbregts *et al* [2000] in the calculation of toxicity potentials in CML-POA [Guineè, 2002].

The principles used in these two approaches will be explained in the following sections, staring with a description of the fate simulation which in both cases is performed with the EUSES/SimpleBox model.

5.1 *Fate modeling with SimpleBox*

Development of characterization factors for life cycle impact assessment is in many ways similar to environmental risk assessment of substances. The procedure outlined in Figure 3.3 (identification, fate (or exposure), effect and characterization) is valid for both ERA and LCIA purposes. In order to quantify effects on different eco-systems the fate of emissions has to be assessed. In both Eco-indicator 99 [Goedkoop & Spriensma, 2001] and CML-POA [Huijbregts *et al*, 2000], fate assessment of eco-toxic substances is carried out with the European System for the Evaluation of Substances (EUSES) risk assessment model.

EUSES is the multi media distribution model for risk assessment of chemicals used by the European Chemicals Bureau[3]. SimpleBox is the distribution module of the EUSES model [Brandes *et al*, 1996]. SimpleBox has been developed over a long period, and the versions used in the Eco-indicator 99 method and in the CML method are not the same. The SimpleBox multi media model includes the three inter-acting environmental scales illustrated in Figure 5.1; regional, continental and global scale.

The different scales are separated into a number of compartments; each representing different phases in the environment. The compartments in the local scale are illustrated in Figure 5.2.

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[3] See European Chemicals Bureau: http://ecb.jrc.it/
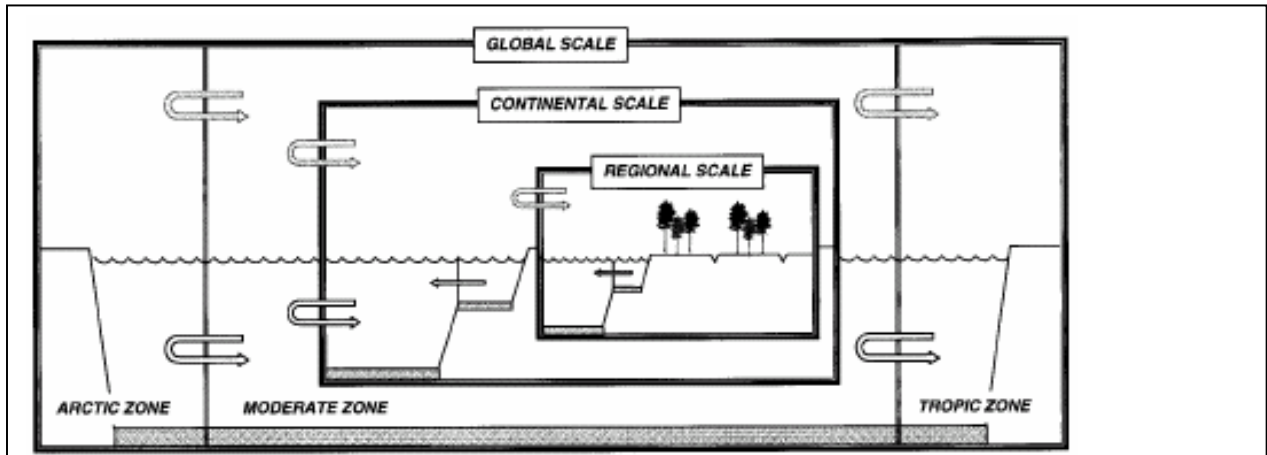
Figure 5.1: The scales in SimpleBox [Brandes *et al*, 1996].
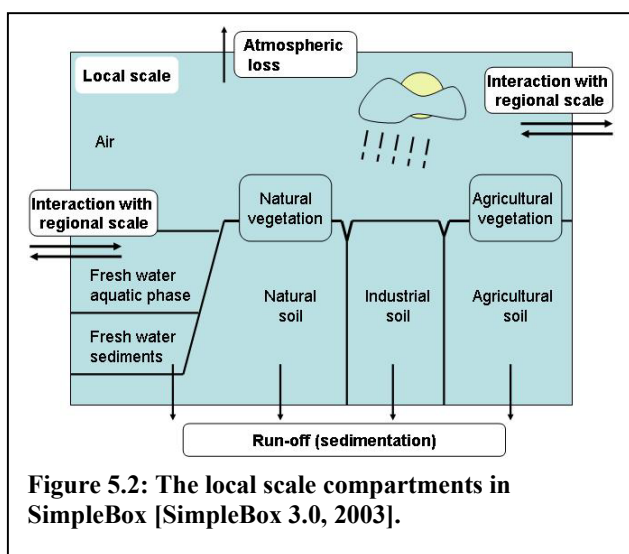
Figure 5.2: The local scale compartments in SimpleBox [SimpleBox 3.0, 2003].

As can be seen from Figure 5.2, there are three compartments for the terrestrial phases; industrial, agricultural and natural soil. The aquatic phases are modeled with four compartments; marine and freshwater aquatic and sediment phases. The marine compartments are not included in the regional scale. Bioaccumulation and predation will give accumulation in the organic compartments; and the last compartment is the atmosphere (air).

Chemical and physical properties of the substances are required input data to the SimpleBox model. Given an annual emission to one of the compartments in the SimpleBox system, the model will calculate the resulting concentrations in all compartments assuming conditions of steady state (equilibrium) within a scale and homogeneous conditions within the compartments. Transport between scales is a result of the size definitions of the scales.

SimpleBox calculates with "a perfectly mixed" environment. This is a good assumption for a situation of continuous distribution of emission points in time and space. However, the fewer emission points the larger will the difference between model and actual situation be. Both Goedkoop & Spriensma and Huijtbregts *et al* discuss the implications of emission points distributed in time, but neither touches the existence of a geographically non-continuous emission scenario. How a geographically non-continuous distribution of emission points relates to the assumed steady state model of SimpleBox is illustrated in Figure 5.3.

Figure 5.3: Boxes illustrate the discharge points and volumes affected by the discharge. Graphs show the distribution of concentration within the box.

Situation a) has only a few emission points and the affected volume is significantly smaller than the total volume of the box, and the concentration is not evenly distributed.

In situation b) the number of emission points is high, and the affected volume is only slightly smaller than the total volume.

Situation c) shows the assumed situation in the SimpleBox model.

5.2 Eco-indicator 99

The Eco-indicator 99 impact assessment method is developed for LCA by Goedkoop & Spriensma [2001]. They use the potentially affected fraction (PAF) of species to assess the effect of toxic substances. PAF has been described previously in this report in Section 3.2. This chapter outlines Goedkoop & Spriensma's method for damage modeling of toxicological effects to eco-systems with the PAF metric.

> *"The PAF can be interpreted as the fraction of species that is exposed to a concentration equal to or higher that the no observed effect concentration (NOEC). It is a measure for toxic stress, and in fact not a real damage..."* [Goedkoop & Spriensma, 2001].

The damage unit for substances in Eco-indicator 99 for toxicological damage to ecosystem quality is PAF·m^2·yr·kg^{-1}.

5.2.1 Fate simulation

The Eco-indicator 99 method uses SimpleBox to calculate the concentration resulting from a continuous release of 10 000 kg/d of a substance. Regional scale is used in the simulations in order to be able to include the process of biological uptake. The sea water compartment is not part of the regional scale. Transport between scales is on the other hand included in the model, but interaction

between regional and continental scale is minimized in order to simulate a "closed Europe" [Goedkoop % Spriensma, 2001b; p. 6]. Concentrations in the sea are therefore not calculated in Eco-indicator 99.

Table 5.1 lists some of the area and volume settings in the SimpleBox simulations in Eco-indicator 99. Note the absence of marine volume.

Table 5.1: Selected SimpleBox settings in [Goedkoop & Spriensma, 2001b; p. 5].

Parameter	Value
Area regional system	$3.6 \cdot 10^6$ km^2
Area fraction of water	0.03
Area fraction of natural soil	0.6
Area fraction of agricultural soil	0.27
Area fraction of industrial soil	0.1
Water depth	3 m

5.2.2 Damage modeling with multiple substance PAF (msPAF)

The impact assessment of the Eco-indicator 99 method uses the principles of PAF of a mix of chemicals; the msPAF described in Section 3.2. It is assumed then that the marginal ecotoxical effect of an increase of concentration for a substance is then not reliant of the PAF curve for the specific substance, but rather of the curve of msPAF.

In order to construct an msPAF curve, an assumed mix of substances is selected to represent the average profile of emissions to the recipient (European average). Actual discharges are then "*standardized into units of average toxicity of the total mixture, so called hazard units (HU)... ()...very similar to the PEC/PNEC ratios.*" [Goedkoop & Spriensma, 2001].

Hazard units are defined as the ratio of concentration to the geometric mean of no observable effect concentrations (NOEC). The geometric mean is the average of logarithmic NOECs, as described previously in Section 3.2. Increase in HU is calculated using the increase of concentration (ΔC). Increase in concentration resulting from an initial discharge is found with SimpleBox. The expression for ΔHU is shown in Equation 5.1

$$\Delta HU = \frac{\Delta C}{10^\alpha} \qquad\qquad \textbf{Eq. 5.1}$$

The situation HU = 1 means that the eco-system is exposed to concentrations equal to the average of logarithmic NOEC, thereby potentially affecting 50% of the species present. This situation implies a msPAF of 0.5. The logarithmic Gaussian curve for the relation of msPAF to HU is constructed assuming a β of 0.4 (se Eq. 3.1 and 3.3). Figure 5.4 shows the curve of ms-PAF as a function of hazard units, with values given in Table 5.1.

Table 4.1: Calculation of marginal PAF to determine the slope for msPAF Europe [Goedkoop & Spriensma, 2001b].

ms-PAF	Hazard units	$\dfrac{\partial PAF}{\partial HU}$
0.05	0.066	0.078
0.1	0.132	0.073
0.0223*	0.317	0.593
0.3	0.482	0.497
0.4	0.688	0.378
0.5	1.000	0.271
0.6	1.453	0.179
0.7	2.182	0.104
0.8	3.585	0.048
0.9	7.566	0.013

*Average European ms-PAF

Figure 5.4: The PAF as a logarithmic function of hazard units [Goedkoop & Spriensma, 2001].
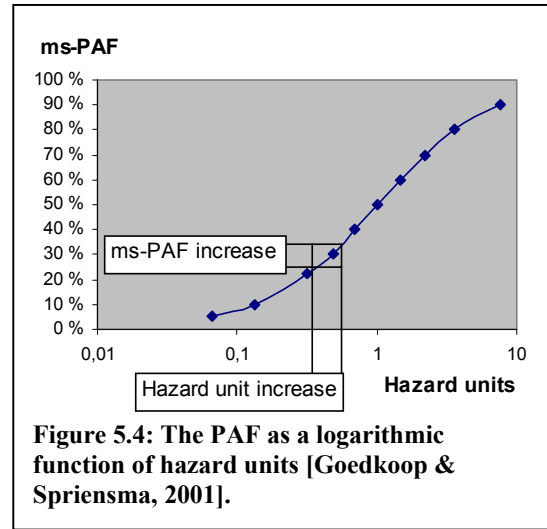
Further it is assumed an average European ms-PAF between 10 and 50 %. The Eco-indicator 99 includes the idea of different cultural perspectives, and the three different perspectives will chose to locate the ms-PAF differently within the interval. In the individual perspective, the msPAF will be the lowest value in the interval; and msPAF will be 0.10. The hierarchical perspective sets ms-PAF as the geometric mean of the two interval boundaries (msPAF=0.24); while in the egalitarian perspective, msPAF will be 0.50.

The geometric mean (24 %) used in the hierarchical perspective gives a slope of 0.59 (=$\partial PAF/\partial HU$). The resulting marginal increase of PAF is found using Equation 5.2.

$$\Delta PAF = \Delta HU \cdot \frac{\partial PAF}{\partial HU}$$
Eq. 5.2

5.2.3 Damage calculation

The increase of PAF per released mass is found by scaling PAF in Equation 5.3 to the original emission rate M (unit: kg/yr) in Equation 5.3, giving the unit of PAF·yr·kg^{-1}.

$$PAF_{kg} = \Delta HU \cdot \partial PAF / \partial HU \cdot \frac{1}{M}$$
Eq. 5.3

Equation 5.3 calculates the damage in one of the compartments. Total damage from continuous emission rate to the initial recipient air compartment is found by aggregating the resulting PAFs in water, and agricultural, industrial and natural soil. The total PAF (unit: PAF·m^2·yr·kg^{-1} of emissions to air is the weighted sum of the PAF contributions to the compartments, with the area of the

compartments as weighting factor (see Equation 5.4).

$$
\begin{aligned}
PAF \cdot m^2(air) = {} & \Delta HU(air, water) \cdot \partial PAF / \partial HU \cdot Areasize\ water \\
& + \Delta HU(air, agri.soil) \cdot \partial PAF / \partial HU \cdot Aresize\ agri.\ soil \\
& + \Delta HU(air, ind.soil) \cdot \partial PAF / \partial HU \cdot Aresize\ ind.\ soil \\
& + \Delta HU(air, nat.soil) \cdot \partial PAF / \partial HU \cdot Areasize\ nat.\ soil
\end{aligned}
\qquad \textbf{Eq. 5.4}
$$

The concentrations in the different compartments will depend on which compartment that is the initial recipient. The procedure of Equations 5.1-5.4 will therefore have to be repeated for the each of the five initial recipient options (air, water and the three soil compartments), resulting in damage factors for emissions to water, emissions to air etc.

5.3 CML Problem Oriented Approach

The risk characterization ratio (RCR) is based on the PEC/PNEC approach explained in Chapter 3.3. This chapter outlines the RCR method of Huijbregts *et al* [2000].

5.3.1 Fate simulation

Fate modeling for substances with the RCR is done with SimpleBox in the same manner as for the PAF, with the exception that Huijbregts *et al* simulate an emission to the regional scale with damages summed for all scales (local, regional and global scales). In the Eco-indicator 99 method, emissions were modeled with damages only within a "closed Europe" in the regional scale.

In RCR the parameter of interest is the absolute concentration resulting from annual emissions; the predicted environmental concentration (PEC).

5.3.2 Damage modeling with the Risk Characterization Ratio (RCR)

Environmental risk assessment, in general and as outlined by the European Commission [1996], is inclined to the use of uncertainty factors in order to make sure proper precautions are made in the use and discharge of potentially harmful chemicals. In LCIA, emissions are translated into actual damages (or in the case of Eco-indicator 99, quantifications of risk), which means that the precautionary principle of risk assessment does not apply. Huijbregts *et al* [2000] therefore use the potentially affected fraction (PAF) of species, described in Section 3.2, as basis for the PNEC. This relates the PNEC to a quantification of risk.
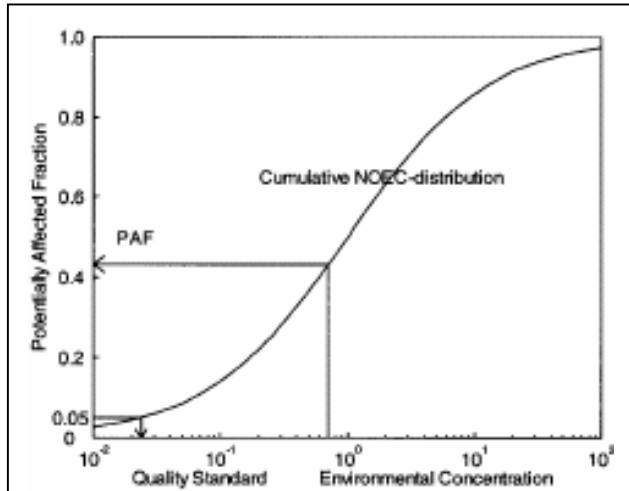
Figure 5. 7: The curve is fitted to follow the cumulative log-logarithmic Gaussian distribution of NOEC values for species in an eco-system. PNEC in the RCR calculations is set at PAF equal to 5%. The figure is from Klepper & Meent [1997].

The PNEC is defined as the concentration giving a PAF of 5 % (single substance PAF); as illustrated in Figure 5.7. The relation is shown in Equation 5.5. The PNEC from Equation 5.5 is then used in the traditional PEC/PNEC-ratio, as shown in Equation 5.6, giving the risk characterization ratio $RCR_{X,C,E}$ in result.

$RCR_{X,C,E}$ is the indicator for substance X on the final recipient C. Concentration in C is the result of emission into initial recipient E. Recipient in this case meaning the compartment and scale in the SimpleBox model.

$$PNEC = C_{PAF=0,05}$$ **Eq. 5.5**

$$RCR_{X,C,E} = \frac{PEC_{X,C,E}}{PNEC_{X,C}}$$ **Eq. 5.6**

5.3.3 Damage calculation

The RCRs are aggregated using metric factors; kg or m^3, describing the size of the compartments or scales. This is shown in Equation 5.7.

$$Weigthed\ RCR_{I,X,E} = \sum_{C7S=1}^{C7S=N} RCR_{I,X,E,C/S} \times W_{I,C/S}$$ **Eq. 5.7**

Summing the weighted contributions the result is a *Weighted RCR$_{I,X,E}$* for impact category *I* from emissions of substance *X* to compartment or scale *E*.

Toxicological impact categories in the CML-POA are 1) human toxicity, and ecotoxicity for the following five compartments: 2) terrestrial, 3) fresh water, 4) sea-water, 5) fresh water sediment, and 6) sea-water sediment. Initial recipients are air, sea water and the three terrestrial compartments (industrial, natural and agricultural soil). This gives a total of 30 characterization factors.

The RCRs of the different substances are in the final stage related to the RCR of a reference substance (*RCR$_{REF}$*), as shown in Equation 5.8. Huijbregts et al use 1,4-dichlorobenzene as reference, giving *Equivalents of 1,4-dichlorobenzene* as the unit for human and eco-system toxicity.

$$TP_{I,X,E} = \frac{Weighted\ RCR_{I,X,E}}{Weighted\ RCR_{REF}}$$

Eq. 5.8

In Equation 5.8, I is the impact category for substance X and initial recipient E.

$$TP_{I,X,E} = \frac{Weighted\ RCR_{I,X,E}}{Weighted\ RCR_{REF}}$$

Eq. 5.8

6 The Dose-related Risk and Effects Assessment Model (DREAM)

6.1 Introduction to DREAM

DREAM (dose-related risk and effects assessment model) is a software tool originally designed for risk assessment of produced water from offshore petroleum installations. It has been developed in co-operation of several research centers (The Netherlands: TNO Research[4]; Norway: Sintef[5] and Akvamiljø[6]) and petroleum companies operating on the Norwegian continental shelf (Statoil, Norsk Agip, TotalFinaElf and Norsk Hydro).

The marine risk assessment methods CHARM [Thatcher *et al*, 2001] and PROVANN [Reed *et al*, 1996] are important precursors to DREAM. The description of DREAM presented in this report is based on the document by Reed *et al* [undated].

"*The general problem to be addressed by DREAM can be subdivided into discrete components as follows:*

> *1. Time-space variations of discharge concentration fields;*
>
> *2. Exposure of organisms with different behaviour patterns;*
>
> *3. Assessment of mixtures of chemicals;*
>
> *4. Assessment of sub-lethal chronic effects.*" [Sintef, undated].

DREAM 2.0 includes the following physical-chemical processes:

- Vertical and horizontal dilution and transport
- Dissolution from droplet form
- Volatilization
- Particulate adsorption/desorption and settling
- Degradation
- Sedimentation to the sea floor

Given that DREAM originally was developed to assess produced water, it includes many processes that relate specifically to oil components in the produced water stream. The processes of oil

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[4] TNO Research: The Netherlands Organisation for Applied Scientific Research, see www.tno.nl.
[5] Sintef, see www.sintef.no.
[6] Akvamiljø (eng.: Aquatic Environment Research Centre), see www.rf.no/akvamiljo.

emulsification, behavior of oil droplets and adsorption/desorption to particles are therefore well addressed in DREAM.

Discharges can be simulated with distribution over time and with several discharge points. The model will calculate several discharges simultaneously, including any eventual overlap in the marine volumes affected. It is, however, a single media model. Volatilization is included in the model, but only in the direction of vaporization, not condensation. In negation to SimpleBox, DREAM therefore models an open system; any effects that might occur after the material is lost from the marine phase will not be assessed.

Characteristics of SimpleBox and DREAM are summarized in Table 6.1.

Table 6.1: Characteristics of fate modeling with SimpleBox and DREAM.

SimpleBox	DREAM
Closed system with interaction between local, regional and global scales.	Open system: material will be lost from further assessment if evaporated.
Multi media and multi scale (including organic compartment).	Single marine phase; includes vaporization, biological uptake, sedimentation and beaching.
Steady state; annual discharges.	Discharges are distributed in time and space.
Only one concentration output.	Concentrations are functions of time.

6.2 Environmental risk assessment with DREAM

In addition to physical and chemical properties, biological processes; e.g. exposure, uptake and depuration, can be assessed with DREAM. The model can simulate distribution to the pelagic and benthic phases of the marine environment. Motion and location of marine species; zooplankton, phytoplankton, benthic organisms and fish, can be plotted and modeled, resulting in locally adapted exposure times and patterns.

DREAM facilitates risk assessment with the PEC/PNEC approach. The most popular application of DREAM in environmental reporting is with the environmental impact factor (EIF). EIF is the volume simulated with concentrations exceeding PNEC, with EIF defined as zero if total volume is less than 100m·100m·10m. Principles of the EIF have been discussed by Johnsen *et al* [2000] and Frost *et al* [2002].

Figure 6. 1: External exposure concentrations for [Karman, 2000]: Top fig: passively moving species; Middle fig.: sessile species; and Bottom fig.: actively moving species
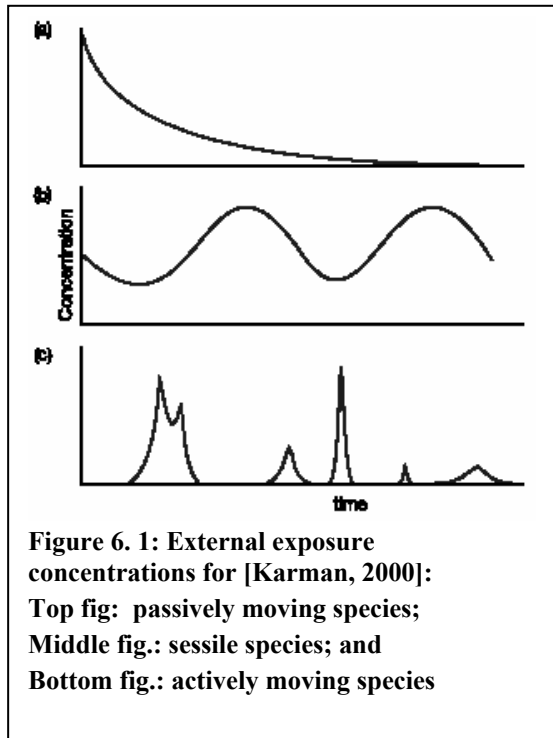
From their characteristics of motion, three types of species will experience different exposure profiles from a marine discharge [Karman, 2000]:

a) Species that move with the water body; passive and continuous exposure.

b) Sessile species; periodic exposure as the plume moves with the tide.

c) Actively moving species (i.e. fish); frequent exposure from movement in and out of the concentration field.

How the exposure profiles look for the three groups of organisms is illustrated in Figure 6.1.

6.3 General equation and concepts

The generalized model equation in DREAM is given below [Reed *et al*, undated]:

$$\frac{\partial}{\partial t}C_i + \vec{V} \cdot \vec{\nabla} C_i = \vec{\nabla} \cdot D_k \vec{\nabla} C_i + \sum_{j=1}^{n} r_j C_j + \sum_{j=1}^{n}\sum_{i=1}^{n} r_{ij} C_i \qquad \textbf{Eq. 6.1}$$

C_i in Equation 6.1 is the concentration of the ith chemical, t denotes time, D_k is the turbulent dispersion coefficient in k (x, y, z) directions, $\vec{V}$ is the advective transport vector, and $\vec{\nabla}$ is the gradient operator. The terms r_j are process rates, including:

- New mass release,
- Evaporation,
- Spreading of surface slicks,
- Emulsification of surface slicks,
- Deposition from water surface onto the coastline,
- Entrainment and dissolution into the water column,
- Resurfacing of entrained oil,
- Volatilisation from water column,
- Dissolution from sediments to water column,
- Deposition from water column to bottom sediments,
- Removal from coastline to water column/surface,
- Mass removal by clean-up.

The terms r_{ji} describe degradation through stages of by-products. In this way, any potentially harmful by-products can be quantified as transfer of mass from one component to another, and be included in the risk assessment.

"Concentrations in the water column are computed from the time- and space-variable distribution of pseudo-Lagrangian particles" [Reed et al, undated]. The particles are of two kinds; i.e. dissolved substances and oil droplets. Oil droplets have non-neutral buoyancy and are pseudo- Lagrangian in that *"they do not move strictly with the currents, but may rise or settle according to their physical characteristics"* [Reed *et al*, undated].

The particles are assumed to be Gaussian "puffs", with concentration distributed in the x, y and z directions around an imaginary centre. The mass is distributed with standard deviations according to Equation 6.2.

$$\sigma_i = \sqrt{2K_i t} \qquad \qquad \textbf{Eq. 6.2}$$

In Equation 6.2, *i* denotes the direction (x, y and z) and *t* the time since release. K_i is the turbulent dispersion coefficient. The calculations of dispersion will be elaborated in a later section.

The distribution of particles result in a three dimensional field of ellipsoid clouds, and the resulting concentration field is the superimposition of the clouds. All particles carry the following attributes:

- x, y and z spatial coordinates;
- mass of the constituents represented by the particle;
- distance to and identity of the nearest neighbour particle;
- time since discharge; and
- spatial standard deviations in x, y and z directions.

Particles representing non-dissolved substances, such as oil droplets and drill cuttings, carry two additional attributes:

- mean droplet diameter; and
- droplet density.

6.4 System description

6.4.1 The physical environment

The physical environment in DREAM; e.g. the marine environment, is defined by the following parameters:

- The coastline,
- Bathymetry (depth), and
- Currents; either two- or three-dimensional current fields. The current fields can be steady state or time varying.
- Wind and wave fields; steady state or time varying, and
- Sea temperature.

Except for the coastline all parameters are user defined. Updates of current, wind and wave fields can be implemented by importation of selected formats or by design through the user interface of DREAM.

6.4.2 Processes

Advection of material in the water column is simulated by spatial interpolation of the mean local velocity and a random turbulent component. The local velocity is a general sum of climatological, tidal, wind and wave (Stokes) driven components.

Dispersion in the horizontal plane is a function of the time since release. A turbulent component w', in the horizontal or vertical direction, is computed as in Equation 6.4 [Reed *et al*, undated]. K in the equation is the turbulent dispersion coefficient.

$$w' = \sqrt{\frac{6K}{\Delta t}}$$
Eq. 6.4

Reed *et al* use a horizontal turbulent dispersion coefficient approximated as follows (K in cm^2/sec and time t in seconds):

$$K_i = 0{,}0027 t^{1,34}$$
Eq. 6.5

As the time since the release increases, the dispersion coefficient will increase resulting in continually increasing forces driving the dispersion of mass; increasing the size and decreasing the concentration in the cloud surrounding each particle. The maximum value applied for K_i is 100 m^2/day (10^6 cm^2/sec).

In the volume affected by waves, viz. above the pycnocline, the vertical turbulent dispersion coefficient is approximated with the following equation:

$$K_z = 0,028 \frac{H^2}{T} \exp(-2kz)$$ **Eq. 6.6**

In Equation 6.6, H is the wave height, T is the wave period and k is the wave number. The wave height will dependant of the wind speed defined for the simulation. Below the pycnocline depth, K_z is assumed constant equal to 10^{-4} m^2/sec.

Figure 6. 2: General layout of the DREAM model [Reed *et al*, undated].
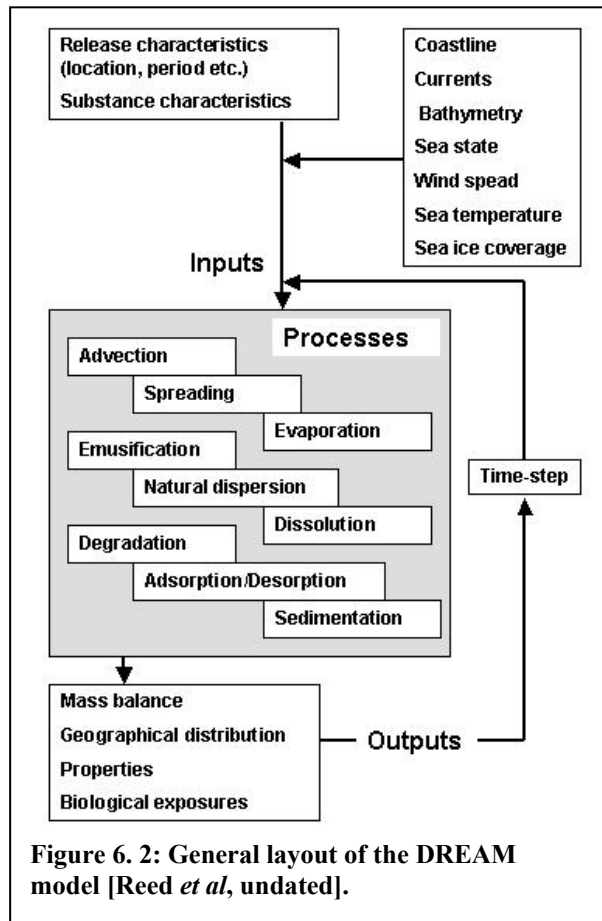
Figure 6.2 shows an overview of the processes included in DREAM. Vertical and horizontal dispersion have been described above. Partitioning between particulate-absorbed and dissolved states is calculated from linear equilibrium theory. Any fraction associated with particulate matter will settle with the particles. Settling speed can be set by the user and should vary with the particle size and density. Dissolved substances will not settle, so this process is only applicable for viscous materials.

Degradation in water and sediment is calculated with first order decay processes. As stated above, intermediate products can be included (Chapter 6.3, Eq. 6.1) in the decay processes.

6.5 User defined parameters in DREAM calculations

6.5.1 Model settings

The number of particles in the calculations set the resolution of the results. It is possible to define number of particles for surface concentrations and subsurface concentrations.

Before simulation, the currents regime to be used has to be defined. Predefined regimes in DREAM include, among others, a North-sea regime and an Atlantic regime. The predefined regimes are limited in size. New regimes can be defined if required, either through the interface of DREAM or

by import of currents data. Once the regime is selected, the volume will de divided into a concentration cell grid. Number of cells in the concentrations grid can be defined between both in the horizontal plane and in the vertical direction.

Calculated concentrations in the cells are stored in a text file and can be taken out of the model for further studies. Cells with concentration below a defined lower concentrations limit will not be stored. The time step, and simulation period, will be the main factors that set the number of calculations necessary; i.e. the run time for the calculations. The time step, as well as the output interval (time step between stored output values) is a user defined parameter.

6.5.2 Discharge scenario settings
DREAM facilitates multiple simultaneous discharge points, and discharges can be of varying durations. Also the discharge depth can be set for each of the discharge points. For some substances long simulation times are necessary to follow the substance concentrations through to non-harmful levels. The simulation time can be set accordingly.

6.5.3 Substance settings
Substances can be combined in release profiles. Each substance is registered with the following characteristics: viscosity, mol weight, density, melting and boiling points, solubility, vapour pressure, octanol-water partition coefficient, and degradation rates. For the purpose of risk assessment, acute and chronic toxicity sensitivities for different species can be included.

6.6 Simulation outputs
The simulation results from DREAM are presented in a two-dimensional graphic illustration which shows the time development of the concentration field. A snapshot of the concentration field is presented in Figure 6.3. Other tools in the software can be used to show the vertical distribution (the insert in Figure 6.3) or specified horizontal layers.

In addition to the graphical presentation, values for the concentration cell grid can be extracted from the model in text-file format. Appendix 1 shows an example of the text-file output. Concentrations are given according to the output interval defined in the model settings. Volumes affected at any time can be found from the number of cells that have concentrations above the defined lower concentrations limit.

A second text-file option is the mass balance development through the simulation. Material is divided between the following compartments; surface, water column, sediment, atmosphere (the

evaporated mass), decay, ashore (the beached mass), clean-up and "outside". The percentage rates are given for the output interval defined in the model settings (see Section 6.5.1). The clean-up compartment is only active if a clean-up percentage (clean-up success rate) is set for the discharge scenario.

DREAM will calculate the environmental impact factor (see Section 6.2) caused by the release. If biological settings are used (see Section 6.2), exposure indicators will be given as well.
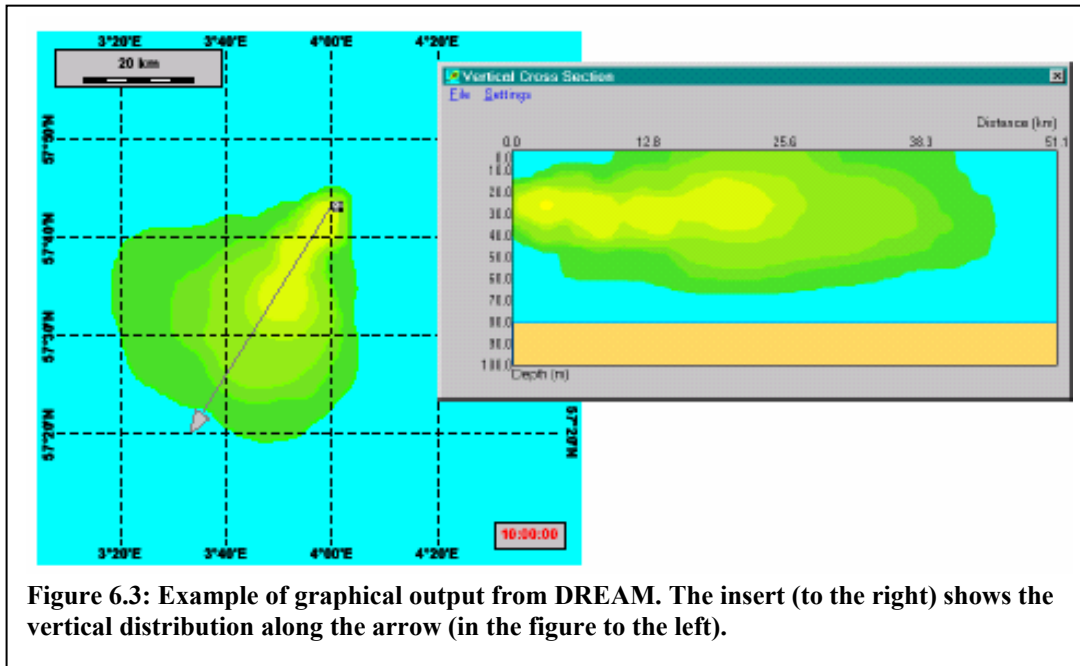

Figure 6.3: Example of graphical output from DREAM. The insert (to the right) shows the vertical distribution along the arrow (in the figure to the left).

7 Dynamic marine exposure PAF (dme-PAF) method

PAF, as defined in the Eco-indicator 99 by Goedkoop & Spriensma [2001], will be used as definition of environmental damage to develop a new method better suited to describe the patchiness of offshore discharges. Fate (exposure) modeling of substances will be done with the marine discharge simulation tool DREAM. By using DREAM, the static steady state concentrations and volumes used in Eco-indicator 99 can be replaced with dynamic values. The resulting PAF is called dynamic marine exposure PAF (dme-PAF).

Calculations with outputs from DREAM can be performed with calculation software like MS Office Excel.

7.1 Methodology

The curve of PAF is assumed a function of hazard units (HU) as in the Eco-indicator 99 method described previously (see Section 5.2.2). Static exposure values in the Eco-indicator method are replaced with time-varying exposure data from DREAM. The hazard unit increase (ΔHU) in Eco-indicator 99 is calculated with Equation 7.1 and is dimensionless.

$$\Delta HU = \frac{\Delta C}{10^{\alpha}}$$ **Eq. 7.1**

ΔC in Equation 7.1 is the compartment concentration resulting of annual continuous discharges to the initial recipient. 10^{α} is the average no effect concentration (see Section 3.2; Eq. 3.2).

It is proposed to replace the concentration increase in Equation 7.1 with a time integrated function to better describe the time dependant exposure from offshore discharges.

DREAM will give time-series of the concentrations in the concentration grid in an output text file; with time step predefined in the model settings (see Section 6.5.1). The concentrations at each time step will first be used to calculate the arithmetic average concentration C_t at time t. The time series of C_t is then used to estimate the integral in a sum function. Units for dynamic HU increase (ΔHU_D) are kept compatible with the Eco-indicator method (dimensionless) by dividing the integrated concentration with the time integral of 10^{α}. The calculation of hazard unit increase in the dynamic approach is shown in Equation 7.2.

$$\Delta HU_D = \frac{\int_0^T C_t - C_B dt}{\int_0^T 10^\alpha dt} \approx \frac{\Delta t \sum_0^T C_t}{T \cdot 10^\alpha}$$

Eq. 7.2

C_t is the average concentration in the cells with concentrations above the predefined *lower concentration limit* (model setting; see Section 6.5.1) at time t; with t ranging from $t=0$ to $t=$T. Δt is constant. The integral is finite, and $C_T=0$.

The marginal increase in PAF caused by the release is found according to Equation 7.3, with ΔHU_D from Equation 7.2. The hierarchical perspective in Goedkoop & Spriensma [2001] will be applied in this study, with an assumed PAF of 24% as the marine eco-system average PAF. This gives a slope factor ($\partial PAF/\partial HU$) of 0.59. The slope factor can be used to include potential local variations concerning the present stress and sensitivity of the marine eco-system.

$$\Delta PAF = \Delta HU_D \cdot \frac{\partial PAF}{\partial HU}$$

Eq. 7.3

As shown in Equation 7.4, the damage per discharged mass is found by dividing the marginal increase in PAF with the discharged mass M (with unit kg). ΔPAF will have the unit PAF·kg^{-1}.

$$PAF_{kg} = \Delta HU_D \cdot \partial PAF / \partial HU \cdot \frac{1}{M}$$

Eq. 7.4

Marine damage from the offshore discharge is found by multiplication of PAF with the affected marine volume (AMV). Local variations have great impact on the damage caused by a release of chemicals, and damage is dependant of the exposure time and volume. AMV works as a localization specific factor, and it is estimated with the time integrated volume; much in the same manner as the time integrated concentration. The volume of cells with concentrations recorded, that is with concentration levels above the *lower concentration limit* (model parameter; see Section 6.5.1) at time t is a given in the text-file output from DREAM. The integral is approximated with the sum function shown in Equation 7.5.

$$AMV = \int_t^T V(t)dt \approx \Delta t \sum_0^T V_t$$

Eq. 7.5

V_t is the affected volume at time t. As in Equation 7.2, the output interval set in the model parameters (see Section 6.5.1) defines Δt, with t ranging from $t=0$ to $t=$T. Like for C_t, the integral of V_t is finite, Δt is constant, and $V_T=0$.

Finally, the marine damage is scaled to fit the PAF defined in Eco-indicator 99. In the Eco-indicator method, the characterization factors are aggregated with area size of the compartments. This was

shown in Equation 5.4 (in Section 5.4.2). In the dynamic approach, the area size of the total marine volume is scaled with the ratio of the affected marine volume and the total marine volume (TMV). Equation 7.6 explains how the aggregation factor for the area size of the marine volume (*MV Areasize*) is calculated in the dynamic approach.

$$MV \; Areasize \, (dynamic) = MV \; Areasize \, (steady-state) \cdot \frac{AMV}{TMV} \qquad \textbf{Eq. 7.6}$$

TMV in Equation 7.6 is in units of m^3, while AMV is in units of $m^3 \cdot yr$. The area size in the dynamic approach therefore includes the time dimension of exposure, and is given in units of $m^3 \cdot yr$.

Because the sea volume is not applied in the fate simulation in the Eco-indicator 99 method, the volume and area size of the marine volume must be found elsewhere. Goedkoop & Spriensma [2001b] use a total system area size of $3.6 \cdot 10^6$ km^2. According to Brandes *et al* [1996; p. 43], typical area fraction of the sea water compartment in both the regional and continental scale is 50 %. This gives a sea water area (MV Areasize (steady-state)) of $3.6 \cdot 10^6$ km^2. The sea water compartment depth is 200 m [Brandes *et al*, 1996; p. 42]. Total marine volume (TMV) is then $7.2 \cdot 10^5$ km^3.

The unit for toxicological eco-system damage in Eco-indicator 99 is $PAF \cdot m^2 \cdot yr \cdot kg^{-1}$. Same units are achieved in the dynamic approach by replacing the steady-state area size with the dynamic area size. The final operation in the calculation of damage in the dynamic approach is given in Equation 7.7.

$$PAF \cdot m^2 \, (marine, \, marine) = PAF_{kg} \cdot \frac{\Delta t \sum_{0}^{T} V_t}{TMV} \cdot MV \; Areasize \, (steady-state) \qquad \textbf{Eq. 7.7}$$

Unit for the final damage is $PAF \cdot yr \cdot m^2 \cdot kg^{-1}$, and it is compatible with the damage definition for eco-system toxicological impacts in Eco-indicator 99.

The total equation for the marine dynamic PAF is summarized in Equation 7.8. Table 7.1 lists and describes the factors used in Equations 7.1-7.8.

$$PAF \cdot m^2 \, (marine, \, marine) =$$

$$\frac{\Delta t \sum_{0}^{T} C_t}{T \cdot 10^{\alpha}} \cdot \frac{\partial PAF}{\partial HU} \cdot \frac{1}{M} \cdot \frac{\Delta t \sum_{0}^{T} V_t}{TMV} \cdot MV \, Areasize \, (steady-state) \qquad \textbf{Eq. 7.8}$$

7 Dynamic marine exposure PAF method

Table 7.1: Parameters used in the calculation operations of the dynamic marine exposure PAF.

Factors	Description
Δt	Time step in the outputs text file; time between stored values of concentration and volume. Δt is constant.
C_t	Average concentration in cells at time t. Only cells with concentrations above the predefined *lower concentration limit* (model selling; see Section 6.5.1) are stored and used in calculations.
T	The time T will be dependant of substance, model and scenario settings. T is the time necessary to eliminate all concentrations above the *lower concentration limit* (model setting; see Section 6.5.1). C_t is zero at t=T.
10^{α}	Geometric mean of no observable effect concentrations (NOEC; toxicological chronic sensitivity).
HU	Hazard units. HU is the ratio of concentration:10^{α}.
$\partial PAF/ \partial HU$	Slope of the PAF curve for the assumed mix of chemicals. In the dynamic approach PAF for the marine eco-system is assumed to the 0.24, giving $\partial PAF/ \partial HU$ of 0.59.
M	M is the discharged mass in units of kg.
V_t	Volume at time t. Only cells with concentrations above the predefined *lower concentration limit* (model selling; see Section 6.5.1) are stored and used in calculations.
AMV	Affected marine volume; the time integrated fraction of the total marine volume affected by the discharge.
TMV	Total marine volume. TMV is the total volume of the marine recipient; $7.2 \cdot 10^5$ km^2.
MV Areasize (steady-state)	Area size of TMV; $3.6 \cdot 10^6$ km^2.

Table 7.2: Methods applied in the Eco-indicator 99 method and in the Dynamic marine exposure PAF; differences and similarities.

Aspect	Eco-indicator 99	Dynamic marine exposure PAF
Fate (exposure) modeling	SimpleBox; steady-state concentrations.	DREAM; time series of concentration and volume.
Effect modeling	$\Delta HU = \dfrac{\Delta C}{10^{\alpha}}$	$\Delta HU_D = \dfrac{\int_0^T C_t - C_B\,dt}{\int_0^T 10^{\alpha}\,dt} = \dfrac{\Delta t \sum_0^T C_t}{T \cdot 10^{\alpha}};$ where C_t is average concentration in affected cells at time t.
Damage modeling	$\Delta PAF = \Delta HU \cdot \dfrac{\partial PAF}{\partial HU}$	$\Delta PAF = \Delta HU_D \cdot \dfrac{\partial PAF}{\partial HU}$
Cultural perspective	Three cultural perspectives; individual ($PAF_{0.10}$), hierarchical ($PAF_{0.24}$) and egalitarian ($PAF_{0.50}$).	Only hierarchical perspective applied. The marginal increase of PAF can be varied to show eco-system sensitivity and stress differences between localities.
Relation to mass	M is discharge rate; resulting in PAF_{kg} with units of $PAF \cdot yr \cdot kg^{-1}$.	M is absolute discharge; resulting in PAF_{kg} with units of $PAF \cdot kg^{-1}$.
Aggregation	Aggregation with area size, resulting in units $PAF \cdot m^2 \cdot yr \cdot kg^{-1}$.	First, affected marine volume (AMV) is estimated: $AMV = \int_t^T V(t)\,dt = \Delta t \sum_0^T V_t$ AMV is used to calculate *Marine Volume Areasize (dynamic)* with the following equation (*TMV* is total marine volume): $MV\ Areasize\ (dynamic) = MV\ Areasize\ (steady-state) \cdot \dfrac{AMV}{TMV};$ where TMV is $7.2 \cdot 10^5$ km^3 and *MV Areasize (steady-state)* is $3.6 \cdot 10^6$ km^2.
Final metric	Resulting in final unit $PAF \cdot m^2 \cdot yr \cdot kg^{-1}$.	Resulting in final unit $PAF \cdot m^2 \cdot yr \cdot kg^{-1}$, and compatible with the Eco-indicator 99 characterization factors.

7.2 The sum function approximation

Figure 7.1: The concentration and volume as functions of time. The columns indicate the sum function approximation of the integral.
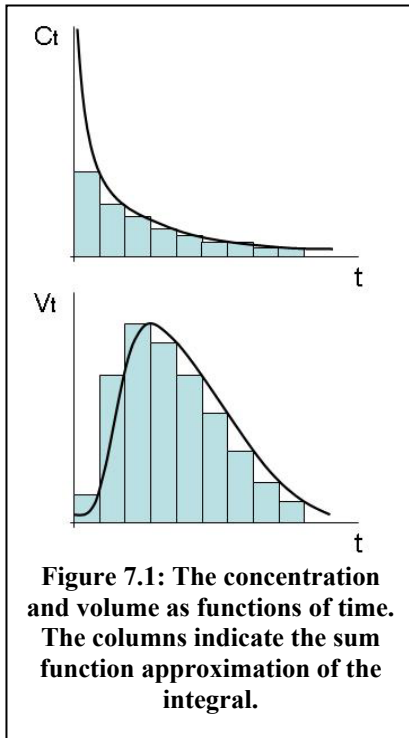
Figure 7.1 illustrates time series of the concentration and volume affected through the simulation time.

From the figure it is obvious that the sum function will systematically underestimate the integral of the concentration. Decreasing the time step Δt will decrease the difference between the integral and the sum function. A decrease in the time step will increase the number of output values as more concentrations will be recorded.

The sum function shows a better fit for approximation of the integral of volume. The curve for V_t is shaped as a "stretched bell", meaning that the volume increases rapidly in the first part of the simulation and decreases slowly in the latter part of the period. The value for the *lower concentration limit* (LCL) decides the rate of decrease of volume, given that mass in cells with concentrations lower than the LCL will be registered as degraded.

Calculations with the sum functions will be performed with MS Office Excel using the PivotTable function.

7.3 Assumptions in the method

Comparison between Figures 7.1 and 6.1 shows that the method proposed in Section 7.1 for the dynamic marine exposure PAF is a valid exposure model for organisms exposed passively and continuously. Table 7.3 lists the general assumptions in the method outlined in Section 7.1.

Table 7.3: General assumptions in the simulation of volume and concentration.

Passively moving organisms.
Concentrations below the *lower concentration limit* are neglected.
Affected volumes from multiple discharge points do not overlap.

The value for the lower concentration limit will greatly affect the volume found in the sum function approximation. It will also influence the time T (see Table 7.1) required to degrade the discharge. Results from test simulations to check the sensitivity of the model will be given in a later section.

8 Calculation of dme-PAF for discharges from the petroleum industry

The motivation of this study is to find ways to include marine effects of offshore discharges in life cycle assessments of input materials to the drilling processes. In other words the method should be designed to be used by petroleum companies. Data available to such companies is the subject of the first section of this chapter. The second section describes the settings used in the DREAM simulations performed.

8.1 Substance data available

Suppliers of products to petroleum processes offshore must present a harmonized offshore chemical notification format (HOCNF) for the products. The HOCNF includes the following list of information about the product's constituents [OSPAR; 2000, 2000c]:

- The likely fate of the substance in general terms; any potential reaction products or intermediates and if it will end up in the sediment, biota, water column or air.
- Safety data sheets, with the information normally included in safety sheets.
- Constituent substances with names, CAS-numbers and concentrations ranging within a specified interval (± 2.5 - 15 % depending on concentration).
- CAS-numbers for monomer if not applicable for polymer.
- For substances not PLONOR-listed (see Section 2.5), acute toxicological properties, according to specified test guidelines, must be assesses for all constituents.
- N-octanol water partitioning coefficient (P_{OW}) according to specified test guidelines.
- Data on biodegradability in the marine environment according to specified guidelines.
- Eventual tainting properties.

Guidelines for the toxicity testing procedures are given by OSPAR [2002a]. The following test organisms have to be screened [SFT, undated]:

- *Skeletonema costatum*
- *Acartia tonsa*
- *Scophtalmus maximus*; if the substance is persistent (< 20 % degradable over 28 days). Can be replaced with screening of *Cyrindon variegatus* (Sheepshead minnow).
- *Corophium volutator;* if the substance will absorb to particles (K_{OC} >1000, organic carbon fraction coefficient.

Companies operating on the Norwegian shelf and SFT have access to the HOCNF data though the CHEMS database[7]. This information is not open to the public, with the implication that such data cannot be published in the format of this report.

A vital part of an LCA, but a very difficult part in the assessment of products used in offshore processes, is to find a (relatively) precise quantification of the material streams. In LCA this is called the life cycle inventory (see Section 5.2.2). In this case it means the product's constituents. It was described above how the percentage of the different constituents need not be presented precisely, but only within certain boundaries. In addition, the compounds used offshore are often of various non-homogenous forms, such as amines or polyols, and the substances in this mix are not defined any further.

Environmental *risk* management is the normal procedure in offshore environmental management. Because of the precautionary principle applied in such assessments, toxicological data beyond the lowest chronic effect level are not relevant for the HOCNF reports. This means that toxicological data for most constituents has to be gathered elsewhere.

8.2 Assumptions and settings

8.2.1 Substance settings

Because of difficulties with finding the required data for relevant substances (see Section 9.1) simulations will be performed for only two substances. Results for volume, concentration and time T from these simulations are intended to be used in Equation 8.8 (see Section 8.1) with the addition of substance specific HOCNF toxicity data (see Section 9.1) to calculate PAF values for substances. The substance to be used in DREAM simulations is glutaraldehyde (synonyms: glutaral; 1,5-pentanedial). Glutaraldehyde is used as biocide in many of the chemical products used offshore. It has fairly high degradation rates in natural eco-systems. Properties for glutaraldehyde are given in Table 9.1.

HOCNF data is used as source for glutaraldehyde toxicity data. All tests used in HOCNF reporting of toxicity are for acute effects with values given in the form of LC_{50} or EC_{50} (see Section 2.1). Geometric average was first calculated for each species, later for the whole set of species data. Unfortunately the toxicity data used in the calculation of acute α could not be published in this report.

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[7] CHEMS is developed and managed by NovaTech. See NovaTech online: http://www.novatech.no.

Chronic α is found as 1/10 of acute value. This is a very rough estimate, but is according to the method of Huijbregts *et al* [2000]. The ratio is also suggested by de Zwart [2002]. Acute to chronic ratios are discussed in detail by Pennington [2002], with the conclusion that a ratio of 10 should be applied with caution.

Table 9.1: Physical and chemical properties of glutaraldehyde[1].

	Formula	CAS No.	Mol weight
Glutaraldehyde	$C_5H_8O_2$	111-30-8	100.12

	Melting p. [^{o}C]	Boiling p. [^{o}C]	Vapour pressure [atm.]
Glutaraldehyde	-14	188	0.0224

	Density [Tonnes/m3]	Solubility	Ecotoxicity: α [g/L][2]
Glutaraldehyde	0.72	perfect	-3,23

	Degradation rate *k* in all phases (water, droplets and sediment)[3]
Glutaraldehyde	0.0396

[1] Data for properties other than toxicity and degradation are from Merck Chemical Database and MDL Information Systems Database, accesses though the Statoil Internal Network.
[2] α (chronic) as described in Section 3.2.
[3] The degradation rate is expressed as e^{-kt} ; where t is days. The degradation is found in the HOCNF data on glutaraldehyde, the average of supplier data from several suppliers.

8.2.2 Discharge scenario settings

The duration of the discharge will depend on the process involved. Three general processes are within the scope of this study. The processes, along with their respective discharge duration, are listed in Table 9.2. All discharges simulated will be at the water surface, so depths for discharges are set at 0 m for all processes.

Table 9.2: Duration of discharges.

Process	Discharge duration[1]
Drilling	2 days
Cementing	1 hour
Completion	1 hour

[1]Rye; personal communication.

Concentration of substance in the discharge is set at 5000 ppm, and discharged mass is 1 tonne.

Figure 7.2: The location of the Heidrun (H) and Efofisk (E) oilfields. The arrows indicate the general direction of the currents in the area. Currents in the North-Sea are generally weaker than in the Atlantic Ocean.
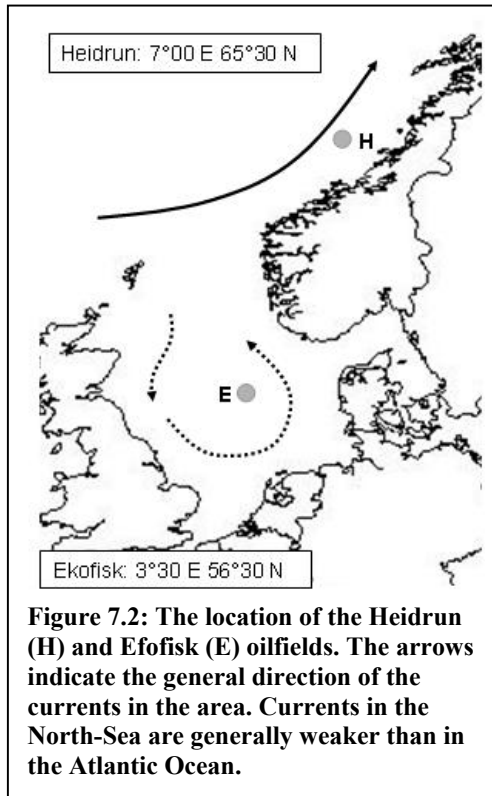
To exemplify different locations with regards to currents and the physical environment two locations are selected:

- Ekofisk: located in the North-Sea. The Ekofisk area is characterized by low currents and a limited marine volume (boundaries are: the British islands, Norway and the European continent).

- Heidrun: located north of Trondheim (North-East Norway). Heidrun is characterized by strong currents (The Gulf Stream) and the absence of boundaries to the marine volume.

Figure 7.2 shows the location of the oilfields.

8.2.3 Model settings

Table 9.4 lists general settings in the simulations of volume and concentration performed in this study. A complete list of settings in the simulations is given in Appendix 2.

Table 9.4: General settings in the simulation of volume and concentration.

Substances are assumed to be perfectly water soluble.

Adsorption/accumulation in the biota is not activated.

Effects caused by potential degradation products are not included.

Lower concentration limit is set at 10^{-4} ppm.

Processes specific for oil compounds are not activated. Such processes are emulsification, processes related to droplet properties, and settling.

8.2.4 Calculation of volume

In the output text file from DREAM, concentrations are given for the cells. Cell size is given by the area size of the currents regime selected, and of the cell numbers set by the user. All cells are defined with constant degree intervals in the latitudal and longitudal directions. Given that the distance of a degree is a function of the latitude this unfortunately means that the cells are not equal in *volume*. The volume of a cell will be calculated for the location of the discharge point, and this volume is used for all cells.

9 Simulation results and model check

9.1 Dynamic marine exposure PAF

Two locations are simulated, both with two discharge periods. Five parallel simulations are performed for each combination. Results of the calculations of PAF are given in Table 9.1. Table 9.2 offers the results of the parameters calculated separately; the total time T and the time integrals of volume (AMV: affected marine volume) and concentration (ΔC). Standard deviations of the parameters can be found in Table 9.3. The complete results from all simulations are given in Appendix 3.

Table 9. 1: Dynamic marine exposure PAF (Dme-PAF) results form the simulations.

	Dme-PAF [PAF·km2·yr/kg]		**Standard deviation**	
	Heidrun	**Ekofisk**	**Heidrun**	**Ekofisk**
Completion/cementing	3,47E-07	2,04E-07	9 %	16 %
Drilling	5,32E-08	4,63E-08	7 %	2 %

Table 9. 2: Results of the separate parameters.

		ΔC [g/L·yr]	AMV [m3·yr]	T [yr]
Heidrun	Completion/cementing	$1,24 \cdot 10^{-10}$	$1,20 \cdot 10^{8}$	0,043
	Drilling	$1,65 \cdot 10^{-11}$	$1,44 \cdot 10^{8}$	0,046
Ekofisk	Completion/cementing	$1,00 \cdot 10^{-10}$	$8,44 \cdot 10^{7}$	0,043
	Drilling	$1,86 \cdot 10^{-11}$	$8,86 \cdot 10^{7}$	0,036

Table 9. 3: Standard deviations in percent for all three parameters.

		ΔC	AMV	T
Heidrun	Completion/cementing	4 %	4 %	12 %
	Drilling	6 %	1 %	15 %
Ekofisk	Completion/cementing	8 %	6 %	20 %
	Drilling	3 %	2 %	7 %

Examples of the development of concentration and affected volume through the simulation are shown in Figure 9.1 (concentration) and 9.2 (volume).

Figure 9.1: Example of development of concentration through time.

Figure 9.2: Example of the development of the affected volume over time.

9.2 Sensitivity analysis

Four parameters are tested; the lower concentration limit, the concentration of the substance in the initial discharge, the mass discharged, and the time step. Complete results can be found in Appendix 4. The Figures 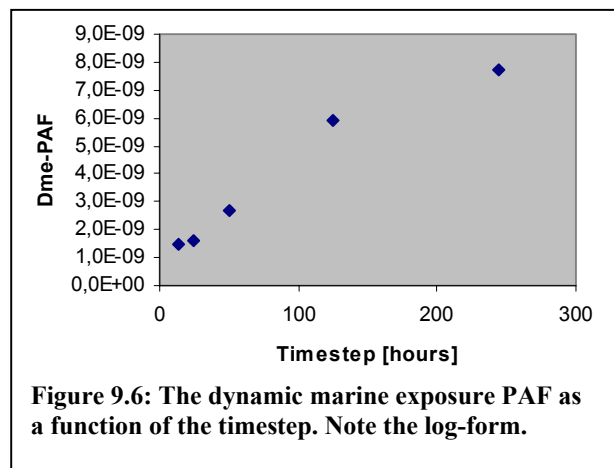9.3-9.6 show dme-PAF as function of (in order): the lower concentration limit, the concentration of glutaraldehyde in the initial discharge, the amount discharged in total, and the time step.

Figure 9.3: The dynamic marine exposure PAF as a function of the lower concentration limit. Note the log-form

Figure 9.4: The dynamic marine exposure PAF as a function of the initial concentration of the substance in the discharge. Note the log-form.

Figure 9.5: The dynamic marine exposure PAF as a function of the mass of the substance in the discharge. Note the log-form.

Figure 9.6: The dynamic marine exposure PAF as a function of the timestep. Note the log-form.
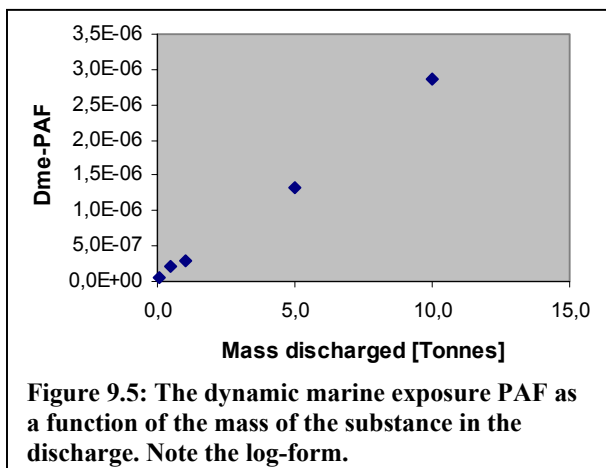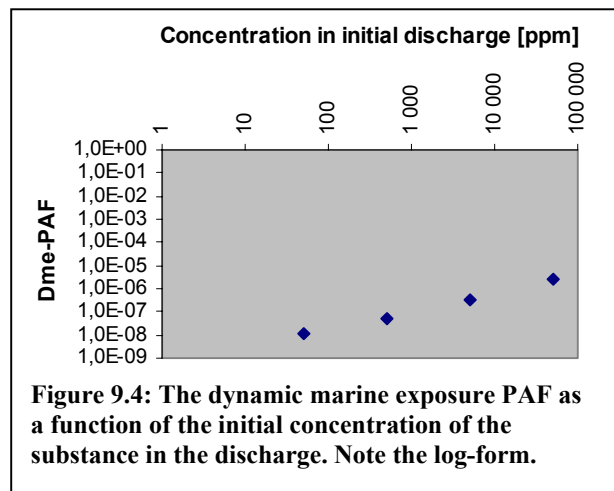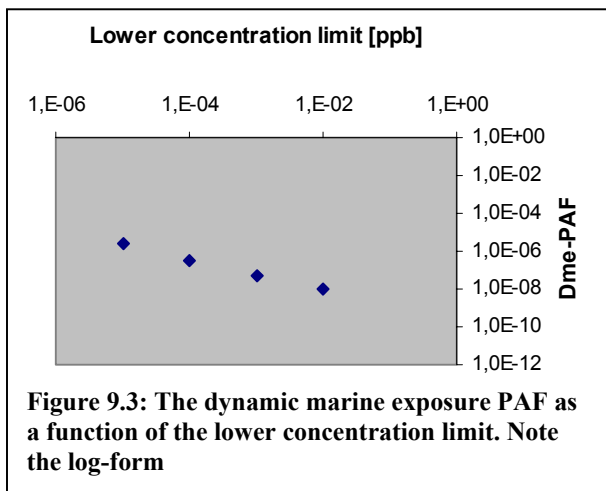
From the figures it is obvious that the resulting dme-PAF is greatly influenced by the settings defined by the user.

Figure 9.7: The influence of the lower concentration limit on the affected volume and the total time T.
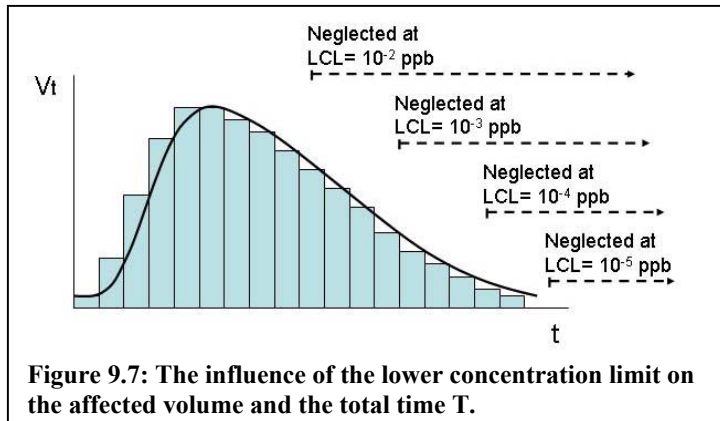
So long as the lower concentration limit (LCL) is not defined as zero the limit will work as an additional "degradation process". Material in cells with concentration below LCL will be recorded as degraded, which effectively decreases the volume affected and the time factor T. How a change in LCL setting will affect the time integral of the volume and the total time T is illustrated in Figure 9.7.

An interesting effect is that increasing the time step actually increases the dme-PAF (see Figure 9.6). The AMV and T are practically constant, or slightly decreased, with an increase of the time step from 13 hours to 245 hours. The increase in dme-PAF is a result of an increase of the time integral of the concentration, mainly caused by the increase of Δt (see values in Appendix 4).

10 Discussion of method and results

10.1 PAF for discontinuous discharges

The methodology proposed in Chapter 7 is compatible with the Eco-indicator 99 method in forms of metric. Still, an important question remains unsolved regarding the starting point of the time integrals. The concentration is very high in the first part of the integral, and this also is the main contribution to the total value of ΔC. A time step of 25 hours is used in the simulations performed in this study in order to maximize the performance of the sum function approximation, and the integral spans the total time from 0 to T. It could be argued that in the first part of the period the exposure is acute. Normally acute toxicity tests span four days. Four days could be set as the starting point of the integral with the argument that exposure in the first few days is acute. Exposure beyond four days would be "prolonged" and therefore chronic. Alternatively both acute and chronic effects could be calculated by dividing the period into an acute period (the first few days) and a chronic period (e.g from day four). Different solutions to the choice of starting point for the exposure assessment and the time step are illustrated in Figure 10.1.
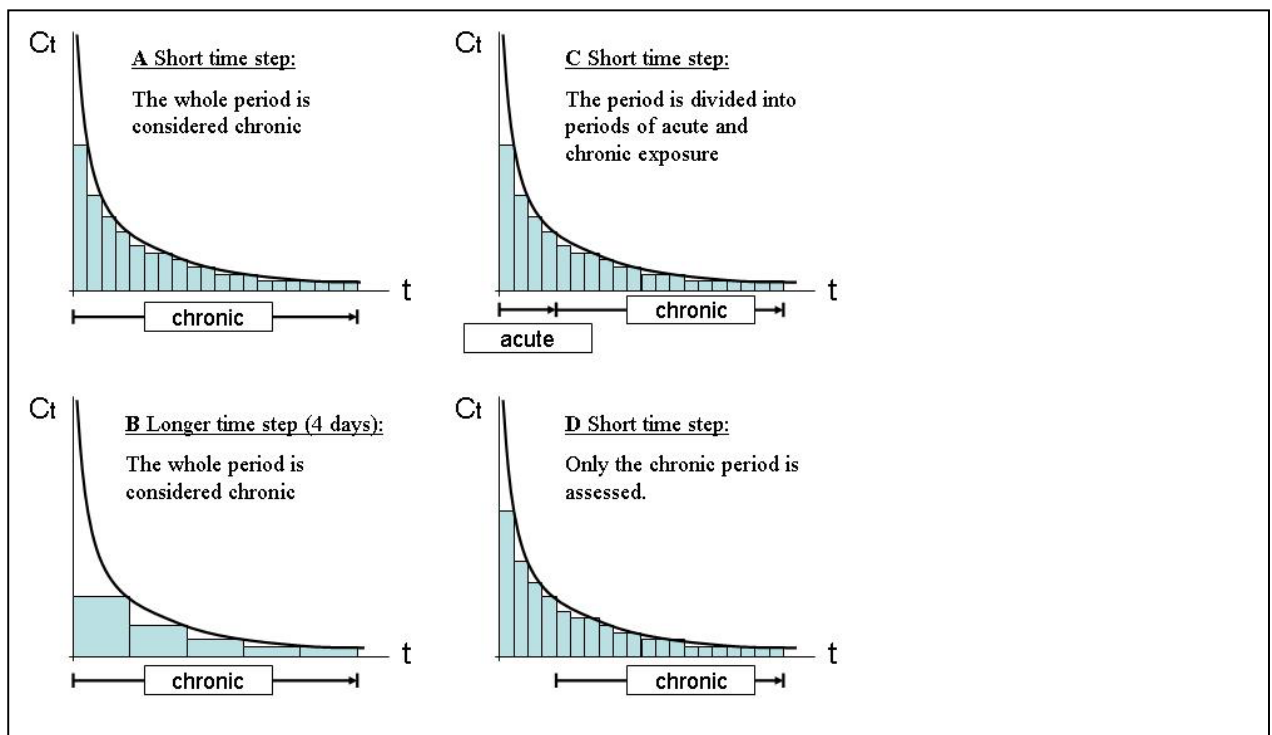
Figure 10.1: How choice of time step influences the time integral. The figure also shows the different solutions mentioned for setting the starting point of the time integral.
In Solution *A*, the whole period is considered chronic. The same is the situation in Solution *B*, only that in this case the choice of time step affects the integral of the volume so that in fact the first few days (four days is proposed) the value for the concentration is neglected.
Two alternative solutions are proposed in *C* and *D*. In *C* the exposure period is divided in a n acute and a chronic period, while in *D* the acute exposure is neglected.

Given the high influence that the first concentration time steps have on the total integral it might be best to omit the acute period and rather start at the beginning of the chronic period. Hazard units are then calculated with Equation 10.1 and the final equation for the dme-PAF will then be as stated in Equation 10.2.

$$\Delta HU_D = \frac{\int_t^T C_t - C_B \, dt}{\int_0^T 10^\alpha \, dt} \approx \frac{\Delta t \sum_t^T C_t}{(T-t) \cdot 10^\alpha} \qquad \textbf{Eq. 10.1}$$

$$PAF \cdot m^2 (marine,\ marine) =$$

$$\frac{\Delta t \sum_t^T C_t}{(T-t) \cdot 10^\alpha} \cdot \frac{\partial PAF}{\partial HU} \cdot \frac{1}{M} \cdot \frac{\Delta t \sum_0^T V_t}{TMV} \cdot MV\, Areasize\ (steady-state) \qquad \textbf{Eq. 10.2}$$

The parameter t in the equation above is the starting point of the time integrals and is proposed as four days. See Table 7.2 for a description for the other parameters.

Eco-indicator 99 defines the factor $\partial PAF/\partial HU$ as a result of both cultural perspective and the multiple substance PAF curve. The slope of PAF varies with the existing eco-system stress, and Goedkoop & Spriensma [2001] assume the average European PAF to be between 10 and 50 % where the different perspectives will apply different values for PAF. In the dme-PAF method proposed in this study, only the hierarchical perspective is applied. The factor $\partial PAF/\partial HU$ includes the aspect of eco-system sensitivity and could be used as a localization factor.

Overlap of affected volumes is not assessed in this study. The PAF proposed in the Eco-indicator 99 method has the advantage that background concentrations need not be quantified because of the definition of a multiple substance PAF and the hazard unit. Functionality of the dynamic marine exposure PAF would be greatly decreased if the method required studies of background concentration of a number of substances.

10.2 Data availability

Information on substance toxicity is available in the HOCNF data. Most substances are listed with data for three species, although some substances are listed with only two. In the case of glutaraldehyde, toxic sensitivity was available for a total of four species, with multiple results for some (from different suppliers). The data is given in the form of LC_{50} or EC_{50}, a format not ideal for assessment of chronic effects. A general weakness of the HOCNF format lies in the fact that the data is produced for risk assessment purposes. This means that only species assumed sensitive are tested, and that only the lowest effect concentrations are relevant for their original purpose. Species sensitivity distributions

require more than three tests to be completely reliable, but because of the highly relevance of the HOCNF data with regards to the selection of substances the HOCNF still are a valuable source of toxicity data.

Physical properties for the substances, on the other hand, will have to be gathered elsewhere. There also is a lot of work related to identifying and quantifying the contents of the chemical products used and discharged offshore. The hardship is a consequence of the restrictions regarding the publication of product data, a secrecy mainly stressed by the suppliers.

10.3 Model settings in DREAM

The following four parameters describe an offshore discharge scenario: location, period of discharge, mass discharged and concentration (of the substance assessed) in the initial discharge. Results for dme-PAF show higher values for the strong-currents location Heidrun than for the Ekofisk location. This is mainly caused by the fact that the affected volume is higher in the Heidrun scenario (see Table 9.2). The other three parameters influence the dme-PAF mainly through the function of the lower concentration limit (LCL). With any LCL above zero, the limit effectively works as an additional degradation process; counting all cells with concentration below the LCL as zero. A LCL of 10^{-4} ppb has been applied in the simulations performed, and even at such low values changes of the LCL greatly influence the results (see Figure 9.3). The lower concentration limit should ideally be set at zero to remove the degradation effects of the limit. Setting the number of cells at 300·300·10 and the lower concentration limit at zero gives a total of 900 thousand cells recorded at every step. This is not a viable option at any time step using MS Office Excel knowing that Excel has a maximum row number of 65 536. So two options arise; either Excel is replaced by software capable of handling the large number of recorded values with a lower concentration limit set at zero, or LCL is set at a value not zero. Defining the LCL at a common level for all substances seems incidental and is not the solution. Another solution could be to base the LCL on toxicity data using an assessment factor, in other words to define an Absolute No-Effect Concentration much like the PNEC only at a lower level. This does not seem like a good solution either. It seems the best way around this problem is to seek other calculation software to replace MS Office Excel.

How the dme-PAF is affected by changes of the mass, concentration or period of the discharge cannot be sufficiently assessed unless LCL is set at zero. It seems however that these factors will influence the dme-PAF, and that toxicity factors should be calculated for different scenarios regarding the concentration, mass and period of the discharge.

10.4 Substance settings in DREAM

All simulations performed in this study assume glutaraldehyde as a perfectly water soluble substance, and all processes other than degradation and distribution in the water column are disactivated. In the final calculation of toxicological impacts the additional processes included in the DREAM model should be activated. Most of the additional processes included in DREAM will decrease the concentration and the affected volume of discharges. Most of the drilling discharges include particles and oil phase. Adsorption of organic substances to the oil phase will effectively remove these effects from the water phase, and the toxicological impact will be local and concentrated to the sediments as the particles fall to the sediment in the region of the drilling site.

11 Conclusions of the study

A method of calculation of potentially effected fraction of species (PAF) has been developed for discontinuous marine discharges. The new dynamic marine exposure PAF (dme-PAF) is compatible with the PAF defined by Goedkoop & Spriensma [2001] in the Eco-indicator 99 method. Fate modeling for dme-PAF is performed with the Dose-related risk and effect assessment model (DREAM). Output from DREAM has to be further assessed with calculation software to calculate the dme-PAF. The DREAM method employs a sum function approximation of the time integral of concentration and volume. It is proposed to start the integrals not at the start of the discharge but after a period of four days to exclude acute exposure from the discharge and to increase the redundancy of the calculations. The model does not include any potential overlaps from multiple discharge points.

Results from simulations indicate that changes in discharge scenario regarding the location of the discharge, as well as concentration, mass and period, has influence on the dme-PAF. Characterization factors should include these aspects.

The DREAM model uses a lower concentration limit (LCL) to reduce the number of recordings in the output. In order to calculate dme-PAFs the LCL should be set at zero. MS Office Excel does not accommodate calculations with more than 65 536 rows of data and therefore sufficient calculations could not be performed for the substance assessed. Other calculation software should be sought to replace Excel.

Glutaraldehyde is assumed a perfectly water soluble substance in the simulations performed in this study. The DREAM model includes processes that should be activated in the final calculations of dme-PAF. If the processes of adsorption and sedimentation of particles was included in the simulations this would decrease the concentration and the affected volume.

Index and abbreviations

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List of appendices

Appendix 1: Example of text-file output from DREAM simulations.
Appendix 2: Complete list of settings in the DREAM simulations.
Appendix 3: Complete results from the DREAM simulations for glutaradehyde.
Appendix 4: Complete results from the sensitivity tests.

Appendix 1: Example of text file output from DREAM.

The columns i(EW) and j(NS) in Table A1.1 denote cell number in the east-west and north-south directions. Size of cells is a result of the total area of the grid (predefined in DREAM) and number of cells (user defined). The number of vertical cells is a user option, and depth is given as cell number in the vertical direction; k(depth). Cells with depths 11 are mean concentration of depths 1-10, while 12 is the maximum concentration in depths 1-10. Table A1.2 shows an example of cell number output from DREAM. Note that all cells are same size in degrees, not in km. Lengths will vary with the latitude.

Table A1.2: Concentrations output.

i(EW)	j(NS)	k(depth)	Date/time	Concentration (ppb)
167	160	1	12.6.1990 17:00	0.234184
167	160	11	12.6.1990 17:00	0.046837
167	160	12	12.6.1990 17:00	0.234184
165	163	1	13.6.1990 18:00	0.186517
166	163	1	13.6.1990 18:00	0.026645
165	163	11	13.6.1990 18:00	0.037303
166	163	11	13.6.1990 18:00	0.005329
165	163	12	13.6.1990 18:00	0.186517
166	163	12	13.6.1990 18:00	0.026645
162	164	1	14.6.1990 19:00	0.003199
163	164	1	14.6.1990 19:00	0.004799
164	164	1	14.6.1990 19:00	0.017595
165	164	1	14.6.1990 19:00	0.084916
166	164	1	14.6.1990 19:00	0.006398
163	165	1	14.6.1990 19:00	0.001600
164	165	1	14.6.1990 19:00	0.023993
165	165	1	14.6.1990 19:00	0.045843
166	165	1	14.6.1990 19:00	0.007998
165	164	2	14.6.1990 19:00	0.004657
165	165	2	14.6.1990 19:00	0.003741
164	164	11	14.6.1990 19:00	0.003519
165	164	11	14.6.1990 19:00	0.017915
166	164	11	14.6.1990 19:00	0.001280
164	165	11	14.6.1990 19:00	0.004799
165	165	11	14.6.1990 19:00	0.009917
166	165	11	14.6.1990 19:00	0.001600
162	164	12	14.6.1990 19:00	0.003199
163	164	12	14.6.1990 19:00	0.004799
164	164	12	14.6.1990 19:00	0.017595
165	164	12	14.6.1990 19:00	0.084916
166	164	12	14.6.1990 19:00	0.006398
163	165	12	14.6.1990 19:00	0.001600
164	165	12	14.6.1990 19:00	0.023993
165	165	12	14.6.1990 19:00	0.045843
166	165	12	14.6.1990 19:00	0.007998
162	165	1	15.6.1990 20:00	0.002741
163	165	1	15.6.1990 20:00	0.002143
164	165	1	15.6.1990 20:00	0.007597
165	165	1	15.6.1990 20:00	0.011066
166	165	1	15.6.1990 20:00	0.002966
161	166	1	15.6.1990 20:00	0.001209
162	166	1	15.6.1990 20:00	0.004791
163	166	1	15.6.1990 20:00	0.012867
164	166	1	15.6.1990 20:00	0.031580
165	166	1	15.6.1990 20:00	0.037175
166	166	1	15.6.1990 20:00	0.012546
162	167	1	15.6.1990 20:00	0.001976
163	167	1	15.6.1990 20:00	0.006399
164	167	1	15.6.1990 20:00	0.014535
165	167	1	15.6.1990 20:00	0.018356
166	167	1	15.6.1990 20:00	0.006362
164	166	2	15.6.1990 20:00	0.002877
165	166	2	15.6.1990 20:00	0.003943
166	166	2	15.6.1990 20:00	0.001417
164	167	2	15.6.1990 20:00	0.001733
etc.				

Appendix 1

Table A1.2: Cell definitions output.

	East-west			North-South			Depth	
Cell No.	Interval [degrees]		Cell No.	Interval [degrees]		Cell No.	Interval [m]	
1	-4,904902	-4,854298	1	51,593807	51,624484	1	0	10
2	-4,854298	-4,803695	2	51,624484	51,655161	2	10	20
3	-4,803695	-4,753091	3	51,655161	51,685838	3	20	30
4	-4,753091	-4,702487	4	51,685838	51,716515	4	30	40
5	-4,702487	-4,651884	5	51,716515	51,747192	5	40	50
6	-4,651884	-4,60128	6	51,747192	51,777868	6	50	60
7	-4,60128	-4,550677	7	51,777868	51,808545	7	60	70
8	-4,550677	-4,500073	8	51,808545	51,839222	8	70	80
9	-4,500073	-4,449469	9	51,839222	51,869899	9	80	90
10	-4,449469	-4,398866	10	51,869899	51,900576			
11	-4,398866	-4,348262	11	51,900576	51,931253			
12	-4,348262	-4,297658	12	51,931253	51,96193			
13	-4,297658	-4,247055	13	51,96193	51,992607			
14	-4,247055	-4,196451	14	51,992607	52,023284			
15	-4,196451	-4,145848	15	52,023284	52,05396			
16	-4,145848	-4,095244	16	52,05396	52,084637			
17	-4,095244	-4,04464	17	52,084637	52,115314			
18	-4,04464	-3,994037	18	52,115314	52,145991			
19	-3,994037	-3,943433	19	52,145991	52,176668			
20	-3,943433	-3,892829	20	52,176668	52,207345			
21	-3,892829	-3,842226	21	52,207345	52,238022			
22	-3,842226	-3,791622	22	52,238022	52,268699			
23	-3,791622	-3,741019	23	52,268699	52,299375			
24	-3,741019	-3,690415	24	52,299375	52,330052			
25	-3,690415	-3,639811	25	52,330052	52,360729			
26	-3,639811	-3,589208	26	52,360729	52,391406			
27	-3,589208	-3,538604	27	52,391406	52,422083			
28	-3,538604	-3,488	28	52,422083	52,45276			
29	-3,488	-3,437397	29	52,45276	52,483437			
30	-3,437397	-3,386793	30	52,483437	52,514114			
31	-3,386793	-3,33619	31	52,514114	52,54479			
32	-3,33619	-3,285586	32	52,54479	52,575467			
33	-3,285586	-3,234982	33	52,575467	52,606144			
34	-3,234982	-3,184379	34	52,606144	52,636821			
35	-3,184379	-3,133775	35	52,636821	52,667498			
36	-3,133775	-3,083171	36	52,667498	52,698175			
37	-3,083171	-3,032568	37	52,698175	52,728852			
38	-3,032568	-2,981964	38	52,728852	52,759529			
39	-2,981964	-2,93136	39	52,759529	52,790206			
40	-2,93136	-2,880757	40	52,790206	52,820882			
41	-2,880757	-2,830153	41	52,820882	52,851559			
42	-2,830153	-2,77955	42	52,851559	52,882236			
43	-2,77955	-2,728946	43	52,882236	52,912913			
44	-2,728946	-2,678342	44	52,912913	52,94359			
45	-2,678342	-2,627739	45	52,94359	52,974267			
46	-2,627739	-2,577135	46	52,974267	53,004944			
47	-2,577135	-2,526531	47	53,004944	53,035621			
48	-2,526531	-2,475928	48	53,035621	53,066297			
49	-2,475928	-2,425324	49	53,066297	53,096974			
50	-2,425324	-2,374721	50	53,096974	53,127651			
51	-2,374721	-2,324117	51	53,127651	53,158328			
52	-2,324117	-2,273513	52	53,158328	53,189005			
53	-2,273513	-2,22291	53	53,189005	53,219682			
54	-2,22291	-2,172306	54	53,219682	53,250359			
55	-2,172306	-2,121702	55	53,250359	53,281036			
56	-2,121702	-2,071099	56	53,281036	53,311712			
57	-2,071099	-2,020495	57	53,311712	53,342389			
58	-2,020495	-1,969892	58	53,342389	53,373066			
59	-1,969892	-1,919288	59	53,373066	53,403743			
60	-1,919288	-1,868684	60	53,403743	53,43442			
61	-1,868684	-1,818081	61	53,43442	53,465097			
62	-1,818081	-1,767477	62	53,465097	53,495774			
63	-1,767477	-1,716873	63	53,495774	53,526451			
etc.			etc.					

Appendix 2: Complete list of settings in the simulations performed.

Table A2.1 lists all model settings in the simulations performed.

Table A2.1: Model settings used in all simulations.

Parameter	Setting
Discharge date and time	June 12. 1990 19:00
Number of surface particles	5000
Number of subsurface particles	5000
Number of cells in concentrations grid	300·300·5
Lower concentration limit [ppb]	$1·10^{-4}$ ppb
Depth of concentration grid [m]	100
Surface film thickness	Default (Emulsification not activated)
Output interval [hours]	25
Calculations time step [hours]	5
Surface drift	Default (not activated)
Near field model parameters	Default
Temperature of discharge [^{o}C]	10
Salinity [g/L]	35
Wind	"Ekofisk" predefined wind file
Ice	Not activated
Background concentration	0
Air temperature [^{o}C]	10
Water temperature [^{o}C]	10
Suspended sediment [mg/L]	0 (Adsorption not activated)
Settling velocity (m/day)	0 (Settling not activated)
Droplet characteristics	Droplet processes not activated

Appendix 3: Complete results from the DREAM simulations for glutaraldehyde.

Table A3.1 lists the settings for the scenarios; period and depth. Volume of cells is a function of the latitude, and in the calculations all cells are assumed with the same volume as at the discharge point. Volume of a cell at the two discharge points is given in Table A3.2. Additional factors required to calculate dme-PAF are listed in Table A3.3.

Results from parallels of the simulations are given in Table A3.4 for the Heidrun location and in Table A3.5 for the Ekofisk location. Results for the two locations are summarized in Table A3.6, and standard deviations for dynamic marine exposure PAF (dme-PAF) are given in Table A3.7. Standard deviations for the total time T and the time integrals of volume and concentration are given in Table A3.8.

The Cementing and Completion scenarios share the same discharge period. This scenario is named C-C in the tables below.

All simulations are performed with a total release of 1 tonne, and a concentration of 5000 ppm of glutaraldehyde in the discharge. Lower concentration limit is 10^{-4} ppb, and timestep is 25 hours.

Table A3.1: Depth and period settings for the calculations

Process	Period	Depth (m)
Cementing	1h	0
Completion	1h	0
Drilling	2d	0

Table A3.2: Factors for the calculation of PAF

dPAF/dHU	0,59	
TMV	7,20E+14	m^3
Areasize (s-s)	3,60E+06	km^2
NOEC (alpha)	-3,23	g/L (log)

Table A3.3: Volume of a cell at the two discharge points.

Location	Volume [m^3]	Latitude [North]	Longitude [East]
Heidrun	$7,328 \cdot 10^6$	65°30 N	7°00 E
Ekofisk	$1,061 \cdot 10^7$	56°30 N	3°30 E

Table A3.4: Parallel calculations for Heidrun

Process	ΔC	AMV	T	Dme-PAF
	g/L·yr	m^3·yr	yr	PAF·km^2·yr/kg
C-C	1,32E-10	1,23E+08	5,14E-02	3,19E-07
C-C	1,19E-10	1,12E+08	4,28E-02	3,13E-07
C-C	1,25E-10	1,22E+08	4,28E-02	3,59E-07
C-C	1,25E-10	1,21E+08	4,28E-02	3,56E-07
C-C	1,19E-10	1,20E+08	3,71E-02	3,90E-07
Drilling	1,60E-11	1,44E+08	4,28E-02	5,43E-08
Drilling	1,60E-11	1,43E+08	4,00E-02	5,77E-08
Drilling	1,83E-11	1,46E+08	5,71E-02	4,72E-08
Drilling	1,63E-11	1,47E+08	4,57E-02	5,28E-08
Drilling	1,61E-11	1,42E+08	4,28E-02	5,40E-08

Appendix 3

Table A3.5: Parallel calculations for Ekofisk

Process	ΔC	AMV	T	Dme-PAF
	g/L·yr	m^3·yr	yr	PAF·km^2·yr/kg
C-C	1,05E-10	8,51E+07	5,71E-02	1,58E-07
C-C	9,50E-11	7,82E+07	3,42E-02	2,19E-07
C-C	1,13E-10	9,20E+07	4,28E-02	2,44E-07
C-C	9,46E-11	8,24E+07	4,00E-02	1,97E-07
C-C	9,50E-11	8,41E+07	4,00E-02	2,02E-07
Drilling	1,82E-11	8,76E+07	3,42E-02	4,70E-08
Drilling	1,95E-11	9,18E+07	4,00E-02	4,52E-08
Drilling	1,83E-11	8,85E+07	3,42E-02	4,77E-08
Drilling	1,87E-11	8,89E+07	3,71E-02	4,52E-08
Drilling	1,83E-11	8,64E+07	3,42E-02	4,67E-08

Table A3.6: Results for dme-PAF for the two locations, with standard deviatins in percent.

	Dme-PAF [PAF·km^2·yr/kg]		Standard deviation	
	Heidrun	Ekofisk	Heidrun	Ekofisk
C-C	3,47E-07	2,04E-07	9 %	16 %
Drilling	5,32E-08	4,63E-08	7 %	2 %

Table A3.7: Results of time integrals and total time

		ΔC [g/L·yr]	AMV [m3·yr]	T [yr]
Heidrun	C-C	1,24E-10	1,20E+08	0,043
	Drilling	1,65E-11	1,44E+08	0,046
Ekofisk	C-C	1,00E-10	8,44E+07	0,043
	Drilling	1,86E-11	8,86E+07	0,036

Table A3.8: Standard deviation for the time integrals and total time

		ΔC	AMV	T
Heidrun	C-C	4 %	4 %	12 %
	Drilling	6 %	1 %	15 %
Ekofisk	C-C	8 %	6 %	20 %
	Drilling	3 %	2 %	7 %

Appendix 4: Complete results from the sensitivity tests.

Unless specified all settings are according to Table A4.1. The Tables A4.2-A4.5 show the time integral of concentration, affected marine volume, total time T and dynamic marine exposure PAF (dme-PAF) as functions of (in order); the lower concentration limit, the concentration of glutaraldehyde in the initial discharge, the amount discharged in total, and the timestep.

Maximum number of rows in MS Office Excel is 65 536. If this is exceeded no calculations can be performed.

Table A4.1: General settings for the simulations.

Time step	25 hours
Mass of substance in discharge	1 tonne
Location	Heidrun
Substance	Glutaraldehyde
Scenario	Cementing/Completion
Initial concentration	5000 ppm
Lower concentration limit (LCL)	1,00E-04 ppb

Table A4.2: Results from variation of the lower concentration limit (LCL)

LCL [ppb]	ΔC [g/L·yr]	AMV [m3·yr]	T [yr]	Dme-PAF [PAF·km^2·yr/kg]
1,E-02	1,33E-10	4,18E+05	5,71E-03	9,8E-09
1,E-03	1,33E-10	6,48E+06	1,71E-02	5,1E-08
1,E-04	1,32E-10	1,23E+08	5,14E-02	3,2E-07
1,E-05	1,20E-10	2,30E+09	1,11E-01	2,5E-06
1,E-06		Recordings > 65536		

Table A4.3: Results from variation of the concentration of glutaraldehyde in the discharge.

Concentration [ppm]	ΔC [g/L·yr]	AMV [m3·yr]	T [yr]	Dme-PAF [PAF·km^2·yr/kg]
50	1,66E-12	6,27E+05	8,56E-03	1,2E-08
500	1,28E-11	6,48E+06	1,71E-02	4,9E-08
5 000	1,25E-10	1,24E+08	4,85E-02	3,2E-07
50 000	1,27E-09	2,33E+09	1,14E-01	2,6E-06
500 000		Recordings > 65536		

Table A4.4: Results from variation of the total mass discharged.

Mass discharged [Tonnes]	ΔC [g/L·yr]	AMV [m3·yr]	T [yr]	Dme-PAF [PAF·km^2·yr/kg]
0,1	1,22E-11	5,86E+06	1,43E-02	5,1E-08
0,5	6,34E-11	4,62E+07	2,85E-02	2,1E-07
1	1,19E-10	1,18E+08	4,85E-02	2,9E-07
5	6,27E-10	9,52E+08	9,13E-02	1,3E-06
10	1,20E-09	2,29E+09	9,70E-02	2,9E-06

Table A4.5: Results from variation of the timestep.

Timestep [hours]	ΔC [g/L·yr]	AMV [m3·yr]	T [yr]	Dme-PAF [PAF·km^2·yr/kg]
13	1,24E-10	1,25E+08	5,34E-02	1,5E-09
25	1,25E-10	1,24E+08	4,85E-02	1,6E-09
50	1,99E-10	1,07E+08	4,00E-02	2,7E-09
125	4,60E-10	1,09E+08	4,28E-02	5,9E-09
245	8,93E-10	9,63E+07	5,59E-02	7,8E-09