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Abstract

The North Sea contains several oil-based drill cuttings piles which have accumulated on the seabed as a result of oil and gas production. An increased awareness of the contaminants within these piles has grown over the years since several platforms are to be decommissioned. Possible relocation of cuttings piles might result in release of contaminants from the drill cuttings, possibly affecting local organisms. It has been of interest to determine rates at which contaminants, total hydrocarbon (THC) in particular, are leaching out to the environment from these piles. This can be done by physical analyses in the laboratory, such as shaking tests, or by mathematical models. The Norwegian Climate and Pollution Agency (Klif) has prepared risk assessment guidelines for contaminated sediments in coastal areas and fjords which includes diffusion calculations. The objective of this thesis is to examine if these guidelines can be used to calculate leaching rates from oil-based drill cuttings piles in the North Sea. Data from drill cuttings piles at Statfjord A was used as basis for the calculations in this study. THC is the main contaminant of concern, determining the leaching rate of THC would therefore be preferred. This was not possible however, due to the fact that THC is not included in the guidelines. The leaching rates are thus calculated based on poly aromatic hydrocarbons (PAH), which often represent the most toxic part of drill cuttings piles. The calculated maximum and mean PAH leaching rates, based on equations given in Klif's guidelines, was determined to be 41,2 kg/year and 3,40 kg/year respectively. Several factors of uncertainty with regards to these calculations, such as extensive use of default values and the possibility that processes not included in the guidelines might contribute to the spreading, and lack of comparison values, makes it difficult to evaluate the accuracy of these leaching rates. However, the estimated time to drain the sediment for contaminants was rapid for some of the PAHs, which might indicate overestimations in the calculations. The environmental impact results show that several of the PAHs are exceeding their respective limit values given in Klif's guidelines. This might indicate that leaching of PAHs from the drill cuttings piles might affect the species living in, on or possibly near the drill cuttings piles.

This study shows that there are several limitations when using Klif's guidelines to determine leaching rates from oil-based drill cuttings piles. Critical parameters are deficient from both the guidelines and the drill cuttings characterization reports to be able to get reliable results. In addition, uncertainty arises due to the fact that the guidelines are based on conditions in harbors and coastal areas and not conditions present in the North Sea. The sum of these uncertainties indicates that the calculated results cannot be considered reliable, and that the present guideline is not feasible to use on oil-contaminated drill cuttings piles. However, the study might provide useful information on factors that should be present to calculate leaching rates from oil-based drill cuttings piles.

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Abbreviations

| | |
|--------|---|
| DC: | Drill cuttings |
| DNV: | Det Norske Veritas |
| EPA: | Environmental Protection Agency |
| IRIS: | International Research Institute of Stavanger |
| Klif: | The Norwegian Climate and Pollution Agency |
| MO: | Microorganism |
| NAF: | Non-aqueous based fluid |
| NIVA: | Norwegian Institute for Water Research |
| NGI: | Norwegian Geotechnical Institute |
| NOEC: | No Effect Concentration |
| OBF: | Oil based fluid |
| OSPAR: | Oslo-Paris Commission |
| PAH: | Poly aromatic hydrocarbon |
| PEC: | Predicted environmental concentration |
| PNEC: | Predicted no-effect concentration |
| ROV: | Remotely operated vehicle |
| SBF: | Synthetic based fluid |
| THC: | Total hydrocarbon |
| TOC: | Total organic carbon |
| TOM: | Total organic matter |
| UKOOA: | United Kingdom Offshore Operators Association |
| WBF: | Water based fluid |

1 Introduction

1.1 Background

Drill cuttings are small rock fragments that are produced when the drill bit cuts into the rock formation during drilling. The cuttings are mixed with drill fluid which contains a variety of different chemicals to optimize the drilling, and then transported to the surface of the rig, where they are separated from the fluid. The fluid can be used again, but the drill cuttings are considered as waste, and have therefore traditionally been discharged to the seabed regardless of its chemical content (Gerrard et al., 1999). The drilling fluid can be divided into three types, water-based (WBF), pseudo/synthetic-based (SBF) and oil-based (OBF) drilling fluid. Oil-based drilling fluid was used and discharged to sea until the 1990s, but after 1993 it was prohibited to discharge this type of fluid to sea due to its negative environmental impacts (Cripps et al., 1998). Even though the drilling fluid and cuttings are separated, some drill fluid will still adhere to the cuttings and thereby be discharged together with the cuttings. After some time, the cuttings will eventually build up as a pile and may cover the lower parts of the platform footings (Gerrard et al., 1999).

Oil-based drill cuttings piles have accumulated in the North Sea since production first started in the 1960's, and an increased awareness of how to handle these piles has grown over the years. Several platforms in the North Sea are also approaching- or have already reached their production termination and might be decommissioned. Some of the platforms can be abandoned at their current locations, but some might have to be removed entirely or partially. In some cases, the cuttings piles will have to be relocated since they might act as a hindrance in the platform removal process (Ekins et al., 2006). When drill cuttings piles are removed from their present location, the contaminants within the pile will be whirled up in the water body and might spread out over a large area. The contaminants will then be more available to species, and potentially pose negative impacts on the environment in the sediment and water column. A biomarker-study on fish impact from the oil industry have shown that haddock, which is a fish that often feeds on the seafloor, has developed DNA-damage due to the formation of DNA adducts (Balk et al., 2011). This could be a result of produced water discharge but also from old drill cuttings piles that has accumulated on the seafloor over the years (Bakke et al., 2012).

The environmental impacts of oily drill cutting piles can be divided into two issues. The occurrence, behavior and spreading of contaminants from the drill cuttings, and the effect these contaminants might have on the species living in the sediment and in the water column (Cripps et al., 1999).

This thesis focus mostly on the first part, but impact on the biological communities will also be addressed.

The Oslo-Paris commission (OSPAR) has set a limit value of 10 tons per year for how much oil that is allowed to leak out from a pile if the pile is to be left *in-situ* (OSPAR Recommendation 2006/5, 2006). Different models and tests can be used to find the leaching rate from drill cutting piles, but establishing a leaching rate in tons per year can be a challenge. The Norwegian Institute for Water Research (NIVA) and Norwegian Geotechnical Institute (NGI) has created risk assessment guidelines for contaminated sediments in harbors and fjords on behalf of The Norwegian Climate and Pollution Agency (Klif). These guidelines include diffusion calculations which give the leaching rate of contaminants from the sediment in $\text{mg}/\text{m}^2/\text{year}$. These guidelines are well proven and used at other contaminated sites, and it has therefore been of interest to examine if these guidelines can be used to determine leaching rates from oil-based drill cuttings piles. This has most likely never been done before, so this thesis is investigating if this approach is feasible. It should be mentioned that the guidelines are normally used as a tool to determine if remediation action should be carried out or not. This is not the case for this thesis, as the guidelines are used primarily to find the leaching rate and possible toxic and ecological impacts.

1.2 Objectives

The objective of this study is to investigate if Klif's risk assessment guidelines for contaminated sediments can be used to estimate hydrocarbon leaching rates from oil-based drill cuttings piles in the North Sea.

1.3 Scope of the study

The following topics were included in this master thesis to achieve the object of this study:

- Through literature studies, develop an understanding of:
 - physical and chemical factors that affect drill cuttings piles.
 - fate and transport of organic contaminants within drill cuttings piles.
 - how organisms living in the surrounding area might get affected by the contaminated drill cuttings piles.
 - Klif's risk assessment guidelines for contaminated sediments
- Through calculations, investigate if the guidelines can be used to find leaching rates from oil-based drill cuttings piles in the North Sea.

1.4 Report outline

The following chapter includes relevant background information on drill cuttings piles (2.1), conditions in the North Sea (2.2), decommissioning activities (2.3), fate and transport of organic contaminants (2.4) and description of Klif's guidelines (2.5). Methodology and equations relevant to Klif's guidelines are described in chapter 3. The results are presented in chapter 4, and they are further discussed in chapter 5, while the final conclusion of this thesis is given in chapter 6.

2. Theoretical background

2.1 Drill cuttings piles.

When a well is drilled to reach an oil or gas reservoir, small fragments of rock is produced when the drill bit teeth cuts into the rock and deepens the hole. These fragments are usually asymmetric with a flake structure and they can vary in size and texture, depending on the nature of the rock and the drill bit. Drill cuttings from the North Sea oil fields generally have a composition of shale and sandstone, and the particle sizes range from 1 μm to 2 cm (Cripps et al., 1999). The chemistry and mineralogy of the cuttings will reflect the sedimentary strata that have been penetrated by the drill during the drilling operations (Neff, 2005).

Drill cuttings have to be removed from the well, and this is done by pumping drilling fluid inside the drill string down the drill pipe. The fluid will exit through holes in the drill bit, suspend the cuttings and return to the surface via the annulus (Neff, 2005), as illustrated in figure 2.1.

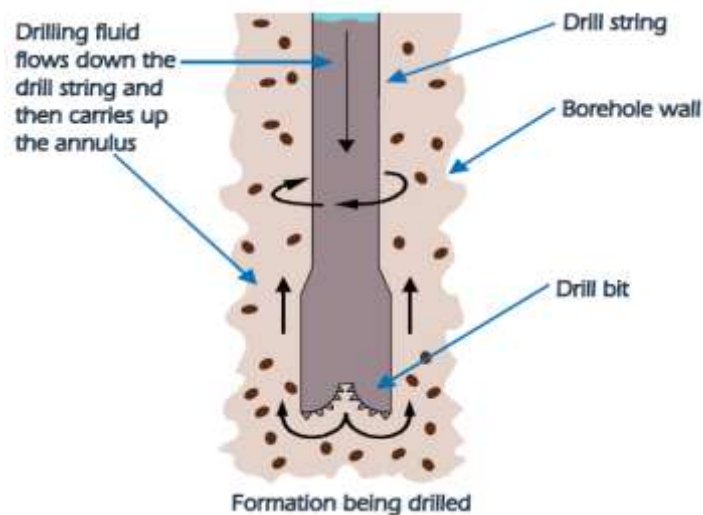


Figure 2.1 Suspension and removal of drill cuttings from the borehole by the drilling fluid during drilling (Melton et al., 2004).

The mud and the cuttings are separated once they come up to the rig. This is done by various techniques such as shale shakers, sand traps, desanders, desilters, centrifuges and mud cleaners. The mud that is separated from the cuttings is either recycled or disposed of onshore (Cripps et al., 1999). It is always a goal to remove as much cuttings from the fluid that is economically possible, before recirculating the fluid back to the borehole (Joel and Amajuoyu, 2009) . Figure 2.2 shows the circulation process of the drilling mud.

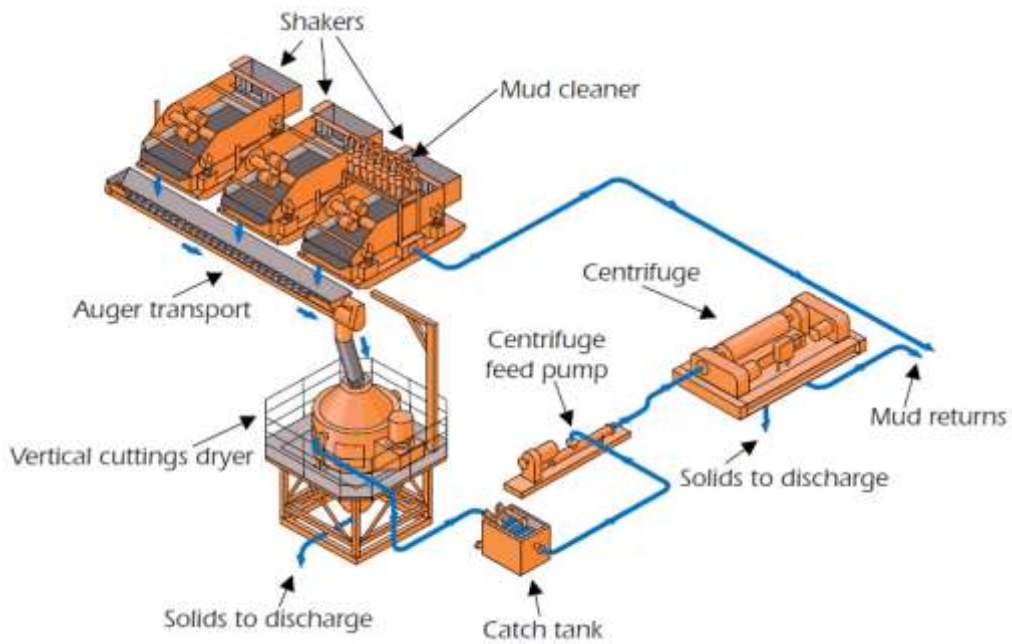


Figure 2.2 Example of circulation and treatment system for drilling mud and drill cuttings (solids) (Melton et al., 2004)

The cuttings are normally discharged to the sea where they will accumulate at the seabed underneath and around the platform. Usually, several wells are drilled at the same location, and drill cuttings discharges will thus be on the same spot, eventually building up a cuttings pile (Cripps, Westerlund et al. 1999).

If the cuttings only form a thin layer on the seabed, it will generally not be considered a pile. To be a pile, it would have to contain a concentrated amount of cuttings in a limited area (Nesse and Hovda, 2001), as illustrated in figure 2.3.

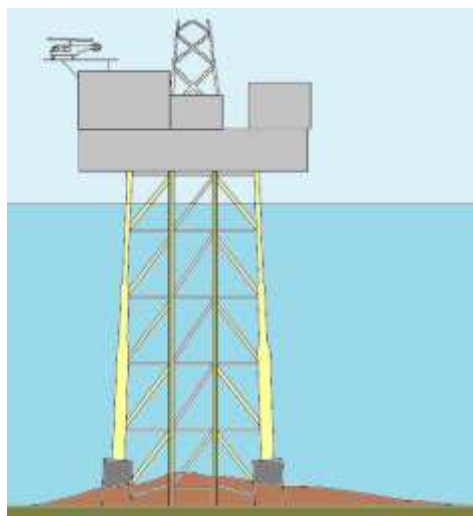


Figure 2.3 Accumulation of a drill cuttings pile under a platform (Land et al., 2000)

Generally, about 1000 tons of drill cuttings are produced for each well drilling (Bakke et al., 2012). The characteristics of drill cuttings piles will be unique for each site, but they can generally be described as “biologically impoverished, poorly sorted silts with a variable mixture of clay particles” (Breuer et al., 2004).

Drill cuttings piles consist of drill cuttings, but also any residual mud that has adhered to the cuttings (typically 10-15 % by weight), (Mairs et al., 1999). Size and shape of the pile will depend on the amount of discharged cuttings, density/particle size, type of drilling mud, depth in the ocean and how they are dispersed in the water column or the seabed by waves and currents (Nesse et al., 1999). Generally, the height of drill cuttings piles in the Northern and Central North Sea range from 2 to 20 meters (Breuer et al., 2004). If there are several wells at the same location, the build-up of cuttings piles can be considerable (Bell et al., 1998). The largest cuttings piles studied are more than 26 meter high, covers an area about 20 000 m² and have an estimated volume of 45 000 m³ (Bakke et al., 2012).

The discharge mode will also influence the dimensions and the constitution of the drill cuttings pile. Three discharge modes are described in “Review of Drill Cuttings Piles in the North Sea” by Bell, Cripps et al (1998); discharge directly onto the sea-bed, discharge from a drilling rig and discharge from a fixed platform. The installation type will also affect the topography and position of the pile. As for a concrete gravity base structure (GBS), the cuttings will pile up outside the storage tanks, while for structures with an open base like steel jackets, it will concentrate right beneath the platform (Bakke et al., 2000). Figure 2.4 shows an example of the location of the cuttings piles discharged underneath a platform.

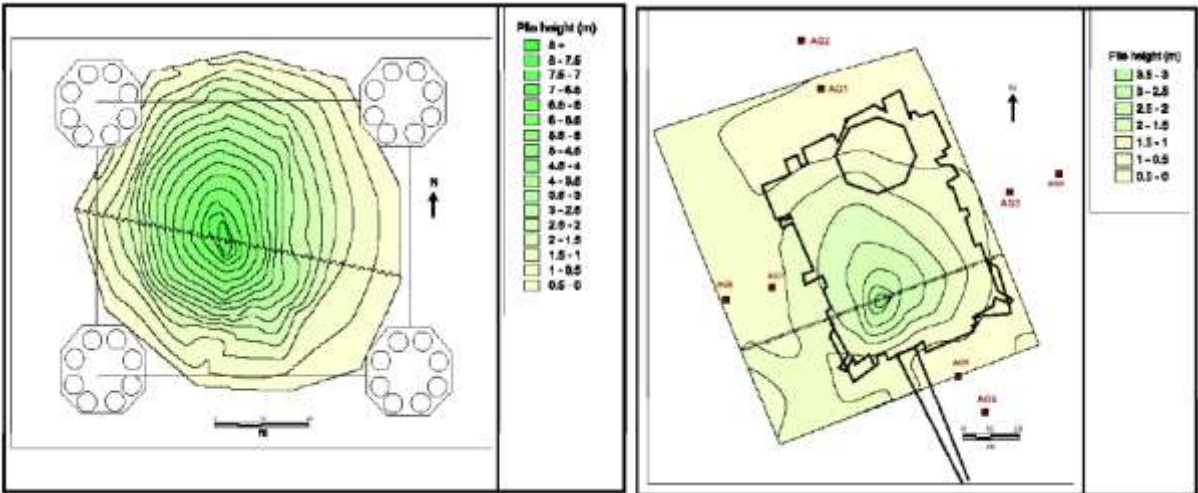


Figure 2.4 Example of drill cuttings piles location relative to the platform (Cripps et al., 2000)

It can be difficult to define the extent of a cuttings pile because the edge of the pile is usually not clearly distinct. This is due to the discharge mode explained above, and also the dynamic nature of the marine environment. This will vary from location to location, even in the North Sea itself there are large differences (Gerrard et al., 1999), as described in chapter 2.2.

Another factor affecting the edge of the pile is the surface of the cuttings piles. If the surface is soft, the pile will be unstable after it has formed and easily be redistributed by bottom currents (Gerrard et al., 1999).

2.1.1 Composition of drill cuttings.

Drill cuttings consist mainly of rock fragments and drilling mud that has adhered to the cuttings. In addition to this, cuttings can contain a variety of other compounds such as sand and cement from casing operations, LSA (low specific activity) scale, heavy metals, hydrogen sulfide from anaerobic degradation, sea water and a variety of debris from construction, maintenance and remedial work (Bakke et al., 2000)

The chemical composition of the piles will vary according to which drilling fluid that has been used, amount of fluid that has adhered to the cuttings at the disposal time, and the geochemistry of the formation that is being drilled (Neff, 2005). Section 2.1.1.1 explains different types of drilling fluids used over the years and which is being used today.

2.1.1.1 Drilling fluids

Since the first exploration well was drilled in the 60's, different kind of drilling muds with different level of toxicity has been applied. In the early years, all drill cuttings where discharged to the seabed. Because of this, there are several piles on the ocean floor today, containing various toxic compounds (Breuer et al., 1999).

There are generally three types of drilling fluid, water based, oil based and synthetic based fluid. A solid phase, usually barite, suspended in a fluid phase is the major component of the drilling fluid. The fluid phase can be seawater, freshwater or brine (WBF) or an organic phase which is either oil-based (OBF) or synthetic drilling fluid (SBF). The oil-based fluid may have diesel or low aromatic mineral oil as the fluid phase, while the synthetic mud most often has an ester (Bell et al., 1998).

According to "Environmental effects of cuttings associated with non-aqueous fluids (NAFs)" by Mairs et al (1999), oil based and synthetic based drilling fluids can be defined as follows:

“OBF: A subset of NAF that includes diesel oil based fluid and mineral oil based fluid which is defined by having polycyclic aromatic hydrocarbon (PAH) content greater than 0.35 %”

“SBF: A subset of NAF that is produced by chemical reactions of relatively pure compounds, and can include synthetic hydrocarbons (olefins and synthetic paraffins), esters, ethers, and acetals. SBFs have PAH contents less than 0.001%”

Figure 2.5 illustrates the differing compounds of water based and non- aqueous based drilling fluid.

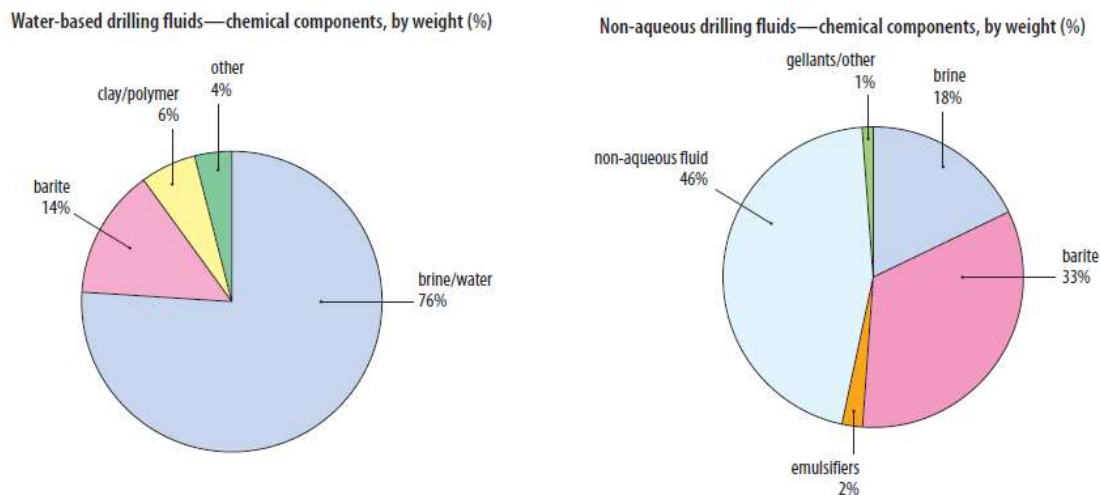


Figure 2.5 Chemical components of water based and non-aqueous drilling fluids, by weight (%) (IPIECA and OGP, 2009)

Non-aqueous fluids has varied in aromatic content and toxicity over the years, such as crude oil, diesel oil, conventional mineral oil, ester, linear paraffin and highly processed mineral oil (IPIECA and OGP, 2009).

Drilling fluid serves several functions for the drilling operations, such as conducting the drill cuttings away from the drill face, balancing the hydrostatic pressure, and providing physical and chemical properties to protect the rock formation that is being drilled. A variety of different compounds are added to the drilling mud to maintain the chemical and physical properties, and the engineer can thus modify to suit specific conditions encountered during drilling. These compounds include viscosifiers, emulsifiers, lubricants, wetting agents, corrosion inhibitors, surfactants, detergents, caustic soda, salts and organic polymers (Bell et al., 1998). Table 2.1 gives an overview of different materials added to the fluid, their composition and function.

Table 2.1 Additives in non-aqueous drilling fluid and their primary function (IPIECA and OGP, 2009, Sheahan et al., 2001, Gerrard et al., 1999)

| Chemical function group | Function | Composition |
|----------------------------|--|---|
| Weighting agent | <ul style="list-style-type: none"> Increase weight of mud, which balance the formation pressure, preventing a blowout | <ul style="list-style-type: none"> Barite, ilmenite, hematite, calcium carbonate |
| Base fluids | | <ul style="list-style-type: none"> Linear paraffins, synthetic iso-alkanes, highly refined mineral oils, olefins |
| Primary emulsifier | <ul style="list-style-type: none"> Stabilize oil-in-water emulsions | <ul style="list-style-type: none"> Hydrophilic and hydrophobic compounds in a carrier fluid <ul style="list-style-type: none"> – soaps, amines, imidazolines, fatty acid derivatives |
| Secondary emulsifier | <ul style="list-style-type: none"> Stabilize oil-in-water emulsions | <ul style="list-style-type: none"> Hydrophilic compounds with a positive end in a carrier fluid <ul style="list-style-type: none"> — polyamides, soaps, amines, imidazolines, fatty acid derivatives |
| Wetting agent | <ul style="list-style-type: none"> Maintain the wetting surfaces of solids in the mud | <ul style="list-style-type: none"> Hydrophilic compounds primarily—sulphonic acid, amides, polyamides |
| Viscosifiers | <ul style="list-style-type: none"> Increase viscosity of mud to suspend cuttings and weighting agent in mud | <ul style="list-style-type: none"> Organophillic montmorillonite, attapulgite or hectorite, synthetic polymers <ul style="list-style-type: none"> —amine treated |
| Rheological modifier | | <ul style="list-style-type: none"> Hydrophobic or polymeric compounds, typically fatty acids in liquid products or acrylate co-polymers in powder products |
| Brine phase | <ul style="list-style-type: none"> Concentrated inorganic salt solutions which balance the interactions of drilling fluid with clay and soluble salts | <ul style="list-style-type: none"> Fresh water primarily with calcium chloride |
| Filtration control | <ul style="list-style-type: none"> Decrease fluid loss to the formation through the filter cake on the wellbore wall | <ul style="list-style-type: none"> Asphalt, lignite, gilsonite |
| Lime | <ul style="list-style-type: none"> Control pH, reducing corrosion and also activating some emulsifiers. | <ul style="list-style-type: none"> Lime (Calcium hydroxide) |
| Thinners | <ul style="list-style-type: none"> Deflocculate clays to optimize viscosity and gel strength of mud | <ul style="list-style-type: none"> Liquid products may contain fatty acids. Powder products include lignites, lingo-sulphonate and tannins |
| Lubricating agent | <ul style="list-style-type: none"> Enhance the rate of penetration of drill string | <ul style="list-style-type: none"> Ester oils, asphalts, graphite cannot be grouped into one hazard |
| Lost circulation materials | <ul style="list-style-type: none"> Block pores and fractures | <ul style="list-style-type: none"> CaCO₃, graphite, walnuts shells, mica, almost any solid plugging material available, cross linking pills sometimes resin based |

Whether water-based or non-aqueous based fluid is used depends upon several factors like the formation to be drilled and technical requirements such as temperature, pressure and shale. Local environmental requirements, waste disposal and economics must also be taken in consideration when choosing the drilling fluid (IPIECA and OGP, 2009).

During the history of drilling operation in the North Sea, WBF, OBF and SBF have been used. At first, the only base fluid used was diesel oil, but it was replaced by mineral oils of lower toxicity in the early 80's due to the negative impacts on the environment. In the early 90s however, it was decided that discharge of oil-based drilling fluid was no longer permitted in the North Sea (Bell et al., 1998)

Today, both water based drilling fluids and non-aqueous drilling fluids (NAFs) are used when drilling different sections of the same well. Generally, water based fluid is used in the upper sections of the well, while the NAFs are used in the deeper, more technically complex portions of the drilling operations, like horizontal drilling (Mairs et al., 1999).

The type of drilling fluid used in the drilling operation determines if the drill cuttings can be discharged to sea or not. Discharge of cuttings with WBF will normally be permitted, but it is assumed that some vulnerable organisms such as corals and sponges can be sensitive to cuttings piles, and this has to be taken into consideration before the cuttings can be discharged in vulnerable areas. Discharge of cuttings with NAFs is not allowed in the North Sea, so it is either re-injected into a well (if a permit is given) or transported and treated onshore (Storting White Paper No 28, 2010).

2.1.1.2 Chemical constituents in drill cuttings

The exact content in the drill cuttings pile can be difficult to identify since the piles are highly heterogeneous, but the hydrocarbon portion of the drilling fluid is considered to be the main contaminant of concern in the drill cuttings piles (Bakke et al., 2000). In the sediment and cuttings around platforms in the North Sea, elevated concentrations of hydrocarbons up to 10 000 times the background concentration has been found (Breuer et al., 2004). Hydrocarbons are compounds which only contains hydrogen and carbon atoms, hence the name. They can be divided into two groups, aliphatics and aromatics. The aliphatics are alkanes, alkenes and cycloalkanes while the aromatics are those containing one or more benzene ring as part of the structure, such as poly aromatic hydrocarbons (PAHs). Crude oil typically contains high concentrations of aliphatic hydrocarbons while the concentration of aromatic hydrocarbons is lower (Williams et al., 2006). Crude oil consists of thousands of these compounds and each one can be identified individually, but they can also be analyzed as the generic term of total hydrocarbons (THC) (Sheahan et al., 2001).

Other important contaminants of concern are PCB's and different metals that can impact the environment (Sheahan et al., 2001). Metals in drill cuttings piles will be a mixture of naturally occurring metals, additives in the drilling fluid, from the platform itself (paint chips, corrosion etc.), and from aeolian input (Breuer et al., 1999). As previously explained, the solid phase in the drilling

fluid is usually the mineral barite. Barite is used in large amounts in drilling muds, especially when deep wells are drilled or when geopressured strata is penetrated (Neff, 2005). Barite consists of barium sulfate (BaSO_4), and most of the barite is grounded to a small uniform size before it is used as a weighting agent in the mud. Due to the impurities in the barites, other metals will also usually be present. Elevated levels of chrome (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) in cuttings piles have been found relative to the natural occurring metals (Breuer et al., 1999). Because barite is contaminated with metals to a various extent, it is considered as the dominant source for metal contamination in the drilling mud. Barite can also serve as a source of reducible sulfate for certain bacteria, if the concentration of barite in the sediment is high. This will release dissolved barium into the sediment pore water, where it can diffuse to the oxic layers of the sediment (Neff, 2005). Metals are not addressed further in this thesis, since the focus is on hydrocarbons. But it is important to be aware of the fact that they are an additional source of contamination from drill cuttings piles.

The fate of the chemicals in cuttings piles are controlled by various chemical reactions like biodegradation, erosion and bioturbation (Tvedten and Tveter, 2009). These reactions are explained further in chapter 2.4

2.1.2 Physical characteristics

Drill cuttings piles will vary greatly in their physical characteristics, depending upon several factors such as sediment signature, types of contaminants, local hydrodynamic conditions and how the benthic community at the current location is. It has however been proposed that cuttings piles generally will have a water content of 20-60 %, a particle size from 10 μm -2 cm and a bulk density of 1,6-2,3 g/cm^3 . Cuttings piles will also show a distinct stratification throughout the pile, and maintain a high stability over the years. The drilling fluid which has been used will influence the morphology of the drill cuttings due to its ability to affect the particle sizes and their tendency to aggregate. The shear strength of cuttings piles can vary greatly, ranging from almost hard cement to a more liquid consistency (Breuer et al., 1999).

Grain size distribution in drill cuttings piles will also vary from pile to pile, but generally the piles consist of silt and clay. It has been found that a crust has formed on the surface of some cuttings piles, which might affect fate and transport of contaminants (Dames & Moore and TNO, 2002).

2.2 The North Sea

This thesis focuses on drill cuttings piles located in the North Sea, and it can therefore be useful to understand how the conditions in the North Sea are. Different factors will affect the piles, depending on their position, as described in this chapter.

2.2.1 General description

Since the early 1960s, the North Sea has been a major resource for the oil and gas industry. The North Sea is located on the continental shelf of northwest Europe. The water in the North Sea flows from the Baltic Sea in the east, through the Skagerrak Strait, and into the Atlantic Ocean in the west. The basin has a surface area of about 750 000 km² and a volume around 94 000 km³, where the depth increases towards the Atlantic Ocean.

The climate in the North Sea is strongly affected by the inflow of oceanic water from the Atlantic Ocean. In addition, the large-scale westerly air circulation, with its frequently low pressure system, influences the North Sea climate. These influences change over time, thus giving the North Sea climate characteristics large variations in wind direction and speed as well as high precipitation and rate of cloudiness.

The discharge into the North Sea from river systems have a catchment area of around 850 000 km², and the annual input of fresh water into the sea from these rivers is about 300 km³. The run-off in the North Sea however is highly variable on an annual basis, and this can affect the transport of contaminants (Ferm and Portmann, 1993).

2.2.1.1 Activities in the North Sea

There are several activities in the North Sea. Fishing covers a large part, as well as shipping, tourism, aquaculture, sand and gravel extraction and military activity. However, the offshore oil and gas industry plays the major role of activities in the North Sea (Ferm and Portmann, 1993). The largest oil developments have mainly been in the northern parts of the North Sea, while the gas deposits are mainly exploited in the shallower southern parts (Ferm and Portmann, 1993).

2.2.2 Seabed topography

The North Sea is relatively shallow, ranging from about 30 to 200 meters in depth, except from the northern extremes and the Norwegian trench (about 700 meters deep). Generally, the southern part of the North Sea is shallower than the north part, i.e. less than 100 m in the south and between 100-200 meters in the north. Figure 2.6 shows the depth conditions in the North Sea (Ferm and Portmann, 1993).

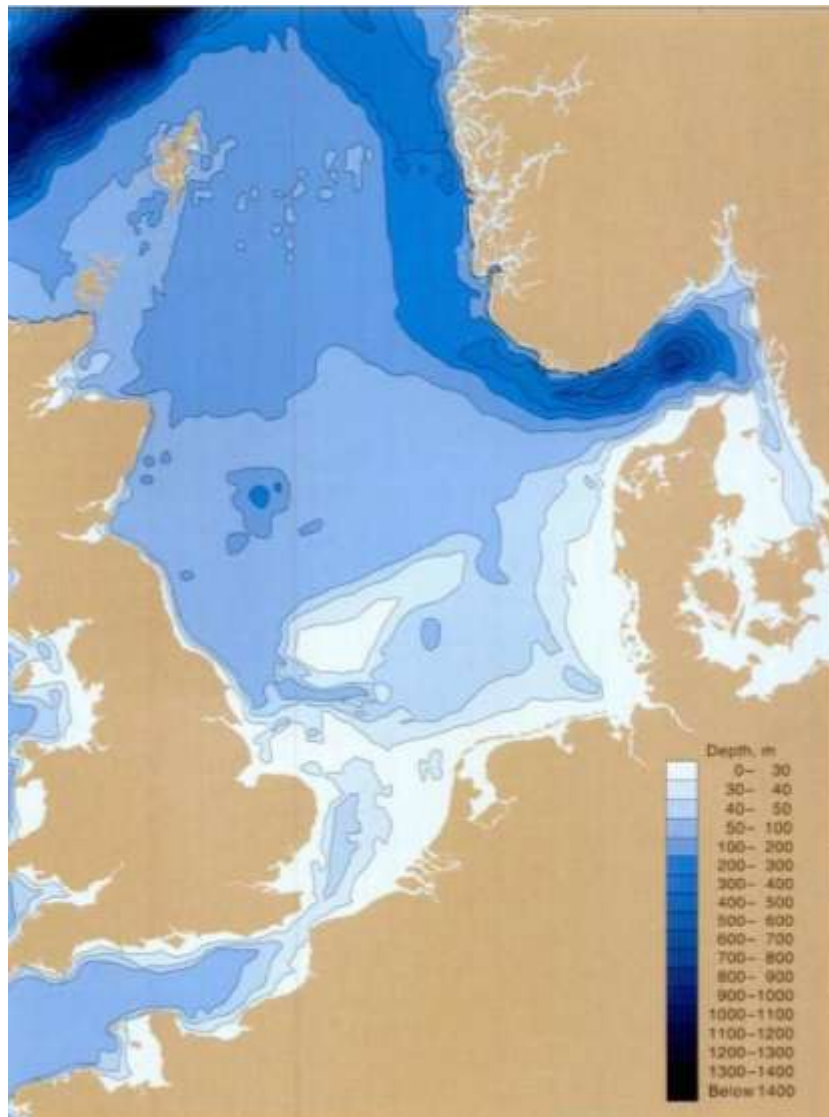


Figure 2.6 Water depth in the North Sea (Ferm and Portmann, 1993)

The shallow southern part of the North Sea has strong currents and waves, so the cuttings will rapidly disperse due to the harsh environment, and the remaining materials will eventually biodegrade. In deeper areas with relatively weak currents, like the Northern and Central North Sea, the cuttings can

flocculate and accumulate in a pile under and around the platform for a long time (Breuer et al., 1999).

Water stratification can impact the formation of cuttings piles. Most of the regions of the North Sea are well mixed vertically in the winter months, but not as well in the remaining months. This is because the solar heat increases in the spring, resulting in a thermocline over large parts of the North Sea, especially in the deeper areas. This thermocline is a gradient that separates the lower layer from the upper, with regards to temperature difference (Ferm and Portmann, 1993). The thermocline will result in a major reduction of the vertical mixing of the water. Even though the movement depends on the season, there is generally less movement in the deeper areas than the shallower parts of the North Sea. This is because tidal- and wind induced currents and wave action is strong in the shallower areas, thus resulting in erosion, re-suspension and dispersal of particles. These conditions means that drill cuttings would rapidly disperse and not have the ability to settle into a pile (Gerrard et al., 1999). The thermocline depth will increase from May to September and differ from area to area, typically 50 meters in the northern region and 20 meters in the western Channel. During the autumn, the thermocline will be destroyed due to storms and seasonal cooling at the surface which mixes the upper and lower layers (Ferm and Portmann, 1993). The sediment in the North Sea generally consists of mud, gravel and different types of sand, as illustrated in figure 2.7.



Figure 2.7 Sediment types in the North Sea (Ferm and Portmann, 1993)

By comparing figure 2.6 and 2.7, it can be noticed that there is a connection between the depth in the basin and the sediment type. Areas with mud and sandy mud characterize deeper areas such as the Oyster Ground, Skagerak and the Norwegian Trench, while the shallower areas generally have sand, coarse sand and gravel sediments (Gerrard et al., 1999).

2.2.3 Contamination

The North Sea is contaminated both naturally, via rivers, the atmosphere, directly by discharges from land, offshore installations, dumping at sea, shipping and aquaculture. One of the major contaminant is hydrocarbons, originating to a large degree from the offshore industry. The hydrocarbon input from the offshore industry mainly comes from drill cuttings, produced water and accidental spills (Ferm and Portmann, 1993). Figure 2.8 gives an overview of oil input to the Norwegian continental shelf from cuttings, produced water and displacement water between 1984 and 2004. As the figure shows, drill cuttings were the major contributor to hydrocarbon input between 1984 and 1991, before discharge of oil-based drill cuttings were prohibited. Produced water has dominated the hydrocarbon input since the early 90s.

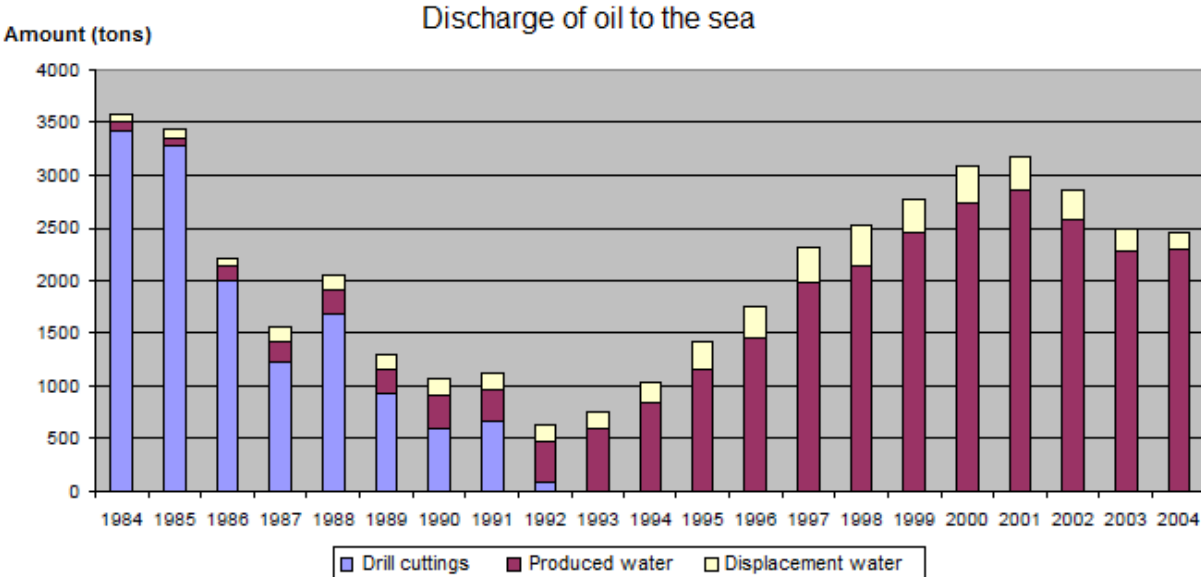


Figure 2.8 Discharges of oil-based drill cuttings, produced water and displacement water in the Norwegian Continental shelf from 1984 to 2004 (Moe et al., 2006)

In addition to the anthropogenic sources, aromatic hydrocarbons of natural origin produced by biosynthesis, natural seepage or other chemical processes may be present in the North Sea sediment. This background concentration of natural hydrocarbons can be defined as the

concentration that would be present if no human activity had influenced the environment. The background concentration will not be considerably high, in comparison, the areas where offshore installations are located, the concentration can be more than 1000 times higher than the background concentration (Gerrard et al., 1999).

2.2.4 Regulations governing drill cuttings in the North Sea.

Regulations relevant to drill cuttings in the North Sea have changed several times over the years. Generally, it was permitted to discharge 100 grams of oil per kilo of drill cuttings into the North Sea, until September 1991. Then the regulations changed, so that discharge of any cuttings with oily residue over 10 grams per kilo was prohibited. This was rather hard to manage in practice, so until 1993 a transition period, where discharge up to 60 grams per kilo, was permitted. In 1994, the transition period ended, only allowing discharge of 1 gram of oil per kilo cuttings for exploration drilling, which practically means that no such discharges are taking place (OLF, 2001). Today, there are technologies which can clean the cuttings to a level below the limit for the discharge from offshore installations (OSPAR, 2010).

In 1996-1997, a zero discharge goal for oil and environmentally hazardous substances to sea from petroleum activities was established in Storting White Paper No. 28, Environment policy for sustainable development. This included no discharge of chemical additives or naturally occurring substances (Storting White Paper No 28, 2010).

OSPAR has identified limits in Recommendation 2006/5 (OSPAR Recommendation 2006/5, 2006) regarding release of oil (THC) from drill cuttings piles to the water column. The limits state that the potential environmental impact due to loss of hydrocarbons from cuttings piles is significant if the leaching rate exceeds 100 tons/year. It is considered insignificant if the rate is below 10 tons/year and the seabed area, at greater than 50 mg/kg over time, do not exceed 500 km². This means that the loss of hydrocarbons cannot exceed 10 tons/year for a cuttings pile to be left *in-situ* at the seabed. This loss of oil is to be evaluated as direct loss to the water column, and not from processes like erosion and biodegradation (Danielsson et al., 2005). Figure 2.9 illustrates the limits and how each situation should be handled.

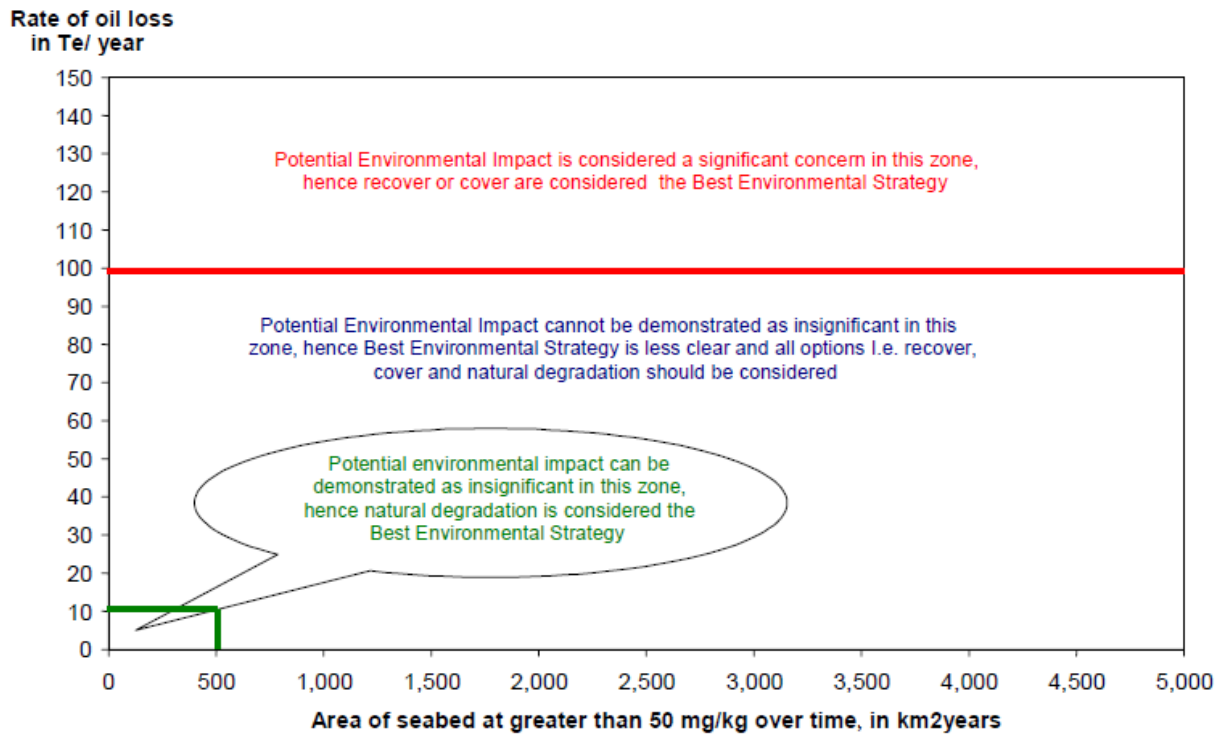


Figure 2.9. Limits for rate of oil loss, identified by UKOOA Joint industry project (Danielsson et al., 2005)

If the drill cuttings piles are disturbed, it can be considered as secondary pollution, thus regulated under the Pollution Control Act (Pollution Control Act, 1981). Disturbance of cuttings piles is relevant in offshore decommissioning activities, explained in chapter 2.3.

2.3 Platform decommissioning

Several oil and gas fields on the Norwegian continental shelf have already, or will soon, enter the last stage of their productive lives, and might therefore be decommissioned.

Decommissioning has been defined by the UK Offshore Operators Association (UKOOA) as: *“The process which the operator of an offshore oil and gas installation goes through to plan, gain government approval and implement the removal, disposal or re-use of a structure when it is no longer needed for its current purpose”*.

The First Ministerial meeting of the OSPAR commission established in 1998 a new binding framework for the decommissioning of disused offshore installations (OSPAR 98/3). It was decided that: *“The dumping, and the leaving wholly or partly in place, of disused offshore installations within the maritime area is prohibited”* (Gibson, 2002).

OSPAR 98/3 requires that the topsides of all installations must be taken ashore, and that all installations emplaced after 9 February 1999 has to be completely removed. In addition, all installations with jacket weight of less than 10 000 tons, must be completely removed so that they can be re-used, recycled or be disposed of onshore. Figure 2.10 illustrates the different components of a typical North Sea deep water platform.

If a cuttings pile has accumulated under the installation, decisions on how to manage the pile have to be evaluated. Some cuttings piles can be very difficult to move, and cover the lower sections of the platform legs, so that complete removal of the platform can be impossible (Gerrard et al., 1999).

The footings can be partially left *in-situ* or removed completely. If they can be left partially, a decision on where to cut, and how to handle the cuttings have to be made. The footings could be decommissioned by removing only the cuttings immediately around them, thus avoiding major disturbance and potential release of oil-based contamination from the cuttings into the marine



Figure 2.10 Components of a typical North Sea deep water platform (Ramsay, 2005)

environment. It is also possible to cut the footings at the same level as the cuttings pile, so that the residual footings will be left in the cuttings pile. The rest of the footings would then be taken to shore and the cuttings pile could be covered or just left *in-situ* (Ekins et al., 2006).

Before the right management option can be considered, the overall environmental impacts following each solution must be properly evaluated. Fate and transport of contaminants will differ from one management option to another. Comparison of the solutions to determine which option that gives least negative impact to the environment should therefore be considered (Tyler et al., 2002). Fate and transport of contaminants is discussed in chapter 2.4.

2.4 Fate and transport of organic compounds in oil-based cuttings piles.

Several factors will affect the drill cuttings piles, therefore the leaching from a pile will normally not be the same from year to year. Different processes like dispersion, erosion, biodegradation and bioturbation will affect the piles, changing the content and toxicity (Kjeilen et al., 1999). Transport and transformation of the compounds can therefore be examined to study the distribution in the environment, and how the compounds in the piles change over time (Leeuwen, 2003). An overview of the processes that will affect drill cuttings piles is illustrated in figure 2.11, and a more detailed description of fate and transport of organic compounds are given in the following chapters.

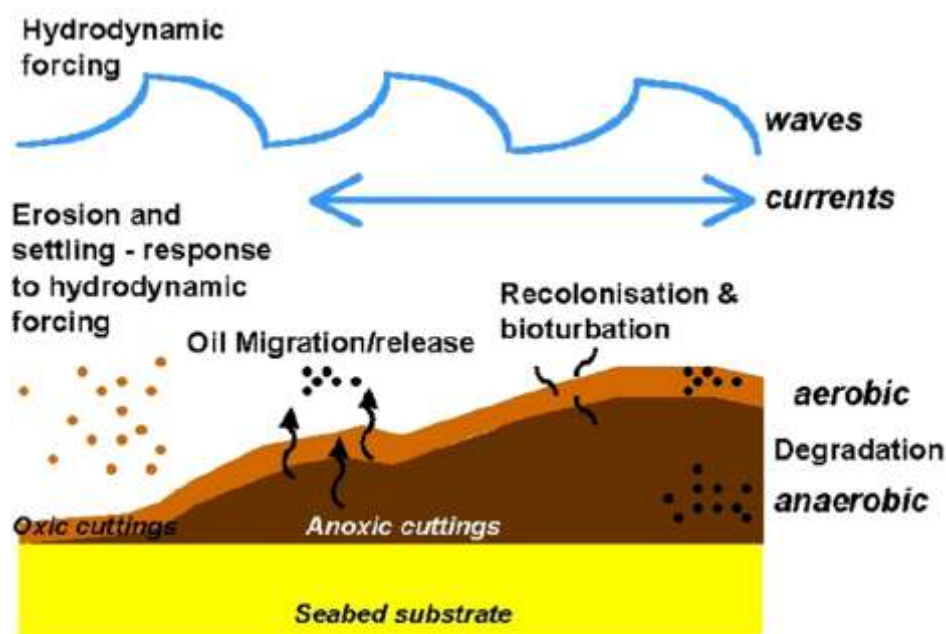


Figure 2.11 Different processes that will affect drill cuttings piles after discharge (Sabeur et al., 2002)

2.4.1 Erosion and sedimentation

Erosion and sedimentation by water is the processes where sediment is detached from its current location, transported to other areas and then deposited due to the external forces like flowing water. Differing factors like climate, topography and land use can influence erosion and sedimentation (Foster and Meyer, 1977). When the sediments are contaminated, as the case with drill cuttings piles, erosion due to currents or storm induced waves might contribute to transport these contaminants to different areas (Tvedten and Tveter, 2009). Particles can be transported either by the body of the moving water which carries the suspended grains along with it, or if the particles are too large to remain suspended, they can be transported by drag force along the sea floor (Kjeilen et

al., 1999). When cuttings piles are disturbed by erosion forces, the exchange of pore water and solids back to the surface will increase, eliminating the equilibrium partitioning. This results in a more rapid release of contaminants from the sediment to the water column. Usually, the clay and silt particles will provide the greatest transportation of particle-bound contaminants. In the context of hydrocarbons, this is due to electrochemical charges which cause the hydrocarbons to be associated to the finer fraction of the sediment rather than the coarser portion. Silt and clay will stay in the water for a longer time after re-suspension than the coarser portion of the sediment, so when hydrocarbons are spread with the particles, heavy particles sink first, eventually followed by silt and clay particles (Nedwed et al., 2006). This is illustrated in figure 2.12.

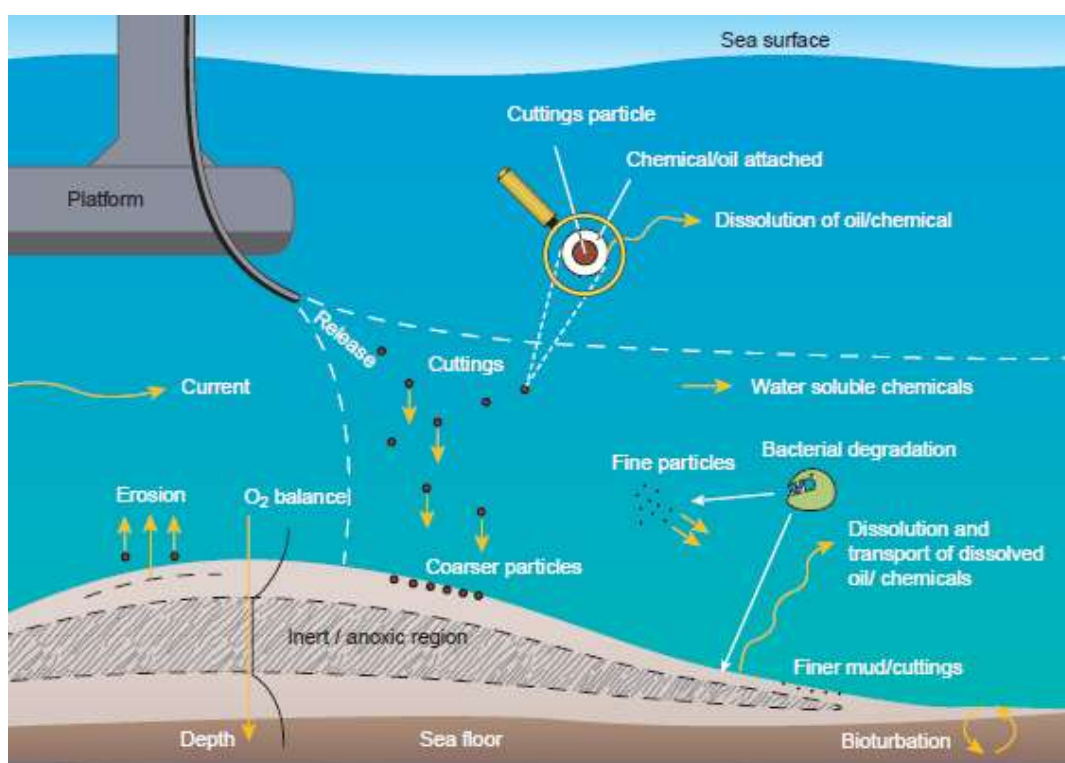


Figure 2.12 Illustration of how drill cuttings behave in the water body after discharge (Rye et al., 2006)

This can be explained by size and density properties, some dense particles carried in suspension will be unstable and therefore fall out of suspension when the right conditions are met, due to gravity. Particles which are smaller and less dense however, can stay in suspension for a longer time because they are more affected by "smaller" forces like electrostatics (Kjeilen et al., 1999). The sinking velocity will also impact the settling rate, as large particles have greater sinking velocity than smaller particles, and will therefore sink first. Other factors that will affect the transport of drill cuttings particles are the speed and direction of the ocean currents (Nedwed et al., 2006).

Bioturbation, which is translocation of sediment particles due to the activity from bottom-living animals, can also contribute to some spreading of contaminants. When animals are eating and stirring up the sediment, contaminated pore water could emerge up to the water column. This is however expected to occur only at the surface and the contribution from this activity is not considered as any considerable contribution to the total spreading (Kjeilen et al., 1999).

Dredging operations during decommissioning of offshore platforms and also trawling activities are external forces that can disturb drill cuttings piles. When cuttings piles are removed from their present location, transported to a surrounding area and resettled to a new location, a lot of the cuttings will be spread out over a large area. The sedimentation process will probably be somewhat similar to the first sedimentation process. However, the new pile will generally be lower than the original pile, the content of the pile will cover a greater area, and some of the finer fraction in the pile might be carried away with currents and waves to locations further away. In addition to controlling removal, transport and sedimentation of contaminated sediment, it might also result in the process where resettled drill cuttings material will mix with surrounding sediment and expose the remaining cuttings to oxygen, which favors aerobic processes in the surface active layer (Dames & Moore and NIOZ, 1999).

2.4.2 Re-colonization and bioaccumulation

Sedimentation of eroded sediment could disturb the seabed and biota, due to physical burying of the benthic communities natural habitat (Mairs et al., 1999). Erosion of cuttings piles might have an ongoing effect on both pelagic and benthic organisms, since they can be exposed repeatedly (Bechman et al., 2006). Heavy sedimentation could result in total destruction of the native fauna, but this will only be the case in those areas closest to the erosion source. Areal extent, thickness and persistence of the drill cuttings as well as the type of community that is affected and the availability these organisms have to re-colonize, will determine the recovery time of the benthic communities (Mairs et al., 1999). In the context of dredging operations, the resettled sediments could be a combination of cuttings and unpolluted sediments giving a concentration that is not likely to restrict the re-colonization of the communities (Tvedten and Tveter, 2009). Initially, those species that are tolerant of hydrocarbons, as well as species that feed on other bacteria which metabolize the hydrocarbons, will re-colonize first. Eventually, the hydrocarbon content in the area will decrease, resulting in return of other species. These species will then reproduce again and as time passes, the community will grow back to a community resembling the initial state (Mairs et al., 1999).

Contaminants within drill cuttings piles are generally particle bound, resulting in slow degradation and leaching rates. Those organisms that feed on the particles and sediment could therefore be

subjected to the toxic effects in a larger degree (Breuer et al., 1999). Species living around the contaminated area can be affected by the bioavailable pollutants through water, food and substrate, due to uptake and retention in the tissues. This is a process called bioaccumulation, and it happens when the uptake rate exceeds the elimination rate (Bjørgesæter, 2009). Bioaccumulation can further result in biomagnification of some compounds, a concentration increase upwards in the food chain which occurs when contaminated benthic species are being eaten by other and often larger animals (Bakke et al., 2011). Bioaccumulation of hydrocarbons from drilling fluids has generally been associated with PAH (Mairs et al., 1999). A study by Balk et al. published in 2011: "Exposure of fish and bivalves to suspended particles of drilling mud: A new continuous flow exposure system" investigated if fish are affected by oil production. Samples were taken from the Tampen-and Sleipner areas, which both have extensive oil production and a high sedimentation rate. One of the effects investigated in the study is the formation of DNA adducts in Haddock (*Melanogrammus aeglefinus*), which is a fish that often feeds on the seafloor (Bechman et al., 2006). DNA adducts are covalently bound addition products that forms during attack of the nucleophile sites in the DNA by electrophilic chemical species (Sheahan et al., 2001). DNA adducts can be used as an indicator for toxic exposure and are considered one of the best biomarkers of PAH exposure. Formation of DNA adducts may result in several genotoxic effects such as development of cancer in following generations or even immediate cell death. The study found elevated levels of hepatic DNA adducts in the haddocks from the Tampen area compared to other sites. This is expected to be a possible result of discharged produced water and accumulations of old drill cuttings piles at the seafloor. The study concludes that there might be a general relationship between the extensive oil production in the investigated areas and the biomarker response found in fish (Balk et al., 2011).

2.4.3 Biodegradation

Biodegradation can be defined as the decomposition of organic matter by living organisms (Bell et al., 1998) and it is an important natural attenuation process (Williams et al., 2006).

The degradation of hydrocarbons is a natural process, performed by several different microorganisms (MOs) in a variety of environments. Degradation of hydrocarbons is a process that converts toxic compounds into less toxic/inert compounds to the environment. Several conditions must be met for biodegradation to occur, the most significant factors are:

- The presence of organisms which have the necessary enzymes to biodegrade
- Environmental conditions like temperature, oxygen levels, pH, redox potential, salinity and the presence of essential nutrients must be applicable.

- The organisms and the chemical compounds must be present in the same environment
- The relevant chemicals must be accessible and bioavailable to the biodegrading microorganisms

Hydrocarbons are good food sources (electron donors) for biodegrading microorganisms because of their content of high-energy electrons. In order to carry out the degradation, the MOs must also have electron acceptors, the most common being oxygen (Williams et al., 2006).

Several different factors like microbial numbers, temperature, organic carbon content, nutrients supply and structure of the substances will affect the biodegradation rate (Kjeilen et al., 1999). This depends to a great deal on the concentration of the compound. If the concentration is very low, biodegradation might not be able to occur, while if the concentration is high, the biodegradation rate can be very rapid due to the great amount of carbon and energy sources. If the concentrations are very high on the other hand, the toxic effects would also be greater, and could act as a reducing agent to the degradation rates.

The presence of other compounds and the fact that crude oil contains thousands of different organic compounds degrading at varying rates will also affect the biodegradation (Cripps et al., 1999).

Degradation can occur in both aerobic and anaerobic environments, meaning with and without oxygen respectively, as illustrated in figure 2.11. In the aerobic layer (surface active layer) of the cuttings piles, which would be the upper portion of the pile, biodegradation of oil is likely to occur naturally. In the absence of oxygen however, which generally will be the conditions present inside/deeper in the pile, degradation will normally be very slow and in some cases biodegradation cannot even be measured. This could be due to high organic load which will result in an increased microbial activity resulting in anoxic conditions, which does not favor biodegradation (Kjeilen et al., 1999). Anoxic conditions occur when the biodegradation rate is greater than the rate of oxygen diffusion into the sediment (Melton et al., 2004). As illustrated in figure 2.11, the aerobic layer on the surface of a drill cuttings pile can be very thin, only a few millimeters to centimeters down in the drill cuttings piles. The pile itself may also affect the anoxic conditions due to characteristics such as low oxygen permeability and high density layers, resulting in restricted/insufficient transfer of oxygen from the surface layers (Kjeilen et al., 1999). Since large parts of the drill cuttings piles are under anaerobic conditions, resulting in slow biodegradation, historic contaminants which has not broken down during the years may still be present in the piles (Breuer et al., 1999). In the event of relocation of drill cuttings piles however, the biodegradation rate might increase due to larger oxygen access which results in aerobic conditions (Tvedten et al., 2012).

2.4.4 Contaminant release

Several processes can contribute to the release of contaminants from the sediment, as explained below:

Diffusion is a physical process where concentration differences are equalized without any contribution from currents or turbulence, i.e. equalization between sediment pore water and the water above the sediment, which will result in a continuous chemical transport from the pore water (high concentrations) to the water-column (low concentrations).

Advection is a diffusion process where the contaminated pore water is transported by weak currents flowing through the sediment.

Bioturbation is the process where benthic species either resuspend the sediment, resulting in pore water migration out to the water column, or pumps water from the sediment to the overlaying water mass during activities like respiration or feeding.

Biodiffusion is a combination of advection and bioturbation, occurring in the upper part of the sediment. The upper part of the sediment is estimated to be 10-28 times more intense than regular diffusion in natural sediments. Biodiffusion will depend on the sediment conditions, if the environment is anoxic, there will be less biological activity, resulting in decreased bioturbation thus less biodiffusion (Bakke et al., 2011).

Diffusion processes are limited by tortuosity and molecular diffusion limits, and they can affect the mobility and bioavailability of contaminants in the sediment (Kravitz et al., 2000). Different factors such as contaminant combination and the age of the contaminants (due to biodegradation) will affect the leaking capacity of organic contaminants in sediments. When the contaminants have migrated out to the water phase, processes like dissolution, sorption (binding), desorption (release) and presence of dissolved organic matter might affect the concentration, depending on the contaminant type (Hansen and Andersen, 2006). Figure 2.13 illustrates the distribution between different phases for benzo(a)pyrene.

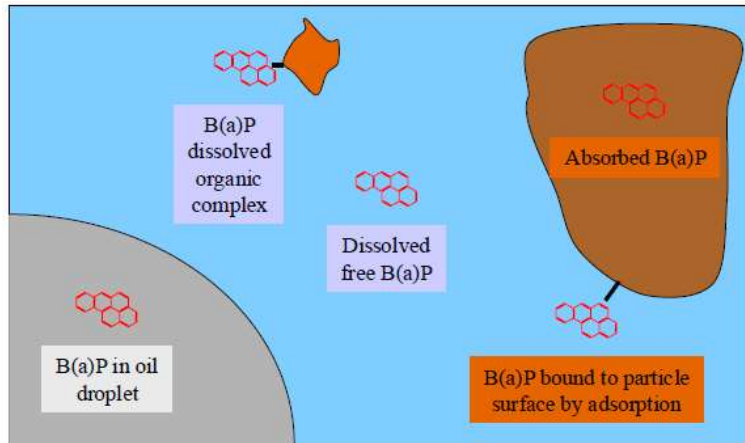


Figure 2.13 Distribution of benzo(a)pyrene between different phases (Hansen and Andersen, 2006)

The sorption potential will affect the leaching rate of contaminants into the water column. If the sorption is strong i.e. strong particle-water partitioning coefficient, the release will be slow, hence for weak sorption the release of contaminants will be faster (Werner et al., 2009). This is illustrated in figure 2.14.

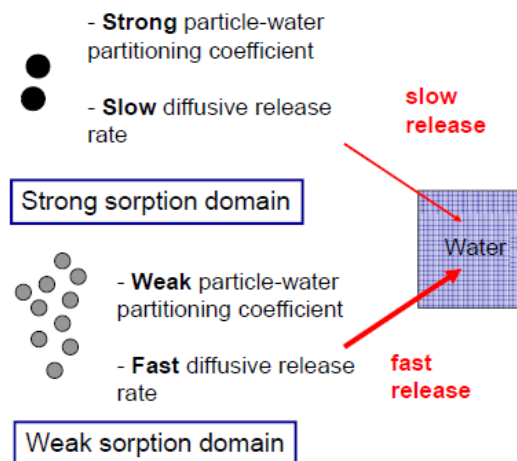


Figure 2.14 The impact sorption has on diffusion rates (Werner et al., 2009)

Studies have shown that after the first oil migration has occurred, the remaining oil which is left on the particles will be tightly bound to the sediment, trapped within the pore water, resulting in a slow biodegradation and leaching rates (Breuer et al., 1999). However, accumulated solubilized compounds that are trapped within stagnant pore waters might be released into the water column if the pile structures are disturbed. This could result in an increased leaching rate from sediment to the water column. It can be difficult to determine accurate leaching rates, but they can be estimated by physical analyses and experiments or by mathematical models (Mitchell et al., 2000). The model used in this thesis is described in chapter 2.5.

2.5 Klif's guidelines for contaminated sediments.

The Norwegian Institute for Water Research (NIVA) and Norwegian Geotechnical Institute (NGI), in cooperation with The Norwegian Climate and Pollution Agency (Klif), has prepared and audited risk assessment guidelines as a tool to find the impact on the environment from contaminated sediments. The risk assessment guidelines can be used by authorities, responsible polluters, consultants, environmental managers and others, to identify the risk from polluted sediments in its present state and to help decide whether remediation is needed or not. The guidelines are intended to be used as an assessment for medium sized fjords-and coastal areas, including harbors, as a part of the procedure for cleanup of contaminated sediments, so that the Norwegian government's goal of clean fjords and harbors along the Norwegian coast can be met (Bakke et al., 2011, Saloranta et al., 2011).

There are three steps, or tiers, in Klif's guidelines. Each step increases in complexity, but will give a better and more realistic conclusion, so that the right actions can be made with reduced uncertainties and thereby less conservative estimates. The risk assessment is meant to be conservative to avoid abandonment of sediments where remediation should be carried out. The main structure of the guidelines is specified in figure 2.15.

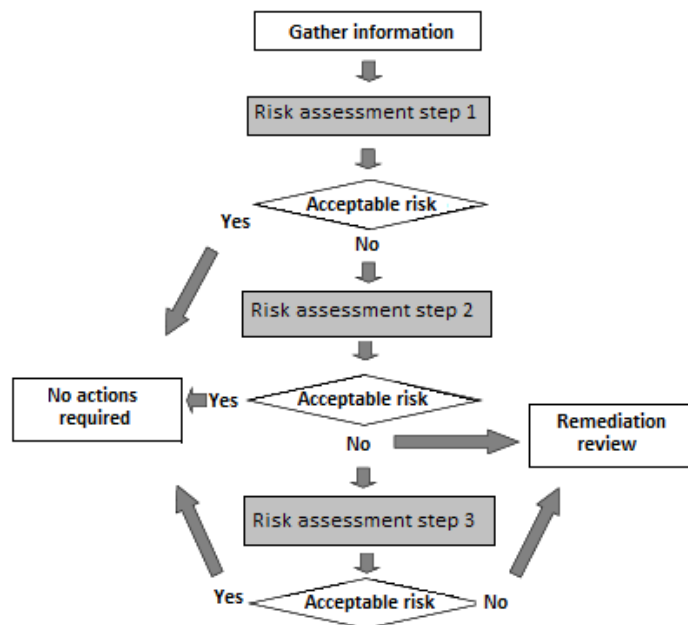


Figure 2.15 Main steps in Klif's guidelines (Bakke et al., 2011)

Tier 1 is a simple risk assessment screening to gather relevant information and compare concentrations and toxicity of the sediment with limit values. This step only involves the ecological risk, not the risk for human health, and it includes no real evaluation. The goal is to rapidly be able to separate those sites which can be abandoned and those that need remediation. If some of the limit values are exceeded, tier 2 should be implemented (Bakke et al., 2011).

Tier 2 is more complex than tier 1 and the goal is to determine whether remediation should be carried out or not. Three types of risk are included in step two, the risk of dispersion of contaminants (2A), the risk to human health (2B) and risk to the ecosystem (2C) (Bakke et al., 2011). This method has been inspired by the Dutch risk assessment approach "Assessment of risk of dispersion to surface water" by Van der Heijdt et al. (2000), (Saloranta et al., 2011).

If tier 2 indicates that remediation should be carried out or if the risk from tier 2 seems unrealistically high, tier 3 can be implemented. The approach in tier 3 is primarily the same as for tier 2, but it is based on detailed local measurements and analyses instead of the more conservative parameters, thus reflect the actual situation better and have more reliable results. Noncompliance in tier 3 results in sediment remediation planning (Bakke et al., 2011).

The risk assessment guide is mainly to be used on sediments consisting of silt and clay. Sampling for quantitative analysis of coarser sand and gravel sediments can be difficult, and the guidelines could therefore not be applicable. Usually, the coarser sediments will not pose a representable environmental threat, since the contaminants normally binds to the finer particles (Bakke et al., 2011)

Since the objective of this thesis is to see if this risk assessment guide can be used to find leaching rates of oil from drill cuttings piles in the North Sea, the following chapters focuses on information which is relevant to this approach.

2.5.1 Limit values

The limit values are set based on conservative assumptions on exposure pathways, bioavailability and the chance of spreading to other parts of the ecosystem. This is to a large degree based on EUs Technical Guidance Document on Risk Assessment (Leeuwen, 2003). Derivation of the limit values for the compounds is explained in the background document. The limit values are based on toxicity data for aquatic environments, and can then be recalculated to sediment concentrations using equilibrium partitions coefficients. A classification system, separating the limit values into five different categories according to the contaminant concentrations has been established, see figure 2.16 (Eek et al., 2011).

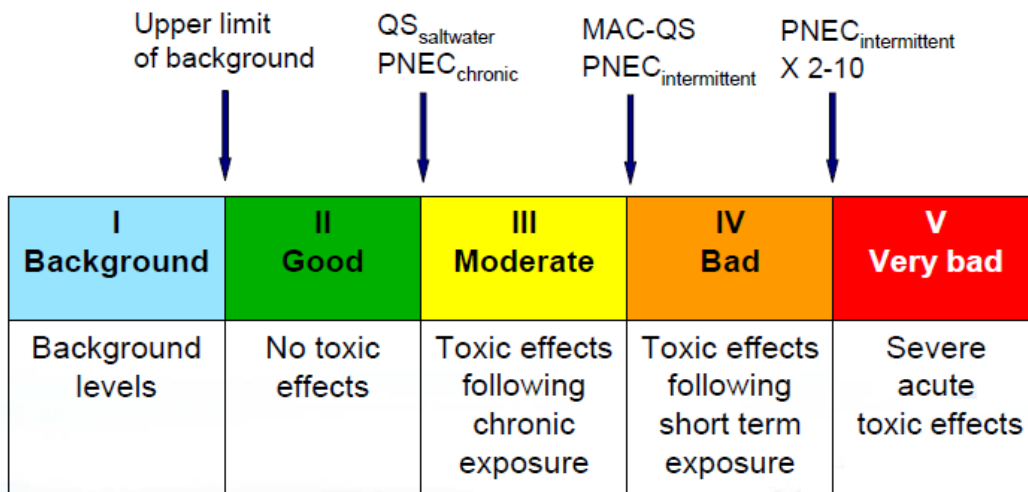


Figure 2.16 Classification of limit values used in Klif's risk assessment guidelines (Bakke et al., 2010)

The sediment background values are recalculated from 2.5 % total organic carbon (TOC) to 1 % TOC, to be more representative for the marine areas with a low TOC content in the sediment, as for the Norwegian coast. For PAH, the background values for water and sediment are taken from OSPAR Recommendation 2005a, b and represents the northern part of the North Sea.

The boundary between class II and class III indicates whether there are toxic effects following chronic exposure or not, so it can be used to determine if remediation of the site is needed or the site can be abandoned as it is. As illustrated in figure 2.16, the upper limit for class II is the Predicted No Effect Concentration (PNEC) with regards to chronic exposure for the compound (Bakke et al., 2007). PNEC can be defined as "an estimate of the highest concentrations of a chemical in a particular environmental compartment at which no adverse effects are expected", in other words a sensitivity estimate the ecosystem have to certain chemicals (Thatcher et al., 2004).

$PNEC_{\text{water}}$ calculation criteria is based on the lowest no effect concentration (NOEC) from chronic tests, divided by an assessment factor. $PNEC_{\text{sediment}}$ can be calculated from toxicity data for organisms living in the sediment, or by equilibrium calculations from $PNEC_{\text{water}}$. In the last case, equilibrium partitioning coefficients is used, either between sediment and water (K_d) or between organic sediment-carbon and water (K_{oc}). The upper limit for class III is the PNEC for acute exposure (intermittent), based on short term tests of acute toxicity. The boundaries for class III-IV for water and sediment are set so that they represent an increasing degree of harm to the organisms in the sediments and water (Eek et al., 2011)

Klif's guidelines includes limit values for 8 metals, 16 PAH, and a number of different organic compounds (Bakke et al., 2011). The limit values for 16 PAH in sediment and water are given in table 2.2 and table 2.3 respectively.

Table 2.2 PAH limit values in sediment according to the guidelines classification system (Bakke et al., 2007)

| PAH | I | II | III | IV | V |
|------------------------|------------|-------|----------|-------|----------|
| | Background | Good | Moderate | Bad | Very bad |
| | µg/kg | µg/kg | µg/kg | µg/kg | µg/kg |
| Naphtalene | 2 | 290 | 1000 | 2000 | > 2000 |
| Acenaphthylene | 1,6 | 33 | 85 | 850 | > 850 |
| Acenaphthene | 4,8 | 160 | 360 | 3600 | > 3600 |
| Fluorene | 6,8 | 260 | 510 | 5100 | > 5100 |
| Phenanthrene | 6,8 | 500 | 1200 | 2300 | > 2300 |
| Anthracene | 1,2 | 31 | 100 | 1000 | > 1000 |
| Fluoranthene | 8 | 170 | 1300 | 2600 | > 2600 |
| Pyrene | 5,2 | 280 | 2800 | 5600 | > 5600 |
| Benzo(a)anthracene | 3,6 | 60 | 90 | 900 | > 900 |
| Crysene | 4,4 | 280 | 280 | 560 | > 560 |
| Benzo(b)fluoranthene | 46 | 240 | 490 | 4900 | > 4900 |
| Benzo(k)fluoranthene | | 210 | 480 | 4800 | > 4800 |
| Benzo(a)pyrene | 6 | 420 | 830 | 4200 | > 4200 |
| Indeno(1,2,3-cd)pyrene | 20 | 47 | 70 | 700 | > 700 |
| Dibenzo(a,h)anthracene | 12 | 590 | 1200 | 12000 | > 12000 |
| Benzo(ghi)perylene | 18 | 21 | 31 | 310 | > 310 |
| PAH16 | 300 | 2000 | 6000 | 20000 | > 20000 |

Table 2.3 PAH limit values for water according the guidelines classification system (Bakke et al., 2007)

| PAH | I | II | III | IV | V |
|------------------------|------------|-------|----------|-------|----------|
| | Background | Good | Moderate | Bad | Very bad |
| | µg/kg | µg/kg | µg/kg | µg/kg | µg/kg |
| Naphtalene | 0,00066 | 2,4 | 80 | 160 | > 160 |
| Acenaphthylene | 0,00001 | 1,3 | 3,3 | 33 | > 33 |
| Acenaphthene | 0,000034 | 3,8 | 5,8 | 58 | > 58 |
| Fluorene | 0,00019 | 2,5 | 5 | 50 | > 50 |
| Phenanthrene | 0,00025 | 1,3 | 5,1 | 10 | > 10 |
| Anthracene | | 0,11 | 0,36 | 3,6 | > 3,6 |
| Fluoranthene | 0,00029 | 0,12 | 0,9 | 1,8 | > 1,8 |
| Pyrene | 0,000053 | 0,023 | 0,023 | 0,046 | > 0,046 |
| Benzo(a)anthracene | 0,000006 | 0,012 | 0,018 | 0,18 | > 0,18 |
| Crysene | | 0,07 | 0,07 | 0,14 | > 0,14 |
| Benzo(b)fluoranthene | 0,000017 | 0,03 | 0,06 | 0,6 | > 0,6 |
| Benzo(k)fluoranthene | | 0,027 | 0,06 | 0,6 | > 0,6 |
| Benzo(a)pyrene | 0,000005 | 0,05 | 0,1 | 0,5 | > 0,5 |
| Indeno(1,2,3-cd)pyrene | 0,000017 | 0,002 | 0,003 | 0,03 | > 0,03 |
| Dibenzo(a,h)anthracene | | 0,03 | 0,06 | 0,6 | > 0,6 |
| Benzo(ghi)perylene | 0,00001 | 0,002 | 0,003 | 0,03 | > 0,03 |

Evaluation of the exceedance of limit values is done by dividing predicted environmental concentrations (PEC), which is an estimate of the expected concentration of a chemical that will expose the environment, on the respective PNEC value (Thatcher et al., 2004). In this case, the PEC value will be the pore water- or sea water concentrations. The PEC/PNEC ratio for each chemical will give an idea of the relationship between the environmental exposure and the sensitivity of the chemical to the environment. If the PEC/PNEC ratio is greater than 1, environmental effects might be expected (Thatcher et al., 2004).

2.5.2 Tier 2 in the risk assessment guideline.

Tier 2 in the risk assessment guidelines consists of three parts, 2A, 2B and 2C, as stated in chapter 2.5. Tier 2A is the risk of spreading, and is based on calculated contaminant transport from the sediment to the water by biodiffusion, resuspension caused by arrivals and departures of ships, and also uptake by organisms and spreading through the food chain, as explained more detailed in chapter 2.4. Tier 2B is the risk for human health, based on the transport routes of contaminants to humans i.e. consumption of fish, contact with sediment, bathing etc. 2C, deals with the risk of effects to the ecosystem, and it is based on contaminant concentrations which organisms in the water and sediment are exposed to, compared to relevant limit values.

An excel worksheet which includes all material data and formulas described in the guide has been created to make the calculation process more effective. Different physical, chemical and biological parameters are included in these calculations. The risk guidelines suggest typical default values for some of the parameters included in the calculations, but local values should be used if possible, since some of the default values are associated with significant uncertainty (Bakke et al., 2011).

The calculations can be used to estimate the importance of the different transport routes for contaminants from the sediment to the ecosystem. Relevant calculations are explained in chapter 3.

Figure 2.17 shows a simplified illustration of the transport routes from the sediment to the ecosystem.

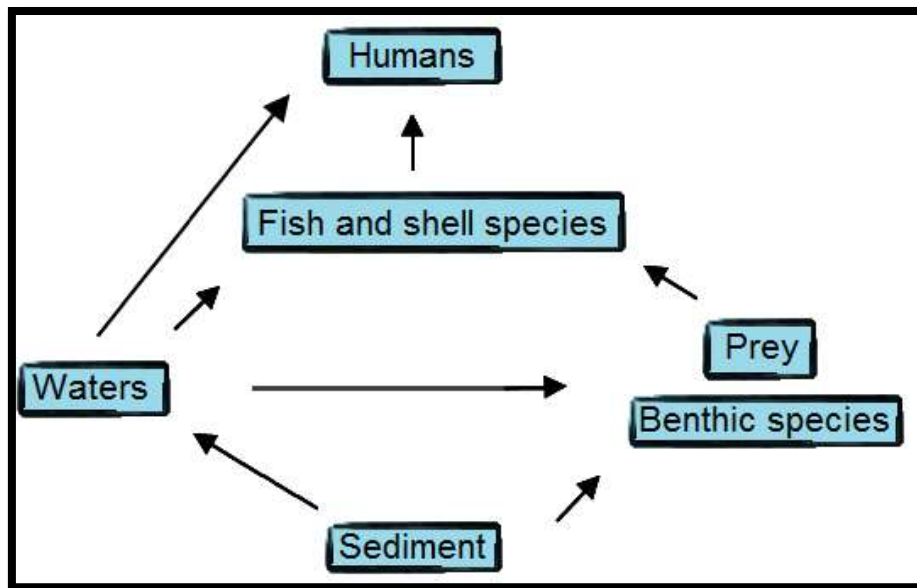


Figure 2.17 Relevant transport routes from the sediment to the ecosystem.
Modified from (Bakke et al., 2011)

Tier 2 also requires a sediment toxicity test for the organisms living in the sediment. This covers the foundation to evaluate the risk for those organisms who are in contact with the sediment over a long period of time (Bakke et al., 2011). Analytical tests are not included in the scope of this study, and this is therefore not further discussed.

2.5.2.1 Acceptance criteria for evaluation of the spreading.

There can be different acceptance criteria to evaluate the spreading of contaminants from the sediment. It could be a specified value i.e. flux of contaminants out of the sediment should not exceed a given amount each year (Bakke et al., 2011). OSPAR Recommendation 2006/5 (OSPAR Recommendation 2006/5, 2006) is one such limit value, of 10 tons of oil/year, as described in chapter 2.2.4.

Other criteria could be that the leaching should not exceed the leaching rate of a predetermined reference sediment more than a given number of times or percent, or have loss of contamination greater than a given limit value in the current location or the surrounding areas (Bakke et al., 2011).

3. Methodology

3.1 Concept

The aim of this study is to investigate if Klif's guidelines for contaminated sediment can be applied to estimate leaching rates from oil-based drill cuttings piles in the North Sea. There has been an increased focus on historic drill cuttings piles due to platform decommissioning, which can alter the piles and result in increased leaching into the environment. To get a better understanding on the impacts cuttings piles can have to the surroundings, gathering and review of information on factors affecting oil-based drill cuttings piles, and how the piles can affect the environment has also been investigated in this thesis.

The leaching rates from the contaminated sediments are given as diffusion, flux from sediment to the water column, in Klif's guidelines. The equations used to find the fluxes are given in chapter 3.2.

3.2 Relevant equations from Klif's risk assessment guidelines

The total flux from the sediment (F_{tot}) consists of flux by diffusion (F_{diff}), ships (F_{ship}) and organisms (F_{org}) as illustrated in figure 3.1 (Bakke et al., 2011)

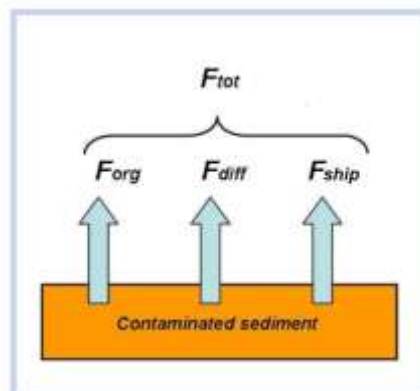


Figure 3.1 Illustration of the 3 fluxes from the sediment included in step 2A (Saloranta et al., 2011).

The equations and explanations are taken from Klif's guidelines (Bakke et al., 2011). The derivation of the equations are given in the Background document, part B (Eek et al., 2011).

Equation 1: Calculation of transport by biodiffusion, F_{diff}.

The spreading by biodiffusion (F_{diff}) is calculated using the following equation. If measured data are not available, the default values written in the brackets can be used.

$$F_{diff} = \frac{n}{\tau} \times a \times D_s \times \frac{C_{pw}}{\Delta x} \times 3,15 \cdot 10^8$$

Where:

F_{diff} = biodiffusion of sediment porewater (mg/m²/year)

n = porosity (fraction of water in sediment) (0,7)

τ = tortuosity (3)

a = factor for increased diffusion due to bioturbation (10)

D_s = molecular diffusion coefficient (cm²/s, specific for each compound, appendix A)

Δx = diffusion length (1 cm)

C_{pw} = porewater concentration (mg/l, C_{pw} = C_{sed} [mg/kg]/K_d [l/kg] or measured, equation 6)

Spreading by diffusion is calculated by multiplying the molecular diffusion with a factor, a, which takes the increased transport due to bioturbation into account, and corrects the increased diffusion length due to the pore-geometry.

Equation 2: Calculation of sediment transport generated by ships, F_{ship}.

Sediments located at water depths shallower than about 20 meters can be spread as a result of the ship propellers during arrival or departure. Resuspension of these sediment particles is calculated with the following equation:

$$F_{ship} = \frac{2 \times N_{ship} \times m_{sed} \times C_{sed} \times (f_{solved} + f_{susp})}{A_{ship}}$$

Where:

F_{ship} = spreading due to arrival and departure of ships (mg/m²/year)

2 = multiplication factor covering arrival and departure of ships

N_{ship} = number of daily ship arrivals per year (port authorities)

C_{sed} = contaminant concentration within the sediment area (mg/kg d.w., measured)

- f_{solved} = soluble contaminant fraction in sediment, ($10/K_d$, specific for each compound, appendix A)
- f_{susp} = fraction suspendable sediment ($< 2\mu m$, measured)
- A_{ship} = total sediment area < 20 meters deep affected by the ship traffic (m^2)
- m_{sed} = mass of resuspended sediment during an arrival or departure of ship (kg) (table 3.1)

Table 3.1 Default values for m_{sed} , based on a standard length < 20 m depth at 120 meters. These default values must be multiplied with the length and divided by 120 before they are applied in equation 2. Sediment type is found based on grain size distribution (Bakke et al., 2011)

| Sediment type | Large harbor | Industry harbor | Small boats harbor |
|------------------|--------------|-----------------|--------------------|
| Silt and clay | 2000 | 1000 | 150 |
| Sand | 200 | 100 | 15 |
| Gravel and stone | 20 | 10 | 1 |

Equation 3: Calculation of transport by organisms, For_g .

Spreading out of the sediment can also occur by benthic organisms which are eaten by fish and other animals, resulting in a possible biomagnification of the contaminants (Bakke et al., 2011). Spreading due to uptake by organisms and predation can be calculated using the equation below. In the absence of measured data, the default values in the brackets can be used.

$$For_g = \frac{C_{bio}}{OC_{cbio}} \times \frac{(OC_{sed} \times (1-d) - OC_{resp})}{1000}$$

Where:

- For_g = spreading due to uptake by organisms ($mg/m^2/year$)
- C_{bio} = total concentration in benthic biota (mg/kg d.w., measured or calculated)
- OC_{cbio} = fraction organic carbon in benthic fauna (0,25 g/g d.w.)
- OC_{sed} = flux of organic carbon settling to the sediment ($200 g/m^2/year$)
- d = fraction of organic carbon not consumed (buried) in the sediment (0,47 g/g)
- OC_{resp} = respiration rate of organic carbon in the sediment ($31 g/m^2/year$)

Equation 4: Calculation of total flux, F_{tot} .

Those areas that are affected by the ship traffic (A_{ship}) and those that are not ($A_{sed} - A_{ship}$) have to be distinguished, so the flux and the annual transport of contaminants from the sediment have to be calculated separately for each area.

Total flux of a compound out of the sediment ($\text{mg}/\text{m}^2/\text{year}$) is calculated by using equation 4:

$$F_{tot} = F_{diff} + F_{ship} + F_{org}$$

Where:

F_{tot} = total flux from the sediment ($\text{mg}/\text{m}^2/\text{year}$)

F_{diff} = flux due to biodiffusion ($\text{mg}/\text{m}^2/\text{year}$)

F_{skip} = flux due to arrival and departures of ships ($\text{mg}/\text{m}^2/\text{year}$)

F_{org} = flux due to uptake by organisms ($\text{mg}/\text{m}^2/\text{year}$)

Equation 5: Calculation of sea water concentrations.

Average toxic sea water concentrations can be calculated if the residence time is known. In the case where the residence time is unknown, default values can be applied, but it can vary greatly and should be calculated based on oceanographic measurements, see chapter 3.3.2. The equation to calculate water mass concentrations is given below:

$$C_{sw} = \frac{(F_{tot} - F_{org}) \times A_{sed}}{V_{sea}} \times t_r = \frac{F_{tot} - F_{org}}{d_{sea}} \times t_r$$

Where:

C_{sw} = concentration in the water mass ($\text{mg}/\text{m}^3 = \mu\text{g}/\text{l}$)

A_{sed} = total sediment area (m^2)

V_{sea} = volume of water over the sediment (m^3 , calculated from area and depth)

d_{sea} = average depth in the sediment area (m, measured)

t_r = residence time of water in sediment area (0,02 years = about 1 week)

Equation 6: Modification of the suggested sediment-to-water partition coefficient, K_d .

For the organic compounds, the sediment-to-water partition coefficient, K_d , is based on the fraction of organic carbon (f_{oc}) and specific organic carbon-water partitioning coefficient (K_{oc}) normalized to organic carbon (Bakke et al., 2011), given in the following equation:

$$K_d = f_{oc} \times K_{oc}$$

F_{oc} can be described as the portion of the organic matter which is available to adsorb the organic contaminants of concern. This means that if the sediment carbon content is high, more organic chemicals might be adsorbed to the sediment and less of those compounds will therefore be available to leach to the water column (IDEM, 2007). K_{oc} describes the potential for movement or mobility which is present for contaminants in the sediment and water (Mackay et al., 2006). Appendix A shows K_{oc} values for 16 PAHs.

The theoretical K_d -values, given in appendix A, is based on an organic carbon content (TOC) of 1 % in the sediment ($f_{oc} = 0,01$). This is a very conservative value, often overestimating the contaminant concentration in the pore water considerable. Some sites have been contaminated for a long time, and the contaminants will then be strongly bound to the particles. In these cases, site-specific measured K_d values should be applied.

If the TOC content increases, the K_d values will also increase, which means that the organic contaminants will be tighter bound to the sediment (Bakke et al., 2011). Larger f_{oc} values will give larger K_d values, which again results in weaker flux (F_{diff}), cf $C_{pw} = C_{sed}/K_d$ explained in equation 1. It might seem as a paradox that higher TOC content results in weaker leaching rates, since increasing amounts of a substance in the sediment will yield a proportional amount of release into the pore water. In the case of organic matter, and in particular for oil with high hydrophobicity, this will be inversely related. The more hydrophobic organic substances contained in the sediment, the higher its binding capacity will be. Due to this, the more of these substances that bind to the organic fraction of the sediment, the more strongly they will be attached, thus less available to leach to the water (Mackay et al., 2006).

Equation 7: Controlling the calculation results, temp.

It is recommended to check the probability of the calculations, and this can be determined by estimating how much time it will take for all the contaminants to be fully drained from the sediment. In a contaminated site, the amount of contaminants leaking out of the sediment each year should only be a fraction of the total amount, if not the contaminants would already have leaked out. If the calculated fluxes are considerable high, resulting in a rapid annual leaking rate, it could indicate that an overestimation of the fluxes has been done or that the sediments are actually gaining additional contaminants.

One can presume that the leaching occurs in the upper 10 cm of the bottom as a default value. Default values for all the parameters except sediment concentration and total contaminant transport from the sediment can also be applied.

$$t_{emp} = \frac{d_{sed} \times C_{sed} \times \rho_{vv} \times f_{dw}}{F_{tot}}$$

Where:

t_{emp} = time for all the contaminants to leak out of the bioactive layer in the sediment (year)

d_{sed} = thickness of bioturbation depth (100 mm/m²)

r_{sed} = sedimentation rate (3 mm/m²/year)

C_{sed} = sediment concentration (mg/kg d.w., measured)

ρ_{vv} = density of wet sediment (1,3 kg/liter)

f_{dw} = fraction dry weight of wet sediment (0,35)

F_{tot} = total contaminant transport out of the sediment (mg/m²/year)

3.3 Additional equations

Equation 8: Total organic matter/total organic carbon conversion factor.

Total organic carbon (TOC) is not always given, and could then be found by converting total organic matter (TOM) into TOC using an accepted factor of 1,724 (Howard, 1965), the equation is given below:

$$TOC = \frac{TOM}{1,724}$$

However, this is based on old information and an assumption that organic matter contains 58 % carbon. This information is also based on soil, but it can be assumed that it would be similar conditions for sediments. This factor is associated with some uncertainty and should be used with caution, only as a rough estimate.

Equation 9: Residence time

In order to calculate the water concentration, equation 5, the residence time must be known. Residence time can be defined as the average time a water mass remains within aquatic systems boundaries (Rueda et al., 2005). This could be found from respective authorities, or it can be calculated based on volumetric flow rates, as shown below.

$$Tf = \frac{V}{Q}$$

Where:

T_f = residence time (s)

V = volume of water (m³)

Q = volumetric flow-rate (m³/s)

(Rueda et al., 2005)

3.4 The excel worksheet

The excel worksheet given as assistance to the equations given in the guidelines, contains equations, constants and default values given in the guideline. The sheet consists of several pages, divided into four parts. Input of site specific values and relevant concentrations as well as homogeneity control are included in part one, whereas part two includes some necessary calculations, K_d values and overview of how much spreading that is allowed if the sediment concentrations are the same as the limit values given in the guidelines. Part three of the worksheet includes the calculated spreading and associated risk, while part four is an overview of the final results. In addition to this, there is a page containing some default values for each compound, and charts representing distribution of spreading mechanisms and distribution of exposure mechanisms (Bakke et al., 2011).

4 Results

4.1 Gathering of relevant input data

The first step to determine if the guidelines could be used to determine leaching rates from cuttings piles was to investigate if relevant information from cuttings piles reports was available. In order to find enough data, several drill cuttings characterization reports were examined. However, requested information was not found in most of these reports since they are not made with the purpose to be used as data input for Klif's guidelines.

One major drawback in the context of drill cuttings piles is that the guidelines do not include THC. Generally, leaching rates from drill cuttings piles are measured by finding the loss of THC as an indicator of the oil contamination. THC would therefore be the preferred parameter to use in the guidelines, however, oil also consists of other compounds, such as PAHs, which often represents the most toxic part of the oil (Bjørgesæter, 2009). The 16 PAH classified by the U.S Environmental Pollution Agency (EPA) (appendix A), is included in the guidelines and has therefore been used to represent the leaching rates from oil-based drill cuttings piles in this thesis.

The leaching rates from sediment to the water column, equation 4, is calculated based on three different fluxes, as described in chapter 3.2. Calculation of transport by biodiffusion, equation 1, requires pore water concentrations from the contaminated area. It was not possible to find pore water concentrations for areas contaminated with drill cuttings, but sediment concentrations were included in the reports, and they were used together with K_d values to find the pore water concentrations. K_d values should preferably be determined on basis of local measurements, but such data was not found for the compounds in drill cuttings piles. Default K_d values are given in the guidelines, but these default K_d values can be modified, using measured TOC values, as described in equation 6. TOC values were therefore calculated based on four measured TOM values from Statfjord A, to give more realistic K_d values. Appendix C shows the modified K_d values.

Equation 2, Calculation of sediment transport generated by ships, could not be applied in the correlation with drill cuttings piles. This equation is based on sediments shallower than 20 meters, and the equation is thus irrelevant for drill cuttings piles which in this case are located at a depth of about 150 meters.

Input data for drill cuttings contamination in this thesis is taken from "Characterization of Drill Cuttings at Statfjord-A" by Tvedten et al., 2012, hereafter referred to as the Statfjord A report. A short introduction to Statfjord A and the drill cuttings are given below.

4.1.1 Statfjord A

The Statfjord oil field is located in the Tampen area in the North Sea, about 200 km northwest of Bergen and close to the United Kingdom border (Boge et al., 2005), see figure 4.1. This area is located in the north part of the North Sea, and the seabed is therefore not as affected by currents and wind generated water movements like the shallower areas in the south, as described in chapter 2.2.

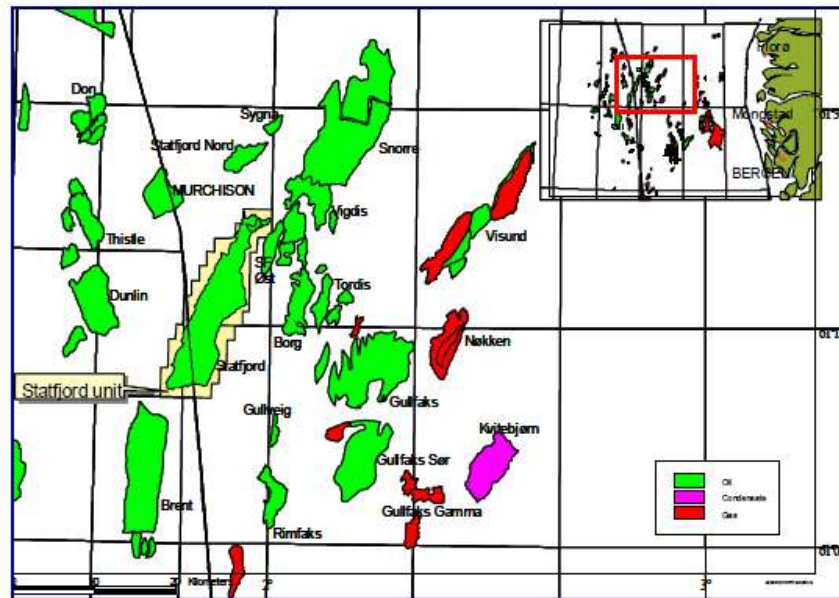


Figure 4.1 Location of the Statfjord field (Boge et al., 2005)

The field was discovered in 1974, the first platform called Statfjord A was installed in 1978 and production started the following year. The platform is a large gravity based structure (BGS) made of concrete, which is about 270 meters tall and located at an area with a water depth around 150 meters (Tvedten et al., 2012). The field has been one of the largest producing oil fields in Europe with regards to recoverable reserves, but it is now reaching its production termination (Boge et al., 2005).

The drilling at Statfjord A has been done through the two platform legs, and discharges of drill cuttings have resulted in accumulation of about 30 000 m³ of drill cuttings on the seabed, covering an area of about 13 000 m². The cuttings have accumulated in two distinct piles, of about 15 meters in height, underneath the platform and some in the surrounding area (Tvedten et al., 2012). Figure 4.2 illustrates the location and extent of the two drill cuttings (DC) piles.

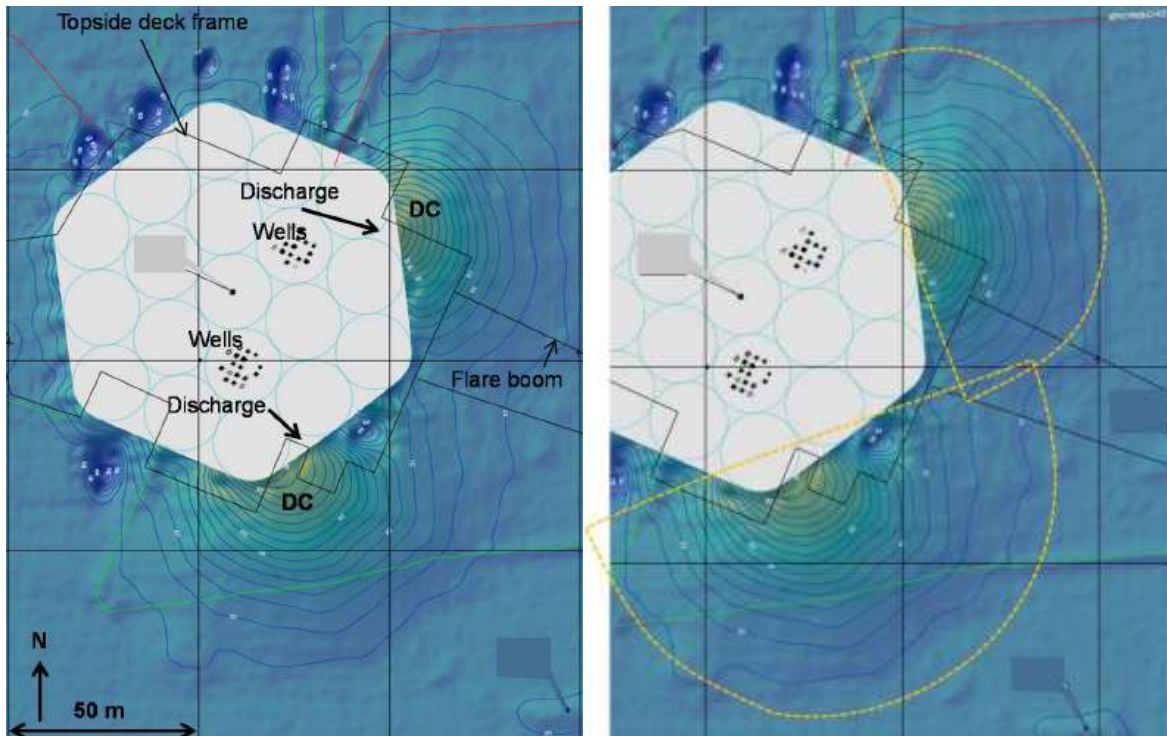


Figure 4.2 Location and extent of the two drill cuttings (DC) piles at Statfjord A (Tvedten et al., 2012)

A rough estimate of the leaching rate of THC from the drill cuttings piles have been made in the Statfjord A report. The leaching rate was estimated to be 0,6 tones/year (Tvedten et al., 2012).

4.2 Input used in the calculations

Input data is provided by information from Statfjord A, with focus on the sediment area where the cuttings piles are located. Default values were used for those parameters which are not included in the following chapters.

4.2.1 Sediment concentrations

Sediment concentrations from 86 samples of 15 PAHs from the Statfjord-report, given in appendix B, were used to carry out the calculations. In the Statfjord report, benzo(b)fluoranthene and benzo(k)fluoranthene was combined into one concentration together with benzo(j)fluoranthene. Since benzo(b)-and benzo(k)fluoranthene have relatively equal K_d values, the concentration for benzo(b/j/k)fluoranthene from the Statfjord report was applied as benzo(b)fluoranthene, and no concentration was applied for benzo(k)fluoranthene.

4.2.2 Total organic carbon (TOC)

As explained in chapter 3.2, K_d values can be modified if TOC values are known, by using equation 6. In this study, one scenario was calculated using the guidelines default K_d values, based on 1 % TOC , and one scenario was calculated using modified K_d values based on average TOC values converted from measured TOM at Statfjord A. TOM data from Statfjord A and the respective TOC conversions are given in table 4.1

Table 4.1 % Total organic matter (TOM) and TOC converted from TOM from 4 samples from Statfjord A (Tvedten et al., 2012)

| Sample | 1 | 2 | 3 | 4 | Average |
|--------|------|------|------|------|---------|
| TOM % | 3,19 | 5,04 | 8,95 | 11,4 | 7,14 |
| TOC % | 1,85 | 2,92 | 5,19 | 6,61 | 4,14 |

Conversion of total organic matter TOC was done by the equation explained in chapter 3.3.

At the time of this study, only four TOM values were available, given in table 4.1. The full TOM analyses were not accessed in time to incorporate them into the calculations.

4.3 Results from the calculations

4.3.1 Mean and maximum sediment concentrations and homogeneity results

The risk assessment includes a homogeneity test for each compound, calculated on basis of the relationship between max-and mean sediment concentrations. A homogeneity value below 2 indicates that the sediment concentrations represent the area well, and that no hotspot-concentrations are occurring (Bakke et al., 2011). Table 4.2 shows the homogeneity results from the sediment concentrations in the cuttings piles.

Table 4.2 Homogeneity control of sediment concentrations from Statfjord A

| Compound | Measured sediment concentrations | | | Homogeneity control |
|------------------------|----------------------------------|-------------------------------|--------------------------------|---|
| | Number of samples | C _{sed, max} (mg/kg) | C _{sed, mean} (mg/kg) | C _{sed, max} / C _{sed, mean} (Values larger than 2 might indicate hotspots) |
| Naphthalene | 86 | 22,2 | 1,68 | 163 |
| Acenaphthylene | 86 | 1,71 | 0,27 | 22,6 |
| Acenaphthene | 86 | 3,85 | 0,58 | 38,5 |
| Fluorene | 86 | 7,33 | 0,61 | 109 |
| Phenanthrene | 86 | 7,66 | 0,92 | 28,7 |
| Anthracene | 86 | 3,76 | 0,41 | 27,4 |
| Fluoranthene | 86 | 5,43 | 0,54 | 28,4 |
| Pyrene | 86 | 9,89 | 1,04 | 21,8 |
| Benzo(a)anthracene | 86 | 3,78 | 0,37 | 93,3 |
| Chrysene | 86 | 1,22 | 0,15 | 33,9 |
| Benzo(b)fluoranthene | 86 | 4,60 | 0,16 | 230 |
| Benzo(a)pyrene | 86 | 3,39 | 0,17 | 53,0 |
| Indeno(1,2,3-cd)pyrene | 86 | 0,02 | 0,02 | 1,00 |
| Dibenzo(a,h)anthracene | 86 | 0,02 | 0,02 | 1,00 |
| Benzo(ghi)perylene | 86 | 0,26 | 0,03 | 13,1 |

Large variations can be observed between the max-and mean concentrations for most PAHs. Naphthalene has considerable higher sediment concentrations than the remaining PAHs, while ideno(1,2,3-cd)pyrene and dibenzo(a,h)anthracene has the lowest. These two latter PAHs had sediment concentrations below the detection limit for all samples, and the concentrations were therefore set to the detection limit of 0,02 mg/kg.

4.3.2 Calculated PAH leaching rates

PAH leaching rates were found using equation 1-4. Both maximum and mean leaching rates were calculated, based on max and mean sediment concentrations given in table 4.2. Table 4.3 and 4.4 shows the PAH leaching rates, using modified and default Kd values respectively.

Table 4.3 Calculated max and mean PAH leaching rates, based on max and mean sediment concentrations from sediment containing drill cuttings, using modified Kd values.

| Compound | Calculated maximum spreading | | | Calculated mean spreading | | |
|------------------------|--|---|--|---|--|---|
| | F _{tot, max} [mg/m ² /yr] | F _{diff, max} [mg/m ² /yr] | F _{org, max} [mg/m ² /yr] | F _{tot, mean} [mg/m ² /yr] | F _{diff, mean} [mg/m ² /yr] | F _{org, mean} [mg/m ² /yr] |
| Naphthalene | 2,68E+03 | 2,62E+03 | 6,17E+01 | 2,03E+02 | 1,98E+02 | 4,68E+00 |
| Acenaphthylene | 1,02E+02 | 9,00E+01 | 1,19E+01 | 1,63E+01 | 1,44E+01 | 1,91E+00 |
| Acenaphtene | 1,00E+02 | 8,34E+01 | 1,67E+01 | 1,50E+01 | 1,25E+01 | 2,49E+00 |
| Fluorene | 1,16E+02 | 9,15E+01 | 2,44E+01 | 9,65E+00 | 7,62E+00 | 2,03E+00 |
| Phenanthrene | 5,84E+01 | 4,05E+01 | 1,79E+01 | 7,04E+00 | 4,89E+00 | 2,16E+00 |
| Anthracene | 2,30E+01 | 1,61E+01 | 6,81E+00 | 2,47E+00 | 1,74E+00 | 7,33E-01 |
| Fluoranthene | 1,40E+01 | 4,16E+00 | 9,84E+00 | 1,38E+00 | 4,11E-01 | 9,73E-01 |
| Pyrene | 4,64E+01 | 1,86E+01 | 2,78E+01 | 4,87E+00 | 1,95E+00 | 2,92E+00 |
| Benzo(a)anthracene | 5,50E+00 | 7,66E-01 | 4,74E+00 | 5,35E-01 | 7,44E-02 | 4,60E-01 |
| Chrysene | 3,90E+00 | 3,11E-01 | 3,58E+00 | 4,80E-01 | 3,84E-02 | 4,42E-01 |
| Benzo(b)fluoranthene | 1,08E+01 | 5,36E-01 | 1,03E+01 | 3,78E-01 | 1,88E-02 | 3,60E-01 |
| Benzo(a)pyrene | 7,77E+00 | 3,86E-01 | 7,38E+00 | 3,79E-01 | 1,88E-02 | 3,60E-01 |
| Indeno(1,2,3-cd)pyrene | 1,62E-02 | 7,57E-04 | 1,55E-02 | 1,62E-02 | 7,57E-04 | 1,55E-02 |
| Dibenzo(a,h)anthracene | 1,95E-02 | 9,05E-04 | 1,86E-02 | 1,95E-02 | 9,05E-04 | 1,86E-02 |
| Benzo(ghi)perylene | 4,85E-01 | 2,26E-02 | 4,62E-01 | 4,78E-02 | 2,23E-03 | 4,55E-02 |
| Σ15 PAH | 3,17E+03 | 2,97E+03 | 2,04E+02 | 2,62E+02 | 2,42E+02 | 1,96E+01 |

Table 4.4 Calculated maximum and mean PAH leaching rates, based on max and mean sediment concentrations from sediment containing drill cuttings, based on Klif's default Kd values.

| Compound | Calculated maximum spreading | | | Calculated mean spreading | | |
|------------------------|--|---|--|---|--|---|
| | F _{tot, max} [mg/m ² /yr] | F _{diff, max} [mg/m ² /yr] | F _{org, max} [mg/m ² /yr] | F _{tot, mean} [mg/m ² /yr] | F _{diff, mean} [mg/m ² /yr] | F _{org, mean} [mg/m ² /yr] |
| Naphthalene | 1,11E+04 | 1,08E+04 | 2,56E+02 | 8,39E+02 | 8,20E+02 | 1,94E+01 |
| Acenaphthylene | 4,22E+02 | 3,72E+02 | 4,94E+01 | 6,76E+01 | 5,96E+01 | 7,92E+00 |
| Acenaphtene | 4,14E+02 | 3,45E+02 | 6,90E+01 | 6,19E+01 | 5,16E+01 | 1,03E+01 |
| Fluorene | 4,80E+02 | 3,79E+02 | 1,01E+02 | 4,00E+01 | 3,15E+01 | 8,42E+00 |
| Phenanthrene | 2,42E+02 | 1,68E+02 | 7,41E+01 | 2,92E+01 | 2,02E+01 | 8,93E+00 |
| Anthracene | 9,50E+01 | 6,69E+01 | 2,82E+01 | 1,02E+01 | 7,20E+00 | 3,04E+00 |
| Fluoranthene | 5,79E+01 | 1,72E+01 | 4,07E+01 | 5,73E+00 | 1,70E+00 | 4,03E+00 |
| Pyrene | 1,92E+02 | 7,69E+01 | 1,15E+02 | 2,02E+01 | 8,08E+00 | 1,21E+01 |
| Benzo(a)anthracene | 2,28E+01 | 3,17E+00 | 1,96E+01 | 2,21E+00 | 3,08E-01 | 1,91E+00 |
| Chrysene | 1,61E+01 | 1,29E+00 | 1,48E+01 | 1,99E+00 | 1,59E-01 | 1,83E+00 |
| Benzo(b)fluoranthene | 4,47E+01 | 2,22E+00 | 4,24E+01 | 1,57E+00 | 7,78E-02 | 1,49E+00 |
| Benzo(a)pyrene | 3,22E+01 | 1,60E+00 | 3,06E+01 | 1,57E+00 | 7,79E-02 | 1,49E+00 |
| Indeno(1,2,3-cd)pyrene | 6,71E-02 | 3,13E-03 | 6,40E-02 | 6,71E-02 | 3,13E-03 | 6,40E-02 |
| Dibenzo(a,h)anthracene | 8,07E-02 | 3,75E-03 | 7,69E-02 | 8,07E-02 | 3,75E-03 | 7,69E-02 |
| Benzo(ghi)perylene | 2,01E+00 | 9,37E-02 | 1,91E+00 | 1,98E-01 | 9,24E-03 | 1,89E-01 |
| Σ 15 PAH | 1,31E+04 | 1,22E+04 | 8,43E+02 | 1,08E+03 | 1,00E+03 | 8,12E+01 |

Naphthalene has by far the greatest diffusion rate for both max and mean concentrations and for the two scenarios based on modified and default Kd values. A decreasing trend in the total leaching rates can be observed, from naphthalene to benzo(ghi)perylene. To illustrate the leaching rate for each PAH, maximum and mean fluxes were plotted for each PAH, and for the two scenarios. The diagram is illustrated in figure 4.3.

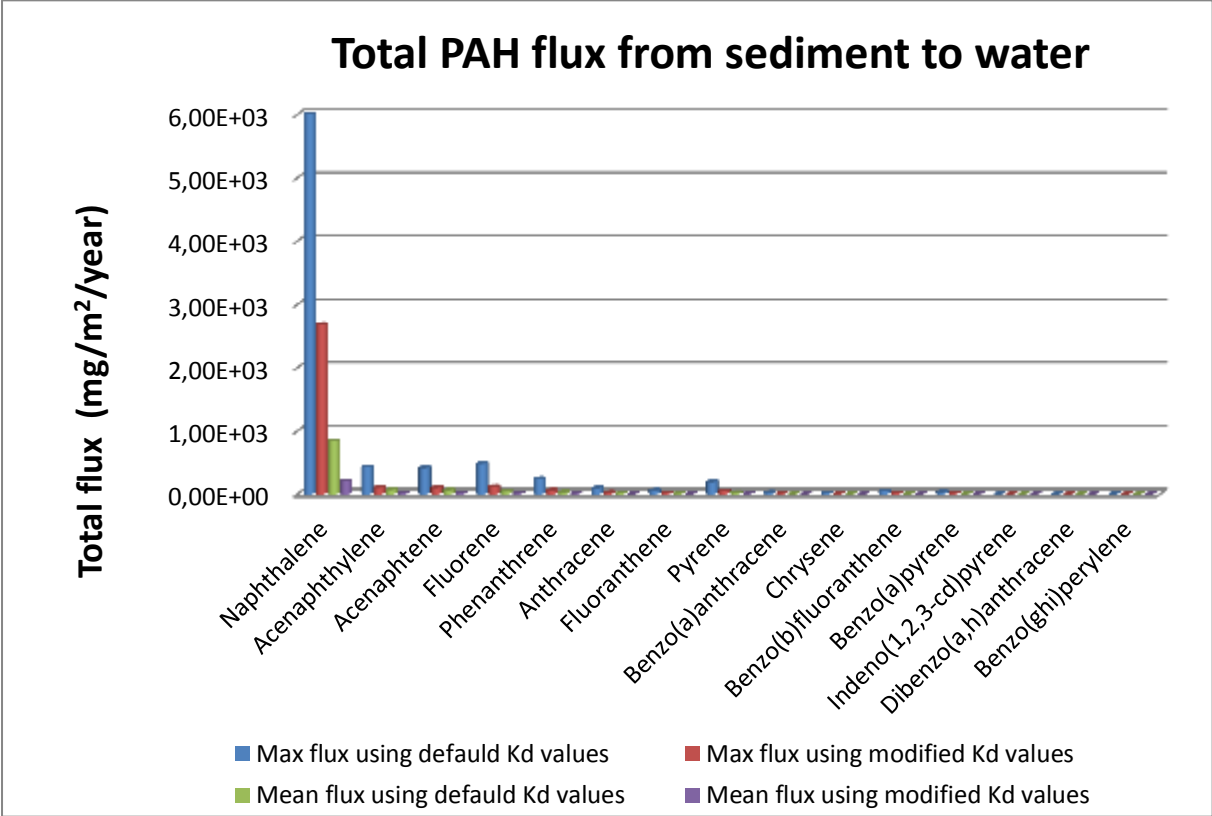


Figure 4.3 Maximum and mean PAH flux, based on max and mean sediment concentrations, for both default and modified Kd values.

As figure 4.3 shows, naphthalene is the major diffusion contributor of the 15 PAHs with a considerable higher leaching rate than the other PAHs. In addition, it can be noticed that the default Kd value gives higher fluxes than the modified Kd values.

4.3.3 Spreading distribution

The total calculated spreading of PAHs from the drill cuttings is based on transport by biodiffusion and transport by organisms only, since spreading generated by ships could not be calculated in this context, as explained in chapter 4.1. As table 4.3 and 4.4 shows, leaching due to biodiffusion is the major contributor to the total spreading. The spreading distribution between these two contributing processes is shown in figure 4.4.

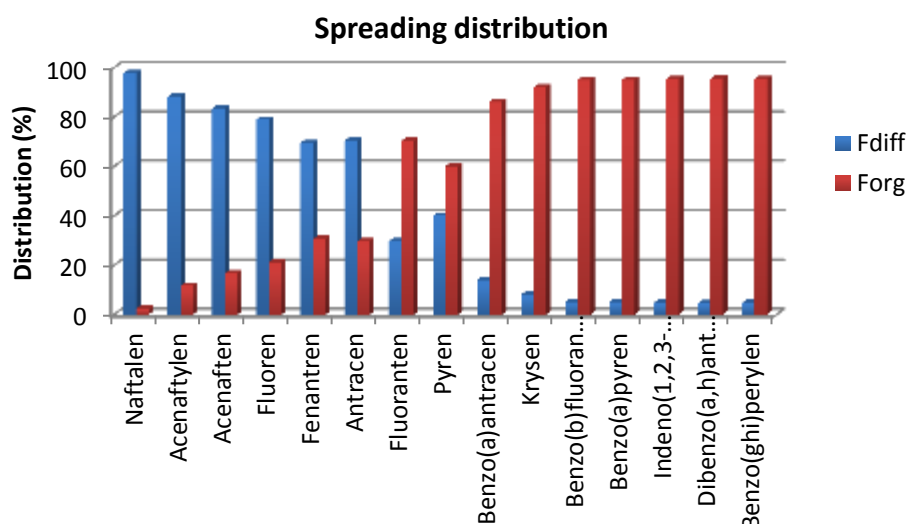


Figure 4.4 Spreading distributions between transport by biodiffusion (Fdiff) and transport by organisms (Forg)

As figure 4.4 shows, the small PAHs are mainly spread by biodiffusion while the heavier PAHs are spread by organisms.

4.3.4 Time to drain the sediment

By using equation 7, time to drain the sediment for each compound can be calculated. This is given in table 4.5 for both modified and default Kd values

Table 4.5 Time to drain the sediment for each of the 15 PAH, for both modified and default Kd values.

| Compounds | Time to drain the sediment for a given compound, t_{emp} (yr) | |
|------------------------|---|------------|
| | Modified Kd | Default Kd |
| Naphthalene | 0,4 | 0,1 |
| Acenaphthylene | 0,8 | 0,2 |
| Acenaphthene | 1,8 | 0,4 |
| Fluorene | 2,9 | 0,7 |
| Phenanthrene | 6,0 | 1,4 |
| Anthracene | 7,5 | 1,8 |
| Fluoranthene | 17,7 | 4,3 |
| Pyrene | 9,7 | 2,3 |
| Benzo(a)anthracene | 31,3 | 7,5 |
| Chrysene | 14,2 | 3,4 |
| Benzo(b)fluoranthene | 19,4 | 4,7 |
| Benzo(a)pyrene | 19,9 | 4,8 |
| Indeno(1,2,3-cd)pyrene | 56,1 | 13,6 |
| Dibenzo(a,h)anthracene | 46,7 | 11,3 |
| Benzo(ghi)perylene | 24,5 | 5,9 |

As table 4.5 shows, the sediment will be drained by the lighter PAHs first, while the heavier PAHs will be more persistent. It can also be observed that when using default K_d values, the time to drain the sediment will be faster than if the modified K_d values are used. Naphthalene, which also has the highest sediment concentration, will drain from the sediment fastest for both modified and default K_d values. For both cases, ideno(1,2,3-cd)pyrene and dibenzo(a,h)anthracene will be most persistent in the sediment, if they are present. These two PAHs had concentrations below detection limit, and they have the greatest K_d values, so the leaching rate will be very slow.

4.4 Comparisons of concentrations and leaching rates against limit values

The environmental impact from the PAHs present in the drill cuttings pile at Statfjord A was found by comparing concentrations and diffusion rates to limit values given in the guidelines. The results from the comparisons are given below.

4.4.1 Sediment concentrations

The sediment concentrations were compared to the limit values given in table 2.2 to get a better understanding of their possible toxicity levels. Results are given in table 4.6, where the blue columns shows the max and mean sediment concentrations from Statfjord A (from appendix B) and the green column shows the limit values used in Klif's guidelines, given in table 2.2. The yellow columns shows the number of times the sediment PAH concentrations exceed their limit values.

Table 4.6 Measured sediment concentrations (blue columns) compared to Klif's limit values (green column), to determine the number of times they exceed the limit values (yellow columns).

| Compound | Measured sediment concentrations | | Limit values (mg/kg) | Measured sediment concentrations compared to limit values (number of times): | |
|------------------------|----------------------------------|--------------------------------|----------------------|--|------|
| | C _{sed, max} (mg/kg) | C _{sed, mean} (mg/kg) | | Max | Mean |
| Naphthalene | 22,2 | 1,68 | 0,29 | 76,5 | 5,80 |
| Acenaphthylene | 1,71 | 0,27 | 0,03 | 51,8 | 8,30 |
| Acenaphtene | 3,85 | 0,57 | 0,16 | 24,1 | 3,60 |
| Fluorene | 7,33 | 0,61 | 0,26 | 28,2 | 2,35 |
| Phenanthrene | 7,66 | 0,92 | 0,50 | 15,3 | 1,85 |
| Anthracene | 3,76 | 0,40 | 0,03 | 121 | 13,1 |
| Fluoranthene | 5,43 | 0,54 | 0,17 | 31,9 | 3,16 |
| Pyrene | 9,89 | 1,04 | 0,28 | 35,3 | 3,71 |
| Benzo(a)anthracene | 3,78 | 0,37 | 0,06 | 63,0 | 6,12 |
| Chrysene | 1,22 | 0,15 | 0,28 | 4,36 | |
| Benzo(b)fluoranthene | 4,60 | 0,16 | 0,24 | 19,2 | |
| Benzo(a)pyrene | 3,39 | 0,16 | 0,42 | 8,07 | |
| Indeno(1,2,3-cd)pyrene | 0,02 | 0,02 | 0,05 | | |
| Dibenzo(a,h)anthracene | 0,02 | 0,02 | 0,59 | | |
| Benzo(ghi)perylene | 0,26 | 0,03 | 0,02 | 12,4 | 1,22 |

Table 4.6 shows that most of the PAHs concentrations exceed the limit values, both for the maximum-and mean concentrations. Anthracene exceeds the limit value the most followed by naphthalene. Some of the heavy PAHs have mean concentrations that do not exceed the limit values, and both mean and max concentrations of ideno(1,2,3-cd)pyrene and dibenzo(a,h)anthracene do not exceed the limit values.

4.4.2 Evaluation of the calculated leaking rate.

Since acceptance criteria for PAHs in drill cuttings piles are limited, the limit values used in Klif's guidelines was used to get an impression of the leaching rate extent. The leaching rates were compared to the permitted leaching rates, which are the leaching rates based on sediment concentrations that equals the limit values. The results based on modified and default Kd values are given in table 4.7 and 4.8 respectively. Blue columns shows the max and mean calculated total spreading (F_{tot}), while the green column shows the permitted spreading, which is the spreading that equals the limit values given in chapter 2.5.1. The yellow columns show how many times the calculated total spreading exceeds the permitted spreading.

Table 4.7 Total calculated spreading (blue columns) compared to permitted spreading (green column), based on modified Kd values, to determine the number of time the calculated spreading exceeds the limit values (yellow columns).

| Compound | Calculated total spreading (F_{tot}) | | Spreading (F_{tot}) if C_{sed} equals the limit values ($mg/m^2/yr$) | F_{tot} compared to permitted spreading (number of times): | |
|------------------------|--|--------------------------------------|--|--|------|
| | $F_{tot, max}$ ($mg/m^2/\bar{a}$) | $F_{tot, mean}$ ($mg/m^2/\bar{a}$) | | Max | Mean |
| Naphthalene | 2,68E+03 | 2,03E+02 | 1,42E+02 | 18,8 | 1,43 |
| Acenaphthylene | 1,02E+02 | 1,63E+01 | 7,38E+00 | 13,8 | 2,21 |
| Acenaphthene | 1,00E+02 | 1,50E+01 | 1,49E+01 | 6,71 | 1,00 |
| Fluorene | 1,16E+02 | 9,65E+00 | 1,42E+01 | 8,19 | |
| Phenanthrene | 5,84E+01 | 7,04E+00 | 1,19E+01 | 4,90 | |
| Anthracene | 2,30E+01 | 2,47E+00 | 5,98E-01 | 38,4 | 4,14 |
| Fluoranthene | 1,40E+01 | 1,38E+00 | 7,94E-01 | 17,6 | 1,74 |
| Pyrene | 4,64E+01 | 4,87E+00 | 2,83E+00 | 16,4 | 1,72 |
| Benzo(a)anthracene | 5,50E+00 | 5,35E-01 | 1,13E-01 | 48,9 | 4,75 |
| Chrysene | 3,90E+00 | 4,80E-01 | 9,77E-01 | 3,99 | |
| Benzo(b)fluoranthene | 1,08E+01 | 3,78E-01 | 5,59E-01 | 19,3 | |
| Benzo(a)pyrene | 7,77E+00 | 3,79E-01 | 9,55E-01 | 8,13 | |
| Indeno(1,2,3-cd)pyrene | 1,62E-02 | 1,62E-02 | 3,74E-02 | | |
| Dibenzo(a,h)anthracene | 1,95E-02 | 1,95E-02 | 5,64E-01 | | |
| Benzo(ghi)perylene | 4,85E-01 | 4,78E-02 | 3,83E-02 | 12,6 | 1,25 |

Table 4.8 Total calculated spreading (blue columns) compared to permitted spreading (green column), based on default K_d values, to determine the number of time the calculated spreading exceeds the limit values (yellow columns).

| Compound | Calculated total spreading (F _{tot}) | | Spreading (F _{tot}) if C _{sed} equals the limit values (mg/m ² /yr) | F _{tot} compared to permitted spreading (number of times): | |
|------------------------|--|--|---|---|-------|
| | F _{tot, max} (mg/m ² /år) | F _{tot, mean} (mg/m ² /år) | | Max | Mean |
| Naphthalene | 1,11E+04 | 8,39E+02 | 1,42E+02 | 78,0 | 5,90 |
| Acenaphthylene | 4,22E+02 | 6,76E+01 | 7,38E+00 | 57,2 | 9,16 |
| Acenaphtene | 4,14E+02 | 6,19E+01 | 1,49E+01 | 27,8 | 4,15 |
| Fluorene | 4,80E+02 | 4,00E+01 | 1,42E+01 | 33,9 | 2,82 |
| Phenanthrene | 2,42E+02 | 2,92E+01 | 1,19E+01 | 20,3 | 2,45 |
| Anthracene | 9,50E+01 | 1,02E+01 | 5,98E-01 | 159 | 17,13 |
| Fluoranthene | 5,79E+01 | 5,73E+00 | 7,94E-01 | 73,0 | 7,22 |
| Pyrene | 1,92E+02 | 2,02E+01 | 2,83E+00 | 67,9 | 7,13 |
| Benzo(a)anthracene | 2,28E+01 | 2,21E+00 | 1,13E-01 | 202 | 19,7 |
| Chrysene | 1,61E+01 | 1,99E+00 | 9,77E-01 | 16,5 | 2,04 |
| Benzo(b)fluoranthene | 4,47E+01 | 1,57E+00 | 5,59E-01 | 80,0 | 2,80 |
| Benzo(a)pyrene | 3,22E+01 | 1,57E+00 | 9,55E-01 | 33,7 | 1,64 |
| Indeno(1,2,3-cd)pyrene | 6,71E-02 | 6,71E-02 | 3,74E-02 | 1,79 | 1,79 |
| Dibenzo(a,h)anthracene | 8,07E-02 | 8,07E-02 | 5,64E-01 | | |
| Benzo(ghi)perylene | 2,01E+00 | 1,98E-01 | 3,83E-02 | 52,4 | 5,16 |

The tables show that several PAHs are exceeding their limit values. Benzo(a)anthracene is the PAH that exceeds the limit value most, followed by anthracene. Naphthalene, which has the highest flux by far, does not exceed as much as one might think, but it also have a much higher limit value and lower toxicity than the other PAHs. It is clear that there are large variations between mean and maximum values and between modified and default K_d values.

4.4.3 Evaluation of the ecological impacts

To evaluate the extent of how the organisms living in the sediment area can be affected by the PAHs, calculated pore water concentrations (PEC) was compared to PNEC_w values. Results are given in table 4.9 and 4.10 for modified and default K_d values respectively.

Table 4.9 Ecological impact determined by comparing the number of times (yellow column) that calculated pore water concentrations (blue columns) exceeds the PNEC_w values (green column). The pore water concentrations are based on modified K_d values.

| Compound | Calculated pore water concentrations (PEC) | | Limit value for ecological risk PNEC _w (mg/l) | Calculated pore water concentrations compared to PNEC _w (number of times): | |
|------------------------|--|------------------------------|--|---|------|
| | C _{pv, max} (mg/l) | C _{pv, mean} (mg/l) | | Max | Mean |
| Naphthalene | 4,12E-01 | 3,12E-02 | 2,4E-03 | 172 | 13,0 |
| Acenaphthylene | 1,59E-02 | 2,54E-03 | 1,3E-03 | 12,2 | 1,96 |
| Acenaphthene | 1,50E-02 | 2,24E-03 | 3,8E-03 | 3,95 | |
| Fluorene | 1,74E-02 | 1,45E-03 | 2,5E-03 | 6,94 | |
| Phenanthrene | 8,08E-03 | 9,75E-04 | 1,3E-03 | 6,22 | |
| Anthracene | 3,22E-03 | 3,47E-04 | 1,1E-04 | 29,3 | 3,15 |
| Fluoranthene | 9,08E-04 | 8,97E-05 | 1,2E-04 | 7,56 | |
| Pyrene | 4,06E-03 | 4,26E-04 | 2,3E-05 | 176 | 18,5 |
| Benzo(a)anthracene | 1,82E-04 | 1,77E-05 | 1,2E-05 | 15,2 | 1,47 |
| Chrysene | 7,40E-05 | 9,13E-06 | 7,0E-05 | 1,06 | |
| Benzo(b)fluoranthene | 1,37E-04 | 4,79E-06 | 3,0E-05 | 4,56 | |
| Benzo(a)pyrene | 9,85E-05 | 4,80E-06 | 5,0E-05 | 1,97 | |
| Indeno(1,2,3-cd)pyrene | 2,06E-07 | 2,06E-07 | 2,0E-06 | | |
| Dibenzo(a,h)anthracene | 2,48E-07 | 2,48E-07 | 3,0E-05 | | |
| Benzo(ghi)perylene | 6,16E-06 | 6,07E-07 | 2,0E-06 | 3,08 | |

Table 4.10 Ecological impact determined by comparing the number of times (yellow column) that calculated pore water concentrations (blue columns) exceeds the PNEC_w values (green column). The pore water concentrations are based on default K_d values.

| Compound | Calculated pore water concentrations (PEC) | | Limit value for ecological risk PNEC _w (mg/l) | Calculated pore water concentrations compared to PNEC _w (number of times): | |
|------------------------|--|------------------------------|--|---|------|
| | C _{pv, max} (mg/l) | C _{pv, mean} (mg/l) | | Max | Mean |
| Naphthalene | 1,71E+00 | 1,29E-01 | 2,4E-03 | 712 | 53,9 |
| Acenaphthylene | 6,58E-02 | 1,05E-02 | 1,3E-03 | 50,6 | 8,10 |
| Acenaphthene | 6,21E-02 | 9,28E-03 | 3,8E-03 | 16,3 | 2,44 |
| Fluorene | 7,19E-02 | 5,98E-03 | 2,5E-03 | 28,7 | 2,39 |
| Phenanthrene | 3,34E-02 | 4,03E-03 | 1,3E-03 | 25,7 | 3,10 |
| Anthracene | 1,33E-02 | 1,44E-03 | 1,1E-04 | 121 | 13,1 |
| Fluoranthene | 3,76E-03 | 3,71E-04 | 1,2E-04 | 31,3 | 3,10 |
| Pyrene | 1,68E-02 | 1,76E-03 | 2,3E-05 | 730 | 76,7 |
| Benzo(a)anthracene | 7,54E-04 | 7,33E-05 | 1,2E-05 | 62,8 | 6,11 |
| Chrysene | 3,06E-04 | 3,78E-05 | 7,0E-05 | 4,38 | |
| Benzo(b)fluoranthene | 5,66E-04 | 1,98E-05 | 3,0E-05 | 18,9 | |
| Benzo(a)pyrene | 4,08E-04 | 1,99E-05 | 5,0E-05 | 8,15 | |
| Indeno(1,2,3-cd)pyrene | 8,53E-07 | 8,53E-07 | 2,0E-06 | | |
| Dibenzo(a,h)anthracene | 1,03E-06 | 1,03E-06 | 3,0E-05 | | |
| Benzo(ghi)perylene | 2,55E-05 | 2,51E-06 | 2,0E-06 | 12,7 | 1,26 |

Pyrene and naphthalene shows significant ecological risk for both scenarios, with high PEC/PNEC ratios. All PAHs except ideno(1,2,3-cd)pyrene and dibenzo(a,h)anthracene, which had concentrations below detection limit, exceed the limit value with the maximum pore water concentrations for both scenarios. The mean pore water concentrations shows less toxicity, but pyrene and naphthalene are still exceeding the limit values to a large extent.

To find the ecological impact to the species living in the surrounding water, sea water concentrations can be compared to PNEC values. Sea water concentrations was not included in the Statfjord A report, but an attempt to calculate them were conducted, where area and depth of the cuttings piles was used to find the residence time, given in equation 9. The results, presented in appendix D, are not considered reliable due to uncertainty with regards to the calculated residence time, and are therefore not applied.

5 Discussion

Input from drill cuttings at Statfjord A was used to investigate if Klif's guidelines for contaminated sediment could be used to determine leaching rates of oil from drill cuttings piles. The results from this study are discussed below.

5.1 Fate and transport of contaminants in drill cuttings piles.

Different physical and chemical processes might affect drill cuttings piles and result in alteration of the fate and transport of the contaminants within the piles. Biodegradation of oil-components are mainly slow within the pile, where oxygen levels are low, and higher at the surface with better availability and surplus of oxygen. Contaminants in the anaerobic layer can thus stay in the piles for many years without being biodegraded. Historic drill cuttings piles are therefore expected to have low biodegradation rates, since the available oxygen has been utilized over the years, and transport in the sediment is slow (Breuer et al., 1999). Contaminants in the pore water can leak out to the overlying water by biodiffusion (Bakke et al., 2011), and this process can potentially be a major contributor of contaminant spreading from drill cuttings piles. Erosion/sedimentation due to natural processes like currents and waves or anthropogenic activities such as dredging or trawling activities can possibly impact the cuttings piles to a large extent. Erosion due to platform decommissioning might play a large role in spreading contaminants to new locations, if the cuttings piles would have to be relocated (Dames & Moore and NIOZ, 1999). Therefore, to let cuttings piles remain as undisturbed as possible and left at its present location is an option which could reduce the leaching potential.

In addition to these factors, additional processes, not included in the guidelines, may affect contaminant release from the sediment. Oil has lower density than water, and convection, which is a density and gravity dependent transport of lighter liquid upwards, might occur if oil is present in a liquid form (Webster et al., 1996). This process is not included in the transport processes represented by the different equations in Klif's guidelines. Thus, it is outside the scope of this thesis to bring this into the calculations. This means that the results is based on an assumption that no other release mechanisms contribute significantly to releases of oil from cuttings piles than those covered in the guidelines. It has been found no literature that may clarify to which extent this assumption holds true, and it can therefore here only be regarded as adding to the uncertainty associated with the calculations.

5.2 Limitations with regards to relevant data

Several limitations were encountered during the process to determine if Klif's guidelines for contaminated sediments could be used on drill cuttings piles. Relevant parameters were difficult to obtain to be able to conduct the calculations with regards to drill cuttings piles. Drill cuttings piles characterization reports do not include specific information meant to be used in the guidelines, so some of the parameters had to be calculated or modified, increasing the uncertainty. Uncertainty is also associated with the extensive use of default values that had to be applied since site-specific data was unavailable. These default values are meant to be used on sediments in harbors and fjords, so to accept them as representative values for the conditions in the North Sea adds to the uncertainty.

The most basic challenge was the fact that THC could not be applied, since it was not included in the guidelines. An attempt to calculate the leaching rate of THC based on equation 1 was conducted, but K_d and D_s values for THC was difficult to obtain. K_d and D_s values can be found based on octanol-water partitioning coefficient, K_{ow} , literature values and molecular weight (Schwarzenbach et al., 2003), but these values were only found for each hydrocarbon compound and not for THC as a whole. Values for THC were needed because the drill cuttings characterization reports generally include sediment concentrations for THC as a group and not for each individual compound.

5.3 Evaluation of the calculated results.

5.3.1 Spreading distribution.

The spreading mechanisms included in Klif's guidelines are spreading due to biodiffusion, spreading generated by ships and spreading due to transport by organisms, as explained in chapter 2.5. Spreading generated by ships, equation 2, could not be calculated since the equation only applies for depths at 20 meters or shallower, and the cuttings piles are located at a depth of 150 meters. Ships would generally not have any impact on the cuttings piles, due to the depth, but other processes could cause the sediment to be whirled up. Natural erosion processes like currents and waves could cause the drill cuttings piles surface to erode and spread to other areas. Human activities such as trawling and other fishing activities could also affect cuttings piles. Possible relocation of cuttings piles during decommissioning seems to be the potentially greatest erosion contributor, and should therefore be taken into account (Nedwed et al., 2006). However, potential calculated oil release due to relocation of drill cuttings piles has not been included in the scope of this study since it is not included in Klif's guidelines.

Spreading due to fish and predation which might have eaten PAH contaminated benthic organisms, equation 3, was calculated based on sediment concentrations, given in appendix B, and default values. The results from this spreading might be associated with uncertainty due to the extensive use of default values. Uncertainty also arises due to the fact that Klif's guidelines have not taken metabolism and biotransformation into account. Although benthic organisms are exposed to- and may accumulate PAHs, it do not necessary mean that they are transferred to higher levels, because fish generally have high ability to biotransform and excrete PAHs (Suede et al., 1994). The importance of spreading due to transport by organisms could therefore possibly be considerable overestimated.

Spreading due to biodiffusion, equation 1, is the major contributor to the total spreading, and this parameter was calculated based on sediment concentrations from Statfjord A. Several default values were applied to calculate the biodiffusion rate, adding to the uncertainty. Figure 4.4 in chapter 4.3.3 illustrates the spreading distribution between biodiffusion and transport by organisms. It can be observed that the small PAHs are mainly dominated by biodiffusion while the spreading of the larger PAHs mainly originates from transport by organisms. This is consistent with the theory explained in chapter 5.3.1, which states that the small PAHs will be affected by diffusion in a larger extent than the heavier PAH, due to the properties which affect how tight the PAHs are bound to the sediment, and thus how available they are to leak out to the water.

5.3.2 Calculated PAH leaching rates

The mean and max leaching rates of 15 PAHs was calculated based on equation 1, given in chapter 3.3. Results are given in table 4.3 and 4.4, and a summary of the mean and max leaching rates (based on mean and max sediment concentrations), in kg/year, for both modified and default Kd values is given in table 5.1. An area of 13 000 m², given in section 4.1.1, was used to convert the units from mg/m²/year to kg/year.

Table 5.1 Mean and max leaching rates (based on mean and max sediment concentrations from Statfjord A) for Σ 15 PAHs in kg/year based on both modified and default Kd values.

| Scenario | Ftot (kg/yr) | | Fdiff (kg/yr) | | Forg (kg/yr) | |
|-------------|--------------|------|---------------|------|--------------|------|
| | Max | Mean | Max | Mean | Max | Mean |
| Modified Kd | 41,2 | 3,40 | 38,6 | 3,15 | 2,65 | 0,25 |
| Default Kd | 170 | 14,0 | 159 | 13,0 | 11,0 | 1,06 |

Table 5.1 shows that the total maximum and mean PAH leaching rates from the drill cuttings at Statfjord A was calculated to be 41,2 kg/year and 3,40 kg/year respectively, using modified K_d values. The maximum leaching rates based on both modified and default K_d values are high compared to the mean leaching rates, however, the mean leaching rates should be hold as most representative for the contaminated area (Bakke et al., 2011). It can also be observed from table 5.1 that the leaching rates based on default K_d values are considerable higher than those based on modified K_d values, this is further discussed in chapter 5.6., and that the leaching rates from transport by organisms are low compared to leaching due to biodiffusion, which is consistent with the theory explained in chapter 5.1.

From table 4.3 and 4.4 a decreasing leaching rate trend were observed from naphthalene to benzo(ghi)perylene, for both maximum and mean values. This might be connected to the decreasing trend that also applies for the molecular weight and K_d values, see appendix A. Naphthalene is the smallest of the 15 PAHs while benzo(ghi)perylene is the largest molecule, see appendix A. This will influence their chemical properties and thus their behavior in the environment. Small K_d values means that the compound is less bound to the sediment and will therefore leak out of the sediment in a greater degree than those compounds with greater K_d values, as previously illustrated in figure 2.14. Those compounds with a greater K_d value, will be tighter bound to the sediment, and thus have a slower leaching rate. To compare, naphthalene has a K_d value of 13 l/kg, while ideno(1,2,3-cd)pyrene has a K_d value of 23442 l/kg with 1 % TOC.

It is difficult to determine whether the total leaching rates are representing the actual conditions, since several factors in the calculations are associated with high uncertainty. The lack of basis to compare the calculated leaching rates to PAH leaching rates from other drill cuttings piles makes it difficult to evaluate the realism of these rates, since most leaching rate reports from drill cuttings piles are focused on THC and not PAH (Dames & Moore and TNO, 2002). It can be concluded though that the PAH leaching rates, based on both modified and default K_d values, are minor compared to the roughly estimated THC leaching rate of 0,6 tons/year from the Statfjord report, see chapter 4.1.1. However, the average total amount of PAH loading in the drill cuttings piles at Statfjord A is found to be only 0,42 tons compared to 584 tons of THC loading (Tvedten et al., 2012), so the PAH contribution will obviously be small compared to THC.

If compared to other areas, the Statfjord area has been one of the largest producing fields in the Norwegian continental shelf over the years (Boge et al., 2005), and the amount of PAH in the piles can therefore be expected to be somewhat higher compared to installations with less production and thus less discharge of drill cuttings.

5.4 Control of the calculations using calculated time to drain the sediments.

As described in chapter 3.2, equation 7 can be used to investigate if the calculated leaching rates seem probable or not. The amount of contaminants leaching out of the bioactive layer in the sediment each year should only be a fraction of the total amount, if not the contaminants would already have leached out. If the calculated leaching rates are high, it could imply that the results might not be reliable (Bakke et al., 2011). The estimated time to drain the sediment, given in table 4.5, varies from one PAH to another, and a pattern was observed, where the lightest PAHs drain out first while the more heavy PAHs stay longer in the sediment. This correlates to the theory illustrated in figure 2.14, where the lighter PAHs (smaller K_d) will have faster diffusion rates due to their chemical properties, while the more heavy PAHs (greater K_d) will be more persistent in the sediment. The PAHs that will remain in the sediment for the longest period, according to table 4.5, is ideno(1,2,3-cd)pyrene and dibenzo(a,h) anthracene. However, these compounds had concentration below detection limit, and the results governing these two PAHs are therefore associated with uncertainty.

When analyzing the results from table 4.5, the rapid drainage time for some of the lighter PAHs is noteworthy. Naphthalene for instance, will be fully drained from the sediment in 146 days based on the modified K_d values and 36,5 days based on the default K_d values. Several of the remaining PAHs also show rapid drainage times. Equation 7, which is used to calculate the time to drain the sediment, is based on the upper 10 cm of the sediment (Bakke et al., 2011). Table B.1 shows that sediment concentrations are still detected in the upper portion of the cuttings surface, and it is thus unlikely that some of the PAHs would be fully drained from the sediment in less than one year. These rapid drainage times might indicate that the calculated leaching rates cannot be considered reliable, due to possible overestimation in the calculations.

However, other processes could influence the time to drain the sediment. The sediments might gain additional contaminants from different sources. In the context of drill cuttings piles, contaminant input could originate from produced water where the chemical constituents have settled on the sediment (Bakke et al., 2012). Another explanation could be that contaminants from deeper areas of the pile migrate up to the surface layer due to processes like diffusion and convection, as explained in chapter 5.1. In addition to this, contaminants which have leaked out to the water could have undergone sedimentation and settled on the surface of the pile due to chemical and physical properties. The probability and extent of these possible contributions is difficult to determine however, and should therefore only be regarded as factors adding to the uncertainty.

5.5 Evaluation of possible environmental impacts

Since the leaching rates of THC could not be calculated, as explained in chapter 4.1, the calculated leaching rates could not be compared to OSPARS threshold (10 tons/year) on the amount of oil that is allowed to leak out of drill cuttings piles each year. Comparison with Klif's limit values were therefor conducted to get a better understanding of the possible impacts the PAH content of the drill cuttings might pose to the environment.

5.5.1 Toxicity of the sediment concentrations

The sediment concentrations were compared to the limit values given in Klif's guidelines, see chapter 2.5.1, to get a better understanding of their possible toxicity levels. Results are given in table 4.6, and it can be observed that most of the PAHs sediment concentrations exceed the limit values, both for maximum-and mean concentrations.

Anthracene is the compound that exceeds the limit value most for both scenarios. The limit value for this PAH is low compared to the other PAHs, so low concentrations could still exceed the limit value. Ideno(1,2,3-cd)pyrene and dibenzo(a,h)anthracene had sediment concentrations below the detection limit of 0,02 mg/kg, and did not exceed the limit values.

There is a large difference in maximum and mean concentrations for most of the PAHs, and as stated in chapter 4.3.1, the samples show signs of poor homogeneity and the possibility of concentration hotspots. Since most of the PAHs exceed their limit values both for maximum and mean concentrations, the PAHs might pose negative impacts on the local sediment organisms.

5.5.2 Calculated leaching rates compared to permitted leaching rates

Since acceptance criteria for PAHs in drill cuttings piles are limited, the limit values used in Klif's risk assessment guidelines was used to get an impression of the leaching rate extent. The leaching rates were compared to how many times they exceed the permitted leaching rates which are the leaching rates that equal Klif's limit values, see table 4.7 and 4.8 .

Most of the PAHs exceed the limit values for the total leaching rate when compared to Klif's limit values. As one might expect, there are more and greater exceedance of limit values with the default Kd values than with the modified Kd values. This illustrates the importance of site specific measured data. Benzo(a)anthracene is the PAH that exceeds the limit value most, followed by anthracene. Naphthalene, which has the highest leaching rate by far, does not exceed as much as one might

think, but it also have a much higher limit value and low toxicity compared the other PAHs (Mumtaz and George, 1995) In table 4.8, it can be observed that ideno(1.2.3-cd)pyrene exceeds the limit values, but this is associated with uncertainty due to the fact that the concentration for this PAH was under the detection limit.

Although several of the PAHs leaching rates exceed the limit values, it must be kept in mind that this is based on drill cuttings piles in the North Sea, and not contaminated sediment in a harbor or fjord. The acceptance criteria are different for those two scenarios and even though the PAHs might exceed the acceptance criteria for harbors and fjords, it does not mean that it will be the same for conditions in the North Sea. The calculated leaching rates are also associated with high uncertainty, and the actual exceedance would probably not be similar to these results if the calculations were based on local measurements.

It is also a question if all processes of importance are included in the leaching calculations, as explained in section 5.1. The contribution from spreading due to organisms, *Forg*, might be overestimated and add to the total leaching rate in a unlikely matter, but this might be a minor difference since the calculated rate of *Forg* is small compared to biodiffusion, see table 5.1. In addition, the possibility that all contributing migration processes might not have been included in the total spreading calculations can add to the uncertainty.

5.3.3 Possible ecological impacts, based on PEC/PNEC ratios.

To evaluate the extent of how the organisms living in the sediment area can be affected by the PAHs, calculated pore water concentrations (PEC) was compared to limit values from Klif's guidelines given in table 2.3 (PNEC_w), as described in section 2.5.1.

Results are given in table 4.9 and 4.10 for modified and default K_d values respectively. Five of the mean pore water concentrations exceeds the PNEC values using modified K_d values, while 10 pore water concentrations exceeds the PNEC values based on the default K_d values. This confirms that the default K_d values are conservative, and might overestimate the results.

Pyrene and naphthalene shows significant ecological risk for both scenarios. When based on modified K_d values, maximum pore water concentrations exceeds the PNEC values 176 and 172 times for pyrene and naphthalene respectively. All PAHs except ideno(1,2,3-cd)pyrene and dibenzo(a,h)anthracene, which had concentrations below detection limit, exceed the limit value with the maximum pore water concentrations for both scenarios. The mean pore water concentrations shows less exceedance of limit values, but also here pyrene and naphthalene are exceeding the limit values to a large extent. This means that especially pyrene and naphthalene could affect the

sediment living organisms. Pyrene is considered one of the more toxic PAH (Mumtaz and George, 1995), and this high pore water concentration might cause toxic effects, as described with the DNA-adducts in chapter 2.4.2, in organisms living in, on or possibly near the cuttings piles.

The heavy PAHs can cause negative effects to organisms even when they are present in the environment at very low concentrations, but the results from this assessment shows that the most heavy PAHs does not exceed the limit values as much as the smaller PAHs, the only exception being benzo(ghi)perylene. However, the heavy PAHs might be more persistent, resulting in bottom dwelling organisms being exposed to the PAHs for a potentially long period. It should also be kept in mind, that this is only the PAH content of the pile, different metals, and other organic contaminants are also usually present in drill cuttings piles potentially adding to the toxicity. The potentially toxic effects are likely to be limited only to the area where the drill cuttings are located.

PEC/PNEC ratio could also be applied on sea water concentrations to investigate the possible effects on the species living in the overlaying water. However, sea water concentrations were not measured and included in the Statfjord A report. They could be calculated using equation 5, but considerable uncertainty was associated with the residence time needed to calculate the sea water concentrations. The default residence time of 0,02 years is based on conditions in harbors and fjords, and would therefore not represent the conditions in the North Sea. The North Sea is an open system with different properties governing the fate and transport of contaminants than the conditions present in harbors or fjords. Residence time could be calculated using equation 9, and an attempt to calculate the residence time was conducted, given in appendix D. However, there was too high uncertainty associated with the values, for them to be used. Area and depths are usually applied for entire harbors and not just one spot in particular. Harbors and coastal areas are usually not as deep as the North Sea where the drill cuttings at Statfjord A are located, but the contaminated areas are generally larger. Using the area covered by drill cuttings of 13 000 m², and a water depth of 150 meters, see table D.1 (Tvedten et al., 2012) would therefore possibly give unreliable results. Table D.2 and D.3 shows that all of the calculated sea water concentrations are low, and that no PAH exceeded the PNEC value for either modified or default K_d values. Based on the leaching rates, and the generally high exceedance of respective limit values for both concentrations and leaching rates, one might have expected exceedance of the limit values for at least some of the PAHs sea water concentrations. This was not the case based on the attempt to calculate the sea water concentrations given in appendix D.

It might have been possible to find a general residence time for the area in the North Sea where Statfjord A is located, but such values were not obtained.

5.6 Reliability of the calculated results

Overall, several factors of uncertainty are present with regards to the results. Parameters such as K_d and TOC, were not obtained from drill cuttings characterization reports, and therefore had to be modified, increasing the uncertainty. Site-specific measured K_d values would have given more reliable results than modified K_d values. This can be illustrated by a PAH contaminated site in Kristiansand where it was found that the total diffusion of PAH from the sediment to water was 300-800 times higher when using theoretical K_d values instead of the measured K_d values (Ruus et al., 2005). This was also the case at a PAH contaminated site in Ransfjorden, where the total diffusion rates were found to be 360-1500 kg/years using default K_d values, and 0,3-1,5 kg/year when using the measured K_d values. Both sites also found that the flux was dominated by different PAHs when using measured K_d values compared to the default K_d values. For the site in Ransfjorden, naphthalene was the dominating PAH when using default K_d values, but when the measured K_d values were applied, fluorine, phenanthrene, anthracene, fluoranthene and pyrene dominated the flux (Helland and Uriansrud, 2006). This illustrates the high uncertainty associated with the results when site-specific measured K_d values are not available. The modified K_d values used in this thesis, given in appendix C, are not as remarkably different from the default K_d values, as they might be if the K_d values were based on site-specific measurements.

The four converted TOC values given in table 4.1 originate from TOM values measured at Statfjord A. These four TOM values were the only available TOM values present at the time of this study and the full TOM analyses were not accessed in time to incorporate them into the calculations. TOC should be based on all available data to represent the actual conditions properly. And the fact that the calculations are based on only four of the samples adds to the total uncertainty. The TOM/TOC conversion method might be unreliable, as it is an old method based on soils and not sediments.

The homogeneity test, given in table 4.2 showed great variance in the mean and max sediment concentrations. Especially benzo(b)fluoranthene and naphthalene have high values. The high benzo(b)fluoranthene value could be affected by the fact that it consists of concentrations from three compounds and not one, as described in chapter 4.2.1. The high difference in max-and mean concentrations might indicate that some of the concentrations can be abnormally high compared to the larger whole. However, data from drill cuttings piles are often heterogeneous in the chemical content (Breuer et al., 2004), thus getting homogeneous data might be difficult to obtain. The guidelines do not require the homogeneity test to be met, but it can be used to get an idea of the possibility that some of the concentrations might be “hot-spots” and distinguish themselves from the other concentrations, resulting in high maximum concentrations compared to mean concentrations.

The reliability of the calculated leaching rates, given in table 4.3 and 4.4, might be associated with uncertainty, since they are based on extensive use of default values meant for conditions in harbors and coastal areas. The results shows great variance when using modified and default K_d values for instance. If site-specific measured K_d values could have been applied instead of the modified K_d values, the uncertainty would have decreased. The leaching rates would probably be reduced if such K_d values were utilized, as shown in the two examples from Kristiansand and Ransfjorden explained above. The uncertainty governing the leaching rates can also be confirmed by the rapid calculated time to drain the sediment for PAHs, given in table 4.5.

Erosion due to currents and waves have not been included in the guidelines, only erosion due to ships, which does not apply for drill cuttings located at a depth of 150 meters. In addition, there is a possibility that migration routes not included in Klif's guidelines, such as convection, might contribute to the total spreading of contaminants, as described in chapter 5.1. The fact that there might be forces acting upon the migration and spreading of contaminants in cuttings piles not included in the equations contributes to these uncertainties. The contribution by spreading due to organisms might also be unreliable, as metabolism and biotransformation of contaminants is not included in the guidelines, explained in chapter 5.1. The guidelines are set to be conservative, but this contribution could have possible effects on the total calculated spreading with regards to PAHs.

The calculations of possible toxicity and ecological impacts, given in chapter 4.4 showed that the PAHs from drill cuttings at Statfjord A might pose negative impacts on the species living in, at or possibly near the drill cuttings. The reliability of these calculations is difficult to evaluate, since they are based on several default- and modified values. However, since PAHs are considered to be the most toxic part of the oil (Bjørnesæter, 2009), negative impacts on species might be expected, although these effects are presumably mostly limited to the actual drill cuttings area.

6 Conclusion

The objective of this study is to investigate if Klif's risk assessment guidelines for contaminated sediment can be applied to estimate leaching rates of hydrocarbons from oil-based drill cuttings piles. Factors affecting oil-based drill cuttings piles and impacts cuttings piles can have on the environment have also been included in this study.

Several limitations govern the use of Klif's guidelines to determine leaching rates from oil-based drill cuttings piles. A major concern is that THC is not included in the guidelines, and loss of oil can therefore not be calculated and compared to the OSPAR threshold of 10 tons of oil/year. Several parameters which should be present, in order to exclude as many of the default values given in the guideline as possible, were deficient from drill cuttings characterization reports. Some of the parameters such as K_d - and TOC can be modified, but great uncertainty is still associated with these values. The lack of erosion, metabolism and biotransformation of contaminants in organisms, and possible convective oil releases (dependent on the form of oil present in the drill cuttings piles) in the guidelines might also contribute to uncertainty, but this is not discussed in any detail in this thesis.

Leaching rates based on biodiffusion and transport by organisms were calculated for 15 PAHs from Statfjord A, and the maximum and mean leaching rates was found to be 41,2 kg/year and 3,40 kg/year respectively, based on modified K_d values. The maximum and mean leaching rates were calculated to be 170 kg/year and 14,0 kg/year if the default K_d values were used. This large difference in leaching rates based on modified and default K_d values implies that the default values might overestimate the results. It is difficult to evaluate the reliability of the results due to the associated level of uncertainty connected to the equations, and the lack of available comparison values from similar analyses. However, the calculated time to drain the sediment of PAHs was considerable rapid for some of the lighter PAHs, which might indicate overestimations of the calculations.

With regards to the calculated environmental impact from PAHs present in the cuttings piles, it can be concluded that the leaching from the sediment might result in possible negative impacts to species living in, on or possibly near the drill cuttings piles. However, it is important to keep in mind that great uncertainty is associated with the calculated values which were compared to Klif's limit values, and this will add uncertainty to the exceedance results and following possible environmental impacts.

The results from this study show that there are several limitations when using the risk assessment guidelines to determine leaching rates from oil-based drill cuttings piles. Critical factors are deficient from both the guidelines and from drill cuttings characterization reports to be able to get reliable results and the guidelines are based on conditions in harbors and fjords and not conditions in the North Sea. This results in large uncertainties with regards to the calculated results. The sum of all the uncertainties indicates that the present guideline is not feasible to use in the context to determine leaching rates from oil-contaminated drill cuttings piles.

Modifications could be conducted to possibly get more reliable results if the guidelines were to be used to find leaching rates from drill cuttings in the future:

- Physical analyses could be implemented with the purpose to gather relevant local information needed to get reliable results.
- Attempt to include THC in the guidelines, so that total loss of oil could be calculated and compared to OSPARS threshold value of 10 tons/year.
- Include erosion generated by factors governing depths where cuttings piles are located such as currents and waves, and possibly incorporate erosion due to anthropogenic activities such as relocation of cuttings piles or trawling activities.
- Include default values based on conditions governing drill cuttings piles rather than sediments in harbors and fjords.
- Evaluate the possibility to include oil release mechanisms not included in the present guidelines, such as convection, that might contribute to the total spreading rates. And to consider how metabolism and biotransformation of certain chemicals might affect the spreading due to transport by organisms.

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Appendix A: Chemical and physical properties for EPAs 16 PAHs

Table A.1 Overview of physical and chemical data for 16 PAH (Bakke et al., 2011)

| Compound | D_s (cm^2/s) | K_d sed (l/kg) 1 % TOC | log Kow | Koc | Molecular weight (g/mole) |
|------------------------|-------------------------------------|-----------------------------|---------|---------|------------------------------|
| Naphthalene | 8,61E-06 | 13 | 3,33 | 1250 | 128,2 |
| Acenaphthylene | 7,69E-06 | 26 | 4,00 | 2570 | 150,2 |
| Acenaphthene | 7,55E-06 | 62 | 4,20 | 6166 | 154,2 |
| Fluorene | 7,16E-06 | 102 | 4,32 | 10233 | 166,2 |
| Phenanthrene | 6,81E-06 | 229 | 4,57 | 22909 | 178,2 |
| Anthracene | 6,81E-06 | 282 | 4,68 | 28184 | 178,2 |
| Fluoranthene | 6,22E-06 | 1445 | 5,23 | 144544 | 202,4 |
| Pyrene | 6,22E-06 | 589 | 5,13 | 58884 | 202,4 |
| Benzo(a)anthracene | 5,71E-06 | 5012 | 5,91 | 501187 | 228,3 |
| Chrysene | 5,71E-06 | 3981 | 5,81 | 398107 | 228,3 |
| Benzo(b)fluoranthene | 5,32E-06 | 8128 | 6,11 | 812831 | 252,3 |
| Benzo(k)fluoranthene | 5,32E-06 | 7943 | 6,11 | 794328 | 252,3 |
| Benzo(a)pyrene | 5,32E-06 | 8317 | 6,13 | 831764 | 252,3 |
| Indeno(1,2,3-cd)pyrene | 4,99E-06 | 23442 | 6,87 | 2344229 | 276,3 |
| Dibenzo(a,h)anthracene | 4,96E-06 | 19498 | 6,75 | 1949845 | 278,4 |
| Benzo(ghi)perylene | 4,99E-06 | 10233 | 6,22 | 1023293 | 276,3 |

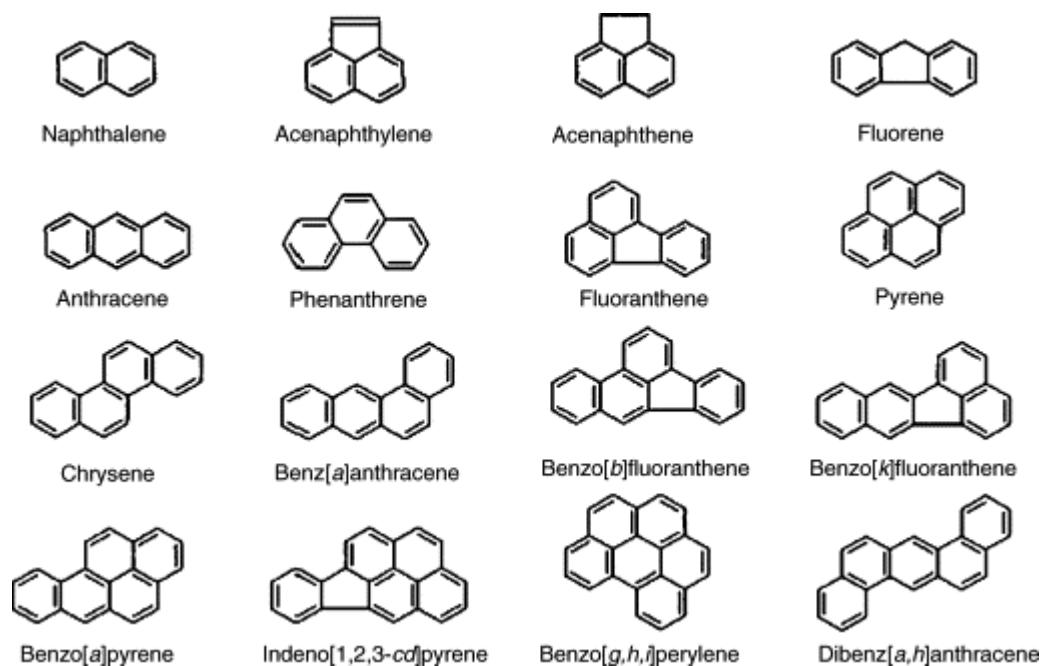


Figure A.1 The chemical structure of EPAs 16 PAHs (Anyakora et al., 2005)

Appendix B: PAH sediment concentration from Statfjord A

Table B. Sediment PAH concentrations (mg/kg dry sediment) analysed from grab samples (G), large gravity corer (LC) and short corer (SC) with the aid of ROV, from the drill cuttings at Statfjord A (Tvedten et al., 2012)

| Component | G10 | | | | G16 | | | | |
|--------------------------|--------|--------|--------|-------------|--------|--------|--------|------------|--------------|
| | 0-1 cm | 1-3 cm | 3-6 cm | sampleprøve | 0-1 cm | 1-3 cm | 3-6 cm | + 6 Bulk a | +6 cm Bulk b |
| Naphthalene | 3.50 | 0.154 | <0.02 | <0.02 | 0.088 | <0.02 | <0.02 | 0.137 | <0.02 |
| Acenaphthylene | 0.049 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | 0.547 | <0.02 |
| Acenaphthene | 0.253 | 0.033 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | 0.190 | <0.02 |
| Fluorene | 0.188 | 0.038 | 0.071 | 0.022 | <0.02 | <0.02 | <0.02 | 0.304 | <0.02 |
| Phenanthren | 1.58 | 0.158 | 0.042 | 0.024 | 0.146 | 0.057 | 0.042 | 0.574 | 0.022 |
| Anthracene | 0.137 | 0.033 | 0.027 | <0.02 | 0.023 | 0.023 | 0.021 | 0.528 | <0.02 |
| Fluoranthene | 1.04 | 0.030 | 0.020 | <0.02 | 0.077 | 0.029 | 0.076 | 1.09 | <0.02 |
| Pyrene | 0.979 | 0.078 | 0.067 | 0.048 | 0.088 | 0.115 | 0.135 | 5.67 | 0.025 |
| Benzo(a)anthracene | 0.905 | 0.065 | <0.02 | <0.02 | 0.023 | 0.020 | <0.02 | 1.28 | <0.02 |
| Chrysene | 0.652 | 0.025 | <0.02 | <0.02 | 0.031 | 0.027 | <0.02 | 1.50 | <0.02 |
| benzo(b/j/k)fluoranthene | 0.745 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | 0.251 | <0.02 |
| Benzo(a)pyrene | 0.376 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | 0.179 | <0.02 |
| Dibenzo(a,h)anthracene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Indeno(1.2.3-cd)pyrene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Benzo(ghi)perylene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | 0.065 | <0.02 |

| Component | G15 | | | | G22 | | | |
|----------------|--------|--------|--------|---------|--------|--------|--------|---------|
| | 0-1 cm | 1-3 cm | 3-6 cm | +6 Bulk | 0-1 cm | 1-3 cm | 3-6 cm | +6 Bulk |
| Naphthalene | 0.021 | 0.032 | 0.083 | <0.02 | 0.420 | 0.079 | 0.057 | <0.02 |
| Acenaphthylene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | 0.116 | 0.114 | <0.02 |
| Acenaphthene | <0.02 | <0.02 | <0.02 | <0.02 | 0.056 | 0.062 | 0.062 | <0.02 |
| Fluorene | <0.02 | <0.02 | <0.02 | <0.02 | 0.060 | 0.162 | 0.138 | <0.02 |
| Phenanthren | 0.039 | 0.054 | 0.059 | 0.039 | 0.292 | 0.506 | 0.362 | 0.042 |
| Anthracene | <0.02 | <0.02 | <0.02 | <0.02 | 0.068 | 0.166 | 0.205 | <0.02 |

| | | | | | | | | |
|--------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| Fluoranthene | 0.054 | 0.158 | 0.026 | 0.033 | 0.188 | 0.228 | 0.362 | 0.048 |
| Pyrene | 0.054 | 0.176 | 0.085 | 0.105 | 0.324 | 1.07 | 1.24 | 0.181 |
| Benzo(a)anthracene | 0.021 | 0.353 | 0.026 | <0.02 | 0.196 | 0.427 | 0.481 | <0.02 |
| Chrysene | 0.032 | 0.443 | 0.078 | <0.02 | 0.268 | 0.609 | 0.653 | <0.02 |
| benzo(b/j/k)fluoranthene | <0.02 | 0.241 | <0.02 | <0.02 | 0.104 | 0.128 | 0.133 | <0.02 |
| Benzo(a)pyrene | <0.02 | 0.248 | <0.02 | <0.02 | 0.084 | 0.091 | 0.114 | <0.02 |
| Dibenzo(a,h)anthracene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Indeno(1.2.3-cd)pyrene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Benzo(ghi)perylene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |

| Component | G21 | | | | G14 | | |
|--------------------------|--------|--------|--------|---------|--------|--------|--------|
| | 0-1 cm | 1-3 cm | 3-6 cm | +6 Bulk | 0-1 cm | 1-3 cm | 3-6 cm |
| Naphthalene | 0.488 | 0.097 | 0.068 | 0.048 | 0.083 | 0.046 | 0.071 |
| Acenaphthylene | 0.027 | 0.030 | 0.032 | 0.173 | 0.022 | 0.043 | 0.123 |
| Acenaphthene | 0.048 | 0.036 | 0.037 | 0.070 | 0.116 | 0.040 | 0.057 |
| Fluorene | 0.043 | 0.054 | 0.047 | 0.140 | 0.044 | 0.069 | 0.166 |
| Phenanthren | 0.397 | 0.230 | 0.116 | 0.423 | 0.560 | 0.082 | 0.644 |
| Anthracene | 0.059 | 0.115 | 0.026 | 0.074 | 0.161 | 0.063 | 0.152 |
| Fluoranthene | 0.091 | 0.236 | 0.210 | 0.670 | 0.987 | 0.340 | 0.455 |
| Pyrene | 0.199 | 0.466 | 0.515 | 1.31 | 1.12 | 0.775 | 1.54 |
| Benzo(a)anthracene | 0.263 | 0.218 | 0.326 | 0.530 | 0.904 | 0.393 | 0.616 |
| Chrysene | 0.333 | 0.290 | 0.420 | 0.725 | 1.22 | 0.544 | 0.838 |
| benzo(b/j/k)fluoranthene | 0.172 | 0.091 | 0.163 | 0.166 | 1.22 | 0.129 | 0.081 |
| Benzo(a)pyrene | 0.204 | 0.091 | 0.110 | 0.121 | 0.455 | 0.086 | 0.133 |
| Dibenzo(a,h)anthracene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Indeno(1.2.3-cd)pyrene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Benzo(ghi)perylene | 0.021 | <0.02 | <0.02 | <0.02 | 0.261 | <0.02 | <0.02 |

| Component | G11 | | | | G26 | | |
|--------------------------|--------|--------|--------|---------|--------|--------|--------|
| | 0-1 cm | 1-3 cm | 3-6 cm | +6 Bulk | 0-1 cm | 1-3 cm | 3-6 cm |
| Naphthalene | <0.02 | 0.023 | <0.02 | <0.02 | 0.022 | 0.115 | <0.02 |
| Acenaphthylene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | 0.031 |
| Acenaphthene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Fluorene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Phenanthren | <0.02 | 0.027 | 0.024 | <0.02 | <0.02 | 0.047 | 0.107 |
| Anthracene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | 0.023 | <0.02 |
| Fluoranthene | <0.02 | <0.02 | 0.027 | <0.02 | <0.02 | <0.02 | 0.040 |
| Pyrene | <0.02 | 0.023 | 0.071 | <0.02 | 0.039 | 0.062 | 0.328 |
| Benzo(a)anthracene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | 0.040 |
| Chrysene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | 0.026 | 0.034 |
| benzo(b/j/k)fluoranthene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Benzo(a)pyrene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Dibenzo(a,h)anthracene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Indeno(1.2.3-cd)pyrene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Benzo(ghi)perylene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |

| Component | G8 | | | | G5 | | | |
|----------------|--------|--------|--------|-------|--------|--------|--------|---------|
| | 0-1 cm | 1-3 cm | 3-6 cm | Rest | 0-1 cm | 1-3 cm | 3-6 cm | 6-17 cm |
| Naphthalene | 0.2 | 0.25 | 0.394 | 0.639 | 0.70 | 0.15 | 0.497 | 0.8 |
| Acenaphthylene | 1.1 | 0.41 | 1.453 | 1.205 | 0.99 | 0.25 | 0.714 | 1.3 |
| Acenaphthene | 1.4 | 0.98 | 2.370 | 1.529 | 3.09 | 1.16 | 1.783 | 3.2 |
| Fluorene | 0.8 | 0.13 | 2.058 | 1.103 | 3.54 | 7.33 | 2.460 | 5.0 |
| Phenanthren | 0.4 | 0.08 | 0.180 | 0.426 | 0.33 | 0.13 | 0.034 | 0.2 |
| Anthracene | 0.1 | 0.09 | 0.139 | 0.392 | 0.30 | 0.13 | 0.040 | 0.0 |
| Fluoranthene | 0.1 | 0.10 | 0.075 | 0.072 | 0.25 | 0.04 | 0.069 | 0.0 |
| Pyrene | 0.2 | 0.17 | 0.105 | 0.089 | 0.19 | 0.04 | 0.069 | 0.1 |

| | | | | | | | | |
|--------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| Benzo(a)anthracene | 0.2 | 0.04 | 0.041 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Chrysene | 0.2 | 0.08 | 0.041 | 0.034 | <0.02 | <0.02 | <0.02 | <0.02 |
| benzo(b/j/k)fluoranthene | 0.1 | 0.02 | 0.023 | 0.030 | <0.02 | <0.02 | <0.02 | <0.02 |
| Benzo(a)pyrene | <0.02 | 0.05 | 0.139 | 0.068 | <0.02 | <0.02 | <0.02 | <0.02 |
| Dibenzo(a,h)anthracene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Indeno(1.2.3-cd)pyrene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Benzo(ghi)perylene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |

| Component | G20 | | | | G4 | | | |
|--------------------------|--------|--------|--------|-------|--------|--------|--------|-------|
| | 0-1 cm | 1-3 cm | 3-6 cm | Rest | 0-1 cm | 1-3 cm | 3-6 cm | Rest |
| Naphthalene | 0.137 | 0.136 | 0.115 | 0.473 | 1.60 | 0.584 | 0.401 | 0.655 |
| Acenaphthylene | 0.267 | 0.224 | 0.263 | 0.204 | 0.353 | 0.336 | 0.435 | 0.263 |
| Acenaphthene | 0.059 | 0.117 | 0.109 | 0.085 | 0.037 | 0.135 | 0.139 | 0.181 |
| Fluorene | 0.052 | 0.029 | <0.02 | 0.031 | 0.079 | 0.057 | 0.053 | 0.049 |
| Phenanthren | 0.150 | 0.141 | 0.099 | 0.816 | 0.189 | 0.122 | 0.201 | 0.700 |
| Anthracene | 0.183 | 0.180 | 0.102 | 0.642 | 0.171 | 0.153 | 0.096 | 0.613 |
| Fluoranthene | 0.431 | 0.375 | 0.408 | 0.519 | 0.274 | 0.257 | 0.354 | 0.655 |
| Pyrene | 0.835 | 0.862 | 0.796 | 1.05 | 0.597 | 0.445 | 0.822 | 1.77 |
| Benzo(a)anthracene | 0.444 | 0.380 | 0.411 | 0.465 | 0.968 | 0.571 | 0.865 | 0.729 |
| Chrysene | 0.202 | 0.170 | 0.211 | 0.196 | 0.469 | 0.257 | 0.349 | 0.268 |
| benzo(b/j/k)fluoranthene | 0.059 | 0.088 | 0.086 | 0.065 | 0.104 | 0.092 | 0.201 | 0.091 |
| Benzo(a)pyrene | 0.196 | 0.132 | 0.128 | 0.181 | 0.469 | 0.209 | 0.282 | 0.243 |
| Dibenzo(a,h)anthracene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Indeno(1.2.3-cd)pyrene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Benzo(ghi)perylene | <0.02 | <0.02 | <0.02 | <0.02 | 0.067 | 0.052 | 0.024 | <0.02 |

| Component | G9 | | | |
|----------------|--------|--------|--------|-------|
| | 0-1 cm | 1-3 cm | 3-6 cm | Bulk |
| Naphthalene | <0.02 | <0.02 | <0.02 | <0.02 |
| Acenaphthylene | <0.02 | <0.02 | <0.02 | <0.02 |

| | | | | |
|--------------------------|-------|-------|-------|-------|
| Acenaphthene | <0.02 | <0.02 | <0.02 | <0.02 |
| Fluorene | <0.02 | <0.02 | <0.02 | <0.02 |
| Phenanthren | <0.02 | 0.038 | 0.060 | 0.023 |
| Anthracene | <0.02 | 0.044 | <0.02 | <0.02 |
| Fluoranthene | <0.02 | 0.022 | 0.087 | 0.044 |
| Pyrene | <0.02 | 0.052 | 0.141 | 0.084 |
| Benzo(a)anthracene | <0.02 | <0.02 | <0.02 | <0.02 |
| Chrysene | <0.02 | <0.02 | <0.02 | <0.02 |
| benzo(b/j/k)fluoranthene | <0.02 | <0.02 | <0.02 | <0.02 |
| Benzo(a)pyrene | <0.02 | <0.02 | <0.02 | <0.02 |
| Dibenzo(a,h)anthracene | <0.02 | <0.02 | <0.02 | <0.02 |
| Indeno(1.2.3-cd)pyrene | <0.02 | <0.02 | <0.02 | <0.02 |
| Benzo(ghi)perylene | <0.02 | <0.02 | <0.02 | <0.02 |

| Component | LC2 | | | | | |
|--------------------------|---------|----------|----------|-----------|------------|------------|
| | 0-20 cm | 20-40 cm | 40-80 cm | 80-100 cm | 100-120 cm | 120-140 cm |
| Naphthalene | 8.15 | 7.84 | 8.41 | 4.88 | 1.42 | 3.91 |
| Acenaphthylene | 0.025 | 0.038 | 0.028 | 0.027 | 0.057 | 0.022 |
| Acenaphthene | 0.908 | 0.924 | 0.774 | 0.563 | 0.917 | 0.577 |
| Fluorene | 1.48 | 0.466 | 0.603 | 0.480 | 0.870 | 0.230 |
| Phenanthren | 4.23 | 3.68 | 2.81 | 2.24 | 2.27 | 1.33 |
| Anthracene | 0.297 | 0.455 | 0.367 | 0.241 | 0.451 | 0.396 |
| Fluoranthene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Pyrene | 0.829 | 0.504 | 0.195 | 0.282 | 0.543 | <0.02 |
| Benzo(a)anthracene | 0.022 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Chrysene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| benzo(b/j/k)fluoranthene | 0.140 | 1.38 | 4.60 | 1.47 | <0.02 | <0.02 |
| Benzo(a)pyrene | 0.227 | 0.929 | 1.22 | 3.39 | <0.02 | <0.02 |
| Dibenzo(a,h)anthracene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Indeno(1.2.3-cd)pyrene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |

| | | | | | | |
|--------------------|-------|-------|-------|-------|-------|-------|
| Benzo(ghi)perylene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
|--------------------|-------|-------|-------|-------|-------|-------|

| Component | LC5 | | | | |
|--------------------------|--------|---------|-----------|------------|------------|
| | 0-8 cm | 8-97 cm | 97-115 cm | 115-165 cm | 165-240 cm |
| Naphthalene | 1.83 | 7.95 | 17.5 | 22.2 | 18.1 |
| Acenaphthylene | 1.11 | 0.045 | 0.808 | 0.183 | 0.123 |
| Acenaphthene | 1.93 | 1.68 | 3.68 | 3.85 | 3.05 |
| Fluorene | 4.25 | 0.704 | 3.99 | 1.88 | 2.83 |
| Phenanthren | 0.671 | 3.60 | 7.66 | 5.12 | 7.13 |
| Anthracene | 0.233 | 0.609 | 0.982 | 1.97 | 0.672 |
| Fluoranthene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Pyrene | 0.124 | 7.70 | 1.88 | 9.89 | <0.02 |
| Benzo(a)anthracene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Chrysene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| benzo(b/j/k)fluoranthene | <0.02 | <0.02 | <0.02 | <0.02 | 0.140 |
| Benzo(a)pyrene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Dibenzo(a,h)anthracene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Indeno(1.2.3-cd)pyrene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Benzo(ghi)perylene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |

| Component | LC6 | | | | |
|----------------|---------|----------|----------|----------|----------|
| | 0-10 cm | 10-20 cm | 20-30 cm | 30-40 cm | 40-50 cm |
| Naphthalene | 0.076 | 0.063 | 0.148 | 0.035 | 0.050 |
| Acenaphthylene | 0.092 | 0.099 | 0.475 | 0.079 | 0.053 |
| Acenaphthene | 0.060 | 0.091 | 0.769 | 0.171 | 0.109 |
| Fluorene | 0.029 | 0.045 | 0.935 | 0.107 | 0.049 |
| Phenanthren | 0.251 | 0.971 | 2.57 | 0.674 | 0.186 |

| | | | | | |
|--------------------------|-------|-------|-------|-------|-------|
| Anthracene | 0.083 | 0.971 | 3.49 | 1.15 | 0.299 |
| Fluoranthene | 0.479 | 0.635 | 1.27 | 0.407 | 0.592 |
| Pyrene | 0.914 | 1.57 | 2.51 | 0.462 | 0.320 |
| Benzo(a)anthracene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Chrysene | 0.054 | 0.037 | <0.02 | <0.02 | <0.02 |
| benzo(b/j/k)fluoranthene | 0.029 | 0.024 | <0.02 | <0.02 | <0.02 |
| Benzo(a)pyrene | 0.032 | 0.059 | <0.02 | <0.02 | <0.02 |
| Dibenzo(a,h)anthracene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Indeno(1.2.3-cd)pyrene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Benzo(ghi)perylene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |

| Component | SC1 | | SC2 | SC5 | |
|--------------------------|--------|---------|--------|--------|---------|
| | 0-2 cm | 2-19 cm | 0-8 cm | 0-2 cm | 2-21 cm |
| Naphthalene | 0.641 | 0.552 | 1.10 | 0.173 | 0.322 |
| Acenaphthylene | 0.201 | 0.639 | 0.070 | 0.048 | 0.564 |
| Acenaphthene | 0.685 | 0.602 | 0.246 | 0.143 | 0.838 |
| Fluorene | 0.247 | 0.196 | 0.428 | 0.068 | 0.250 |
| Phenanthren | 0.832 | 2.03 | 0.974 | 0.245 | 1.90 |
| Anthracene | 1.00 | 0.835 | 0.147 | 0.136 | 1.19 |
| Fluoranthene | 0.667 | 1.55 | 1.08 | 0.194 | 3.85 |
| Pyrene | 0.756 | 1.60 | 0.249 | 0.476 | 3.79 |
| Benzo(a)anthracene | <0.02 | <0.02 | <0.02 | 0.762 | 2.72 |
| Chrysene | 0.022 | 0.024 | <0.02 | 0.109 | 0.370 |
| benzo(b/j/k)fluoranthene | 0.032 | 0.060 | <0.02 | 0.031 | 0.027 |
| Benzo(a)pyrene | 0.043 | 0.073 | 0.064 | 0.102 | 0.154 |
| Dibenzo(a,h)anthracene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Indeno(1.2.3-cd)pyrene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Benzo(ghi)perylene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |

| Component | SC7 | | SC10 | | SC11 | |
|--------------------------|--------|--------|--------|---------|--------|--------|
| | 0-5 cm | 5-8 cm | 0-5 cm | 5-23 cm | 0-5 cm | 5-9 cm |
| Naphthalene | 0.065 | 0.252 | 0.452 | 1.17 | 1.85 | 10.6 |
| Acenaphthylene | 0.086 | 1.17 | 0.659 | 1.29 | 0.292 | 1.71 |
| Acenaphthene | 0.056 | 0.623 | 0.519 | 1.77 | 0.385 | 2.53 |
| Fluorene | 0.035 | 1.25 | 1.88 | 1.83 | 0.949 | 0.384 |
| Phenanthren | 0.282 | 1.29 | 0.683 | 0.306 | 1.91 | 1.07 |
| Anthracene | 0.137 | 2.74 | 0.201 | 0.267 | 0.915 | 1.64 |
| Fluoranthene | 0.489 | 5.43 | 0.066 | 0.064 | 2.53 | 0.605 |
| Pyrene | 1.13 | 4.77 | 0.098 | 0.047 | 2.21 | 2.04 |
| Benzo(a)anthracene | 1.12 | 2.49 | <0.02 | <0.02 | 0.983 | 0.518 |
| Chrysene | 0.223 | 0.250 | <0.02 | <0.02 | 0.091 | <0.02 |
| benzo(b/j/k)fluoranthene | <0.02 | 0.137 | <0.02 | <0.02 | 0.130 | 0.070 |
| Benzo(a)pyrene | 0.067 | 0.113 | 0.024 | 0.028 | 0.125 | 0.333 |
| Dibenzo(a,h)anthracene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Indeno(1.2.3-cd)pyrene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Benzo(ghi)perylene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |

| Component | SC15 | | SC16 | | SC17 | | SC19 | |
|--------------------|--------|--------|--------|---------|--------|---------|--------|---------|
| | 0-2 cm | 2-7 cm | 0-3 cm | 3-12 cm | 0-2 cm | 2-17 cm | 0-5 cm | 5-16 cm |
| Naphthalene | 0.116 | 0.153 | 0.706 | 0.214 | 0.083 | 0.155 | <0.02 | <0.02 |
| Acenaphthylene | 0.039 | 0.151 | 0.098 | 1.19 | 0.080 | 0.084 | <0.02 | <0.02 |
| Acenaphthene | 0.039 | 0.200 | 0.052 | 1.26 | 0.067 | 0.087 | <0.02 | <0.02 |
| Fluorene | 0.026 | 0.311 | 0.101 | 1.03 | 0.067 | 0.035 | <0.02 | <0.02 |
| Phenanthren | 0.223 | 1.389 | 0.621 | 5.07 | 0.224 | 0.287 | 0.036 | 0.031 |
| Anthracene | 0.042 | 0.842 | 0.110 | 3.76 | 0.090 | 0.074 | <0.02 | <0.02 |
| Fluoranthene | 0.223 | 3.23 | 0.391 | 4.12 | 0.282 | 0.303 | 0.107 | 0.148 |
| Pyrene | 0.213 | 0.582 | 0.508 | 7.81 | 0.647 | 0.555 | 0.071 | 0.033 |
| Benzo(a)anthracene | 0.265 | 0.752 | 0.758 | 1.43 | 0.343 | 0.348 | <0.02 | <0.02 |

| | | | | | | | | |
|--------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| Chrysene | 0.035 | 0.165 | 0.144 | 0.631 | 0.083 | 0.132 | <0.02 | <0.02 |
| benzo(b/j/k)fluoranthene | <0.02 | <0.02 | <0.02 | <0.02 | 0.032 | 0.026 | <0.02 | <0.02 |
| Benzo(a)pyrene | 0.090 | 0.265 | 0.251 | 0.201 | 0.032 | 0.100 | <0.02 | <0.02 |
| Dibenzo(a,h)anthracene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Indeno(1.2.3-cd)pyrene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Benzo(ghi)perylene | <0.02 | <0.02 | 0.043 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |

| Component | SC27 | | SC28 | SC29 | SC36 | |
|--------------------------|--------|--------|--------|--------|--------|--------|
| | 0-4 cm | 4-6 cm | 0-6 cm | 0-5 cm | 0-4 cm | 4-9 cm |
| Naphthalene | 0.093 | 0.090 | <0.02 | 0.048 | 0.060 | 0.094 |
| Acenaphthylene | 0.140 | 0.116 | 0.026 | 0.072 | 0.071 | 0.026 |
| Acenaphthene | 0.140 | 0.060 | <0.02 | 0.070 | 0.060 | <0.02 |
| Fluorene | 0.061 | <0.02 | 0.029 | 0.041 | 0.021 | <0.02 |
| Phenanthren | 0.695 | 0.645 | 0.104 | 0.590 | 0.217 | 0.221 |
| Anthracene | 0.625 | 0.520 | 0.057 | 0.235 | 0.036 | 0.059 |
| Fluoranthene | 0.985 | 1.20 | 0.070 | 0.585 | 0.310 | 0.375 |
| Pyrene | 2.31 | 1.79 | 0.761 | 2.76 | 0.441 | 0.395 |
| Benzo(a)anthracene | 0.855 | 0.650 | 0.169 | 0.892 | 0.648 | 0.294 |
| Chrysene | 0.169 | 0.139 | 0.052 | 0.043 | 0.078 | 0.061 |
| benzo(b/j/k)fluoranthene | <0.02 | <0.02 | <0.02 | 0.197 | 0.153 | <0.02 |
| Benzo(a)pyrene | 0.471 | 0.151 | <0.02 | 0.168 | 0.075 | 0.064 |
| Dibenzo(a,h)anthracene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Indeno(1.2.3-cd)pyrene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Benzo(ghi)perylene | 0.044 | <0.02 | <0.02 | 0.072 | <0.02 | <0.02 |

| Component | SC37 | | SC42 | SC51 | |
|----------------|--------|---------|--------|--------|----------|
| | 0-8 cm | 8-20 cm | 0-3 cm | 0-1 cm | 1-7.5 cm |
| Naphthalene | 1.98 | 9.14 | 0.067 | 0.086 | 0.070 |
| Acenaphthylene | 0.466 | 1.53 | <0.02 | 0.047 | 0.340 |
| Acenaphthene | 1.03 | 1.99 | <0.02 | 0.037 | 0.136 |

| | | | | | |
|--------------------------|-------|-------|-------|-------|-------|
| Fluorene | 0.153 | 0.915 | <0.02 | 0.023 | 0.112 |
| Phenanthren | 1.48 | 1.99 | 0.104 | 0.243 | 0.390 |
| Anthracene | 0.369 | 2.24 | 0.024 | 0.047 | 0.556 |
| Fluoranthene | 0.611 | 3.65 | 0.091 | 0.186 | 1.55 |
| Pyrene | 1.10 | 4.46 | 0.146 | 0.365 | 4.44 |
| Benzo(a)anthracene | 0.837 | 3.78 | 0.115 | 0.306 | 0.607 |
| Chrysene | 0.130 | 0.384 | <0.02 | 0.073 | 0.254 |
| benzo(b/j/k)fluoranthene | 0.127 | 0.067 | 0.055 | <0.02 | 0.088 |
| Benzo(a)pyrene | 0.150 | 0.510 | <0.02 | 0.286 | 0.131 |
| Dibenzo(a,h)anthracene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Indeno(1.2.3-cd)pyrene | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Benzo(ghi)perylene | 0.023 | <0.02 | 0.022 | 0.083 | <0.02 |

Appendix C: Modified K_d values.

Table C.1 Modified K_d values, based on the average TOC content measured in the drill cuttings at Statfjord A

| Compound | K _{d sed} (l/kg) modified to applied %TOC |
|------------------------|--|
| Naphthalene | 54 |
| Acenaphthylene | 108 |
| Acenaphthene | 257 |
| Fluorene | 422 |
| Phenanthrene | 948 |
| Anthracene | 1167 |
| Fluoranthene | 5982 |
| Pyrene | 2438 |
| Benzo(a)anthracene | 20750 |
| Chrysene | 16481 |
| Benzo(b)fluoranthene | 33650 |
| Benzo(a)pyrene | 34432 |
| Indeno(1,2,3-cd)pyrene | 97050 |
| Dibenzo(a,h)anthracene | 80722 |
| Benzo(ghi)perylene | 42365 |

Appendix D: Calculation of sea water concentrations.

Area, depth and current speed near the contaminated area at Statfjord A is given in table D.1.

Table D.1 Physical parameters from the cuttings piles at Statfjord A (Tvedten et al., 2012)

| Parameter | Value |
|-----------------------------|--------|
| Area (m ²) | 13 000 |
| Depth (m) | 150 |
| Average current speed (m/s) | 0,13 |

Residence time for the water in the drill cuttings area was found by current speed and volume information. The mean seabed currents at Statfjord A are measured to be around 8-17 cm/s (Tvedten et al., 2012), which is relatively moderate. By multiplying the average value of 13 cm/s by the contaminated area, the flow rate was found to be 1690 m³/s. The residence time was then found to be 3,65 x 10⁻⁵ years, using equation 9.

Table D.2 Calculated seawater concentrations (PEC) compared to PNEC_w based on modified K_d values.

| Compound | Calculated sea water concentrations (PEC) | | Limit value for ecological risk PNEC _w (mg/l) | Calculated sea water concentrations compared to PNEC _w (number of times): | |
|------------------------|---|------------------------------|--|--|------|
| | C _{sw, max} (mg/l) | C _{sw, mean} (mg/l) | | Max | Mean |
| Naphthalene | 6,28E-07 | 4,75E-08 | 2,40E-03 | | |
| Acenaphthylene | 2,16E-08 | 3,46E-09 | 1,30E-03 | | |
| Acenaphthene | 2,00E-08 | 2,99E-09 | 3,80E-03 | | |
| Fluorene | 2,20E-08 | 1,83E-09 | 2,50E-03 | | |
| Phenanthrene | 9,72E-09 | 1,17E-09 | 1,30E-03 | | |
| Anthracene | 3,88E-09 | 4,17E-10 | 1,10E-04 | | |
| Fluoranthene | 9,98E-10 | 9,86E-11 | 1,20E-04 | | |
| Pyrene | 4,46E-09 | 4,68E-10 | 2,30E-05 | | |
| Benzo(a)anthracene | 1,84E-10 | 1,79E-11 | 1,20E-05 | | |
| Chrysene | 7,47E-11 | 9,21E-12 | 7,00E-05 | | |
| Benzo(b)fluoranthene | 1,29E-10 | 4,51E-12 | 3,00E-05 | | |
| Benzo(a)pyrene | 9,26E-11 | 4,52E-12 | 5,00E-05 | | |
| Indeno(1,2,3-cd)pyrene | 1,82E-13 | 1,82E-13 | 2,00E-06 | | |
| Dibenzo(a,h)anthracene | 2,17E-13 | 2,17E-13 | 3,00E-05 | | |
| Benzo(ghi)perylene | 5,43E-12 | 5,35E-13 | 2,00E-06 | | |

Table D.3 Calculated seawater concentrations compared to PNEC_w based on default K_d values.

| Compound | Calculated sea water concentrations (PEC) | | Limit value for ecological risk PNEC _w (mg/l) | Calculated sea water concentrations compared to PNEC _w (number of times): | |
|------------------------|---|------------------------------|--|--|------|
| | C _{sw, max} (mg/l) | C _{sw, mean} (mg/l) | | Max | Mean |
| Naphthalene | 2,60E-06 | 1,97E-07 | 2,40E-03 | | |
| Acenaphthylene | 8,94E-08 | 1,43E-08 | 1,30E-03 | | |
| Acenaphthene | 8,29E-08 | 1,24E-08 | 3,80E-03 | | |
| Fluorene | 9,09E-08 | 7,57E-09 | 2,50E-03 | | |
| Phenanthrene | 4,03E-08 | 4,86E-09 | 1,30E-03 | | |
| Anthracene | 1,60E-08 | 1,73E-09 | 1,10E-04 | | |
| Fluoranthene | 4,13E-09 | 4,08E-10 | 1,20E-04 | | |
| Pyrene | 1,85E-08 | 1,94E-09 | 2,30E-05 | | |
| Benzo(a)anthracene | 7,61E-10 | 7,39E-11 | 1,20E-05 | | |
| Chrysene | 3,09E-10 | 3,81E-11 | 7,00E-05 | | |
| Benzo(b)fluoranthene | 5,32E-10 | 1,87E-11 | 3,00E-05 | | |
| Benzo(a)pyrene | 3,83E-10 | 1,87E-11 | 5,00E-05 | | |
| Indeno(1,2,3-cd)pyrene | 7,52E-13 | 7,52E-13 | 2,00E-06 | | |
| Dibenzo(a,h)anthracene | 8,99E-13 | 8,99E-13 | 3,00E-05 | | |
| Benzo(ghi)perylene | 2,25E-11 | 2,22E-12 | 2,00E-06 | | |