NorthPestClean: Remediation Stop Criteria
Phase A: Conceptual development and identification of data needs

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**Summary**

The Remediation Stop Criteria project is part of the EU Life project, NorthPestClean. The NorthPestClean project aims at demonstrating the efficacy of *in situ* alkaline hydrolysis for remediation of organophosphate insecticides at a contaminated site, Høfde 42 (Groyne 42), located at the Danish West Coast. This report is the outcome of the initial phase of the Remediation Stop Criteria project, which has focused on conceptual development of the risk assessment approach.

In this phase of the project, the existing data with relevance for the later risk assessment and determination of remediation stop criteria have been summarised. A simplified conceptual model has been introduced based on the available data on geology, hydrology and distribution of contaminants. The conceptual model can be used at the current level of understanding, but the risk assessment modelling will be more certain if additional information on the contaminant levels is obtained.

The alkaline hydrolysis transforms the organophosphate insecticides into more water soluble compounds. These are expected to be largely removed during the drainage cycles of the remedial method. The most important focus compounds in connection with the risk assessment are assessed to be the organophosphate parent compounds (ethyl parathion, methyl parathion, malathion and ethyl sulfotep), which are highly toxic and present as DNAPL. Additional focus compounds can include: the main hydrolysis products (EP2-acid, MP2-acid and *p*-nitrophenol), ethyl amino parathion, 4-chloro-*o*-cresol, and mercury if mobilised by alkaline hydrolysis. The focus compounds can be altered if more relevant compounds are identified in connection with the pilot scale remediation in 2012.

The risk assessment will be based on the reverse risk assessment approach, where the long-term criteria for the North Sea (environmental quality standards) are transformed into acceptable contaminant levels at the source area (remediation stop criteria). The approach includes the definition of the acceptable impacts on the North Sea and a combination of models to determine the dilution of the leachate from the source area. The dilution in the North Sea will be determined based on a local 2D depth integrated numerical model (MIKE21 by DHI), which considers tidal effects, regional weather systems and local wind condition. The dilution between the source area and the discharge point to the North Sea will be determined by 3D numerical modelling (FEFLOW) and simple leaching calculations. Six scenarios are suggested for the 3D modelling, namely: the baseline situation, uniform deterioration of the barriers (excluding or including the cover membrane), no barriers (removal immediately after the remediation or slow deterioration) and no remediation (worst case).

In 2013, the described risk assessment modelling will be used to determine the necessary remediation stop criteria (incl. points of compliance) to prevent any adverse ecological impacts in the North Sea after *in situ* alkaline hydrolysis.
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1 Introduction

1.1 Background

The Remediation Stop Criteria project is part of the EU Life project, NorthPestClean, where a pilot scale remediation is conducted at the contaminated site, Høfde 42 (Groyne 42), located at the Danish West Coast.

The contamination at the site mainly consists of organophosphate insecticides, which were deposited at the site in the 1950’s and 1960’s. The majority of the contamination was removed in 1981, where the unsaturated zone was removed by excavation /1/. The remaining contamination resulted in continuous contaminant discharge to the North Sea, which in 2006 resulted in the hydraulic isolation of the source area by a sheet pile barrier. Different remediation technologies have been screened and in situ alkaline hydrolysis has been selected for the pilot scale remediation project /2/.

The NorthPestClean project will demonstrate the efficacy of in situ alkaline hydrolysis and provide the knowledge required to design a full scale remediation of the site. As part of the overall project, the Remediation Stop Criteria project will provide the knowledge needed to determine when sufficient remediation has been achieved. This is achieved when the deterioration of the sheet pile barrier does not result in unacceptable ecological impacts in the North Sea.

1.2 Project aims

The major aim of the project is to develop measurable remediation stop criteria for the remediation of the Groyne 42 site based on risk assessment. Specifically:

- A risk assessment for the site including: i) an assessment of the post cleanup leaching of contaminants from the site; ii) an assessment of the transport pathways to the North Sea; and iii) an ecological assessment based on the PEC (Predicted Environmental Concentration) and the PNEC (Predicted No Effect Concentration) values in the North Sea.

- Recommendations for remediation stop criteria for the site. These criteria will be based on the risk assessment and will define how to assess when sufficient remediation of the site has been achieved. Points of compliance will be identified and the relevant reporting parameters will be defined. The points of compliance are the locations and times at which to monitor remediation outcomes.
The project will run until December 2013 and it consists of two phases: an initial phase (phase A) in 2011 and a final phase (phase B) in 2013. In phase A, the concepts will be developed in order to identify the data needs. In phase B the actual assessment will be made. In the intermediate period (2012) additional data can be acquired and the concepts adjusted accordingly. This report presents the outcome of phase A.

Phase A will:

- summarise the existing data with relevance for the later risk assessment and the final development of remediation stop criteria.
- present the conceptual model that the assessment will be based on.
- present the selected focus compounds of the risk assessment.
- present the elements of the planned risk assessment.
- explore the uncertainty of the current data and suggest supplementary data to be acquired in 2012 before initialisation of phase B.
2 The conceptual system

The data behind the conceptual model will be summarised in the following chapter. The conceptual model for the system is based on the current available data (autumn 2011) on the geology at the site, the hydraulic conditions and the characterisation of the contamination.

2.1 Geology

The risk assessment will be focused on the area from the dune ridge around 150 m inland and into the North Sea (Figure 1). The meadows and lagoons behind the dunes will not be considered. Several geological investigations have been carried out in the focus area. Data are available in the form of geological borehole logs and interpreted cross sections /e.g. 3-5/. Also, data on more recent detailed investigations are available for smaller areas in the central part of the source area (pilot scale remediation areas) /6-8/.

![North Sea](image.png)

Figure 1. Overview map of the contaminated site and the surrounding areas including the meadows and lagoons behind the dunes. The focus area with the contaminated site is represented by the red square.

The following presents the layers generally found in the geological sequence. At the bottom of the geological sequence, starting at around -9 m above mean sea level (amsl), a thick clay layer is encountered (Pleistocene marine deposits). Between the
water table and the downwards delineating clay layer, the geological sequence consists of marine deposits (sand and silt). At the former depot area, the sequence above the water table consists of sand fillings from the excavation in 1981, where the majority of the contamination at the site was removed /1, 3/.

At an elevation of -1.5 m amsl to -3.6 m amsl a low permeable organic silt layer (0.1-0.7 m thick) is encountered /3, 6/., which separates the upper secondary aquifer from the lower secondary aquifer. The silt layer is assessed to be uninterrupted throughout the area /3/.

Investigations from 2008 show that the silt layer has a low content of clay (~5 %) and a high content of silt (> 30 %) /9/.

The marine deposits in the upper secondary aquifer mainly consist of medium grained sand, while the deposits in the lower secondary aquifer mainly consist of silty fined grained sand and sandy silt layers /6/.

In part of the area, a sandy sludge layer (0.2-0.4 m) is located right above the ground water table at elevations of 0.6 m amsl to 1.3 m amsl. The layer is most likely the remaining part of a sludge layer at the bottom of the former wastewater percolation area /8/.

The extent of the sandy sludge layer has not been delineated. However, it is not a continuous layer as it has largely been removed in connection with the excavation in 1981.

Based on the geological investigations, a simplified geological sequence for the saturated zone is presented in Figure 2. The geological sequence consists of four to five layers: a thin clayey silt layer (layer 2), an upper secondary aquifer with medium grained sand (layer 1), a lower secondary aquifer with silty sand/sandy silt (layer 3), and a downward delineating clay layer. These layers are found throughout the contaminated site. A fifth layer consisting of sandy sludge is present in a smaller part of the source area.

The greatest uncertainties in connection with the geological sequence are the extent of the sandy sludge layer and the thickness and the elevation of the silt layer, which varies significantly between the boreholes at the site.

For modelling purposes the layers will be represented by uniform hydraulic properties and constant thicknesses.
2.2 Hydrogeology

The location next to the North Sea results in special hydraulic conditions, where outbound groundwater meets intruding seawater. Due to the coastal location, the water table and the flow at the site are under the influence of tidal and weather conditions. The conditions are further influenced by the hydraulic isolation of the source area by installation of a cover membrane and a sheet pile barrier. These installations influence both the flow and recharge patterns at the site.

The hydraulic head has been measured at the field site. However, the information on the hydraulic interaction between the upper and the lower secondary aquifer is limited. The difference in hydraulic head between the two aquifers appears to be small. Under natural conditions, without the sheet pile barrier, there appears to be a downwards gradient at the source area in most situations, while an upwards gradient is likely closer to the sea. However, variations may occur depending on the conditions in the North Sea /12/. After placement of the sheet pile barrier, an upwards gradient is likely to exist in the source area due to the lowering of the water table.
Several hydraulic parameters have, with varying certainty, been measured or estimated in connection with the numerous investigations at the site. These include: water table statistics /1, 13/, hydraulic conductivity /3, 14-17/, hydraulic gradient and flow velocities /3, 18/, porosity /11, 15/, dispersion coefficients and dispersivities /3, 19/, and discharge to the North Sea /3/. Data on daily precipitation and other climate data can be obtained from the climate station in Thyborøn close to the site (~4 km) /20/.

Table 1 gives an overview of the hydraulic parameters associated with each of the four continuous layers in the geological sequence presented in Figure 2. The properties of the sandy sludge (layer 5) are generally unknown.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1: Medium sand</td>
<td>$K_1$</td>
<td>[m/s]</td>
<td>$4 \times 10^{-4}$</td>
<td>/10/</td>
</tr>
<tr>
<td></td>
<td>$\varepsilon_1$</td>
<td>[-]</td>
<td>0.44</td>
<td>/15/</td>
</tr>
<tr>
<td>2: Organic silt</td>
<td>$K_{2,\text{vertical}}$</td>
<td>[m/s]</td>
<td>$4 \times 10^{-6}$</td>
<td>/15/</td>
</tr>
<tr>
<td></td>
<td>$\varepsilon_2$</td>
<td>[-]</td>
<td>0.39</td>
<td>/15/</td>
</tr>
<tr>
<td>3: Sandy silt</td>
<td>$K_3$</td>
<td>[m/s]</td>
<td>$1 \times 10^{-4}$</td>
<td>/10/</td>
</tr>
<tr>
<td></td>
<td>$\varepsilon_3$</td>
<td>[-]</td>
<td>0.39</td>
<td>/15/</td>
</tr>
<tr>
<td>4: Clay</td>
<td>$K_4$</td>
<td>[m/s]</td>
<td>$8 \times 10^{-10}$</td>
<td>/14/</td>
</tr>
<tr>
<td></td>
<td>$\varepsilon_4$</td>
<td>[-]</td>
<td>0.40 (estimate)</td>
<td></td>
</tr>
<tr>
<td>5: Sandy sludge</td>
<td>$K_4$</td>
<td>[m/s]</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$\varepsilon_4$</td>
<td>[-]</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

In connection with the hydraulic parameters, the estimation of the hydraulic conductivity is considered to include a significant uncertainty. The hydraulic conductivities at the site have been estimated in different ways incl. consolidation experiments, grain size distribution, slug tests and drawdown in aquifer piezometers. Generally, the hydraulic conductivities vary within two orders of magnitude. For tests of the same type, this variation is reduced to be within the same order of magnitude. The uncertainty is estimated to be relatively small for the upper secondary aquifer, which is relatively homogeneous and has a hydraulic conductivity that is rather consistently in the order of $10^{-4}$ m/s. The uncertainty is greater for the lower secondary aquifer where fewer measurements have been made. The lower secondary aquifer is also expected to be less homogeneous due to the alternating layers of sand and silt. The greatest uncertainty is connected with the organic silt layer, where the hydraulic data are very scarce.
2.3 Contaminants

The contamination at the site consists of a mixture of more than 60 xenobiotic compounds /21/. These compounds are mainly: organophosphate insecticides (e.g. parathion, malathion, sulfotep) and degradation products (e.g. *p*-nitrophenol, di- and triesters); chlorinated herbicides (e.g. MCPA) and degradation products (e.g. cresols); and heavy metals (i.e. mercury and arsenic) /22/. The DNAPL has a density of around 1.1 kg/L /3/. Analysis has shown the following DNAPL composition: ethyl parathion (40-57 %), methyl parathion (10-16 %), ethyl sulfotep (3-8 %), malathion (2-8 %), amino parathion (<1 %), *p*-nitrophenol (<1 %), di- and triesters (~10 %), mercury (~0.5 %), chlorinated aromatics (1-2 %), benzine (6-8 %) and BTEX (2-3 %) /3, 23/.

2.3.1 Contaminant mass and distribution in the source area

The contamination above the water table has previously (1981) been removed at the field site. The remaining contamination in the saturated zone has spread by migration of mobile DNAPL and dissolution in the groundwater.

The contaminant mass (free phase, sorbed and dissolved) has previously (2005) been estimated for selected compounds /4/. The parent compounds are mainly present as DNAPL or sorbed to the sediment, while the less hydrophobic degradation products primarily are found dissolved in the water phase. An overview of the estimated contaminant mass is presented in Table 2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>DNAPL</th>
<th>Sediment</th>
<th>Groundwater</th>
<th>Total</th>
<th>Outside barrier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl parathion</td>
<td>6,000</td>
<td>160,000</td>
<td>41</td>
<td>170,000</td>
<td>2,700</td>
</tr>
<tr>
<td>Methyl parathion</td>
<td>1,700</td>
<td>53,000</td>
<td>71</td>
<td>55,000</td>
<td>120</td>
</tr>
<tr>
<td>Malathion</td>
<td>160</td>
<td>18,000</td>
<td>46</td>
<td>18,000</td>
<td>51</td>
</tr>
<tr>
<td>Ethyl sulfotep</td>
<td>320</td>
<td>6,300</td>
<td>25</td>
<td>6,700</td>
<td>330</td>
</tr>
<tr>
<td>Mercury</td>
<td>60</td>
<td>1,700</td>
<td>22</td>
<td>1,800</td>
<td>350</td>
</tr>
<tr>
<td>Amino parathion</td>
<td>110</td>
<td>3,500</td>
<td>170</td>
<td>3,800</td>
<td>990</td>
</tr>
<tr>
<td><em>p</em>-nitrophenol</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>EP2-acid</td>
<td>-</td>
<td>-</td>
<td>13,000</td>
<td>13,000</td>
<td>-</td>
</tr>
<tr>
<td>MP2-acid</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4-chloro-<em>o</em>-cresol</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2. The estimated remaining mass [kg] at the site in 2005 before the installation of the impermeable barriers /4/. The contamination left in the area outside the current sheet pile barrier was also estimated. Estimations were done for several compounds, which are not all included below. (-) if no estimates.
For most of the contaminants, the mass in the groundwater only represents a smaller fraction of the total mass. The mass was estimated based on the concentration contour lines for the contaminants. This estimate is assessed to have a relatively low uncertainty compared to the estimations for DNAPL and soil /4/.

The contaminant mass in the sediment has been based on all the soil concentrations measurements at the site until 2005. The estimation has been based on a division of the area into seven regions (cross section with concentrations), three horizontal zones (the source area, an inner peripheral zone and an outer peripheral zone) and four vertical layers /4/. The most abundant data are found for the upper layers of the inner peripheral zone as the investigations have aimed at delineation of contamination in the upper secondary aquifer. The estimates for this area are therefore less uncertain than for the rest of the site. Investigations in the source area in connection with the pilot scale remediation have shown, that a reevaluation of the initial mass in the source area would be reasonable as some compounds may have been underestimated (e.g. mercury), while other may have been overestimated /8/.

The DNAPL mass is estimated based on observations from the field. The estimation is based on a typical DNAPL saturation (2 wt%) right above (5 cm) the silt layer in the hotspot /3-4/. The estimation has a significant uncertainty as the observations of DNAPL show a great spatial (horizontal and vertical) variation within the hotspot area. Details on the horizontal and vertical distribution of contaminants are presented in the following.

**Horizontal distribution**

The area in which DNAPL may be present has previously been estimated (Figure 3). DNAPL has been detected in a little more than half of the boreholes in an area of 11,000 m² resulting in an estimated DNAPL area of 6000 m². The observations have mainly been made in the upper secondary aquifer above the organic silt layer /4/.

The earlier field investigations for the entire area conclude that the DNAPL primarily has been detected as pools in the depressions in the surface of the silt layer /3/, while later investigations conclude that the distribution of DNAPL in the source area does not entirely follow the inclination of the surface of the silt layer /6/.

The old chemical depot and percolation area (~3000 m²) is an expected hotspot area with both residual and mobile DNAPL. Also, the highly contaminated sandy sludge layer is expected to be present in this part of the area. The sandy sludge layer contains very high concentrations of mercury as well as organic compounds /8/.
Figure 3. The possible extent of the DNAPL area (shaded green); DNAPL detection is indicated by larger red dots /4/. The blue area indicates the old chemical depot and percolation area. The sheet pile barrier is indicated by the thicker black line.

Based on the estimated distribution of DNAPL, all the DNAPL should be within the 21,000 m² area bordered by the sheet pile barrier (Figure 3). The criteria for the placement of the sheet pile barrier have roughly been based on soil concentrations of the parent compounds (mainly ethyl parathion) that exceed 500 mg/kg and solute concentrations that exceed 1 mg/L /24/. Hence, some contamination has been left in the area outside the sheet pile barrier (cf. Table 2). For the organic parent compounds (parathion, malathion and sulfotep) less than 5 % is estimated to be left outside, while a higher percentage is estimated for the degradation products (e.g. 25-30 % for amino parathion) /4/.
**Vertical distribution**

The vertical distribution depends on the location in the source area. In the centre of the source area, the contamination has spread both vertically and horizontally resulting in high concentrations in the full depth of the upper secondary aquifer (and in the sandy sludge layer above it) /3, 8/. In the periphery of the source area the high concentrations are primarily found in a thin horizontal layer above the organic silt layer /3/.

The presence of DNAPL below the silt layer is a recurring issue that is still connected with a high degree of uncertainty. Several investigations have tried to clarify whether the DNAPL has migrated below the silt layer /e.g. 3, 6, 25/. The earlier investigations have a poor vertical discretisation, which limits an adequate assessment. However, the later investigations, with better vertical discretisation (0.5 m between samples), conclude that the silt layer has not had a sufficient effect as a vertical barrier. The migration of DNAPL to the lower geological layers has only been slowed down, not prevented /6, 25/. DNAPL has been detected from approximately one meter above the silt layer to half a meter below it. The silt layer itself has accumulation large quantities of DNAPL (average of 2,000 mg ethyl parathion per kg soil) /6/. However, poor vertical discretisation still applies to the geological deposits in the lower secondary aquifer.

The previous estimations assigned 98 % of the contamination to the upper secondary aquifer. The DNAPL observations are most frequent above the organic silt layer, and it was assumed that the DNAPL found in the lower secondary aquifer was transferred below the silt layer as a result of penetration of this layer by drilling activities /3-4/. The newer investigations show that a combination of migration through the organic silt layer and downwards transport in connection with drilling may have resulted in the presence of DNAPL in the lower secondary aquifer.

The new investigations estimates a worst case scenario with as much as an additional 50 % of the estimated mass in the silt layer and right below it /6/. However, this worst case scenario is connected with a high degree of uncertainty as it is based on seven sonic drillings in a small part (400 m²) of the most contaminated area. The concentration levels have been extrapolated to the entire source area based on the assumption that the average concentration of ethyl parathion (2000 mg/kg) in the silt layer is representative for the entire silt layer (0.5 m thick) and for the topmost part (0.5 m) of the lower secondary aquifer within the entire area (21000 m²). Also, the drilling method itself is associated with some uncertainty resulting in smearing of DNAPL in the cores.

A more realistic estimate may be that these high concentrations are only found in part of the DNAPL area (<6000 m²) as DNAPL observations are generally much less frequent in and below the organic silt layer. Compared to the contaminant mass in the...
upper secondary aquifer this may result in additional 5-10 % mass in the silt layer and the lower secondary aquifer. Currently, the possible presence of DNAPL in and below the silt layer can not be disregarded, but the actual amount is highly uncertain.

Although some uncertainty is connected with the mass estimation for the upper secondary aquifer, it is clear that the greatest uncertainties on the contaminant mass are connected with the initial contaminant mass in the silt layer and in the lower secondary aquifer. Presently, it is not expected that the remediation will include these layers, although no final decision will be made before 2013. The risk assessment will be based on a remediation scenario similar to the current pilot scale project, where only the upper secondary aquifer is targeted by the remediation. It would therefore be desirable to decrease the uncertainty on the initial contaminant mass before the risk assessment is performed. Also, the extent of the sandy sludge layer is basically unknown. The concentrations in this layer are known to be very high, and the extent beyond the pilot scale remediation area is therefore of importance.

### 2.3.2 Down-gradient contamination

The down-gradient concentrations have been measured for 22 compounds at the foreshore immediately down-gradient of the sheet pile barrier and for 40-50 compounds in the surf of the North Sea. The measurements were done in situations where the concentrations are expected to be high (low tide after several days with eastern winds) /26/.

**Foreshore**

Annual samples have been collected at the foreshore since the installation of the sheet pile barrier (2007-2011). The samples are collected from five monitoring wells along the western side of the sheet pile barrier (Figure 4). The monitoring wells are screened right above and right below the organic silt layer /27/.

The monitoring shows that initially (2007) ethyl parathion (2-120 µg/L) and ethyl sulfotep (2-190 µg/L) are present at the foreshore, while both methyl parathion and malathion are below the detection limits (2-10 µg/L). Initially, the most dominant degradation products were: EP2-acid (0.2-178 mg/L), MP2-acid (0.2-108 mg/L), ethyl amino parathion (0.02-27 mg/L), MP1 (0.2-16 mg/L), EP1 (0.2-6 mg/L), p-nitrophenol (0.1-0.6 mg/L), EOOSPS (0.01-0.5 mg/L), EOOSPO (0.01-0.4 mg/L) and EOOOPS (0.01-0.8 mg/L) /27/.
The measurements at the foreshore show both spatial and temporal differences in the concentrations of some of the compounds. The highest concentrations are generally found at MB4 and MB5 (Figure 4). High solute concentrations are found both above and below the silt layer. The initial concentrations are generally higher above the silt layer as the upper secondary aquifer is more contaminated. For some of the contaminants the concentrations decline significantly after the hydraulic isolation of the source. This is mainly observed for the compounds with low initial concentrations (parent compounds) and for very mobile compounds (diesters).

The concentration reduction is especially observed above the silt layer and between the first two sampling campaigns (2007-2008). Following this period the concentrations are generally higher below the silt layer, which would indicate a greater interaction between the upper secondary aquifer and the North Sea. At the sampling campaign in 2010, the concentrations of several of the contaminants have
been reduced below the detection limits. The most limited temporal changes are observed for amino parathion and ethyl sulfotep, which still show the same concentration range in 2010. For these two compounds the fraction of contamination left outside the sheet pile barrier is relatively high compared to the total contaminant mass (cf. Table 2), which can result in high concentrations for an extended period.

Chlorinated compounds (e.g. MCPA and 4-chloro-o-cresol) are not included in the measurements at the foreshore, but both mercury and arsenic were measured. For mercury (0.05-1.4 µg/L) the concentrations did not change significantly, while arsenic (0.8-470 µg/L) seemed to decrease initially (2007-2008) and then showed more steady levels (~10 µg/L) in the following years.

**North Sea**

Samples have been collected from the North Sea since 2004. The measurements were most frequent before the installation of the sheet pile barrier in 2006. Since the installation, measurements have been annual at the same time as the sampling at the foreshore. The samples are most frequently collected in the surf at three points close to groyne 42, while occasional samples have been collected at groyne 36-37, groyne 39-40, groyne 40-41, groyne 43-44, groyne 44-45, and groyne 47-48 /28/.

In the North Sea, 24 compounds were measured above the detection limit (0.005-50 µg/L) during 2004 and 2005, while only 8 compounds (Hg, As, ethyl sulfotep, amino parathion, MCPA, and the triesters EOOSPS, EOOSPO and EOOOPS) were above the detection limit from 2007-2010 /28/. After the installation of the sheet pile barrier, the concentrations of the organic compounds were significantly reduced (>80% or to below the detection limits), which confirms the containment of most of the contaminant mass by the sheet pile barrier.

Generally, there is a good correlation between the compounds with the highest concentrations at the foreshore and the compounds with the highest concentrations in the North Sea. The difference in concentrations between the two points indicates a dilution (incl. degradation) of roughly 3-4 orders of magnitude.

Great temporal variations are seen during the period with frequent sampling (2004-2005). Unlike the later measurement, not all of these measurements were taken under the conditions with the expected highest concentrations. On occasion, the concentrations before the installation of the sheet pile barrier are as low as the concentrations after the installation /28/. Annual measurements may not be sufficient to established baseline concentrations of the contaminants in the North Sea, which will be of importance in connection with the risk assessment. The baseline concentrations of some of the contaminants (i.e. amino parathion and ethyl sulfotep) may not leave much additional room for contamination from the leachate after the sheet pile barrier has deteriorated.
2.4 The conceptual model

A conceptual model has been based on the data summarised in this chapter. The conceptual model is based on certain simplifications with regard to geology, hydrology and the distribution of contaminants. This has been done to obtain a more homogeneous system that can be used in connection with the risk assessment and modelling of the processes at the site. An overview of the current conceptual model for the system is presented in Figure 5.

Figure 5. Conceptual model for the situation at the contaminated site.

In connection with risk assessment and determination of remediation stop criteria the following is assumed to apply to the system:

- The geological sequence in the saturated zone can be described by four to five homogeneous layers: a sandy sludge layer in the unsaturated zone (0.3 m), an upper sandy aquifer (3.5 m), a thin organic silt layer (0.3), a lower silty/sandy aquifer (6.0 m) and a downward delineating clay layer. For modelling purposes each layer is assumed to have a constant thickness and elevation.

- The hydrogeological conditions at the site are influenced by the impermeable barriers (cover membrane and sheet pile barrier), which affects both the recharge patterns and the flow patterns in the subsurface. Apart for the barriers, the hydrogeology is affected by the fluctuating condition in the North Sea. This also affects the interaction between the two aquifers. After the remediation, when the barriers have started to deteriorate, it is assumed that a downwards gradient exists in the source area, while an upwards gradient exists at the foreshore closer to the North Sea. Hydraulic parameters associated with the geological layers are presented in Figure 2 and Table 1.
• The contamination has spread from the unsaturated zone down through the upper secondary aquifer and into the organic silt layer and the lower secondary aquifer. The contaminants are present in several phases (sorbed, DNAPL and dissolved).

• The sheet piled source area (21000 m²) can be divided into a heavily contaminated hotspot area with both residual and mobile DNAPL (6000 m²) and a larger area with lower concentrations. A sandy sludge layer with high concentrations of the contaminants is present in part of the unsaturated zone above the DNAPL area (~1000 m²).

• The majority of the contamination is found in the upper secondary aquifer. Minor quantities are also found in the sandy sludge, the organic silt layer and the lower secondary aquifer. Without further characterisation of the contamination, it is assumed that the initial mass in the upper secondary aquifer is represented by the 2005 estimates (cf. Table 2), while additional 5 % are present in each of the other three layers.

The largest uncertainties in connection with modelling and risk assessment are often associated with the conceptual model. In this connection the conceptual uncertainties are greatest for the sandy sludge layer, the organic silt layer and the lower secondary aquifer, while the upper secondary aquifer is relatively well described. The greater uncertainty applies to all aspects of the conceptual model i.e. the extent of the layers (sandy sludge), the initial contaminant mass, and the hydraulic parameters. Rougher estimates have been made in connection with these layers and a better initial characterisation could significantly improve the conceptual model.

The layers with the highest uncertainties are not included in the current remediation plans, whereby continuous leaching from these layers may have a great impact on the long-term down-gradient risks, although the majority of the contamination is currently found in the upper secondary aquifer.
### 3 Selection of the focus compounds

The selection of focus compounds for the risk assessment will be presented in the following chapter. This selection reflects the compounds that are assessed to pose the greatest risk after corrosion of the sheet pile barrier has resulted in leakages from the source area. The selection is based on the toxicity of the compounds and the expected prevalence of the compounds after the planned remediation at the site.

#### 3.1 Toxicity

The ecotoxicity of the mixture of contaminants at the site is very high /e.g. 29-32/. There is a great variation between the toxicity of the individual contaminants and studies focused on the removal of the parent compounds have shown significant toxicity reductions /31-33/. The formation of the generally less toxic degradation products is therefore desirable.

Predicted no effect concentrations (PNECs) have been calculated for around 50 of the contaminants /34/. These have later been updated and transformed into potential environmental quality standards /22, 35-36/. The environmental quality standards consider not only toxicity, but also persistence and bioaccumulation of the compounds /36/. The standards are thereby designed to ensure that compliance protects all the compartments of the water environment. Environmental quality standards can be expressed as the maximum allowable concentrations, MAC-EQS, and/or the annual average (AA-EQS) (cf. Table 3).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Annual average (AA-EQS)</th>
<th>Maximum allowable concentrations (MAC-EQS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl parathion</td>
<td>0.0003</td>
<td>0.03</td>
</tr>
<tr>
<td>Methyl parathion</td>
<td>0.009</td>
<td>0.03</td>
</tr>
<tr>
<td>Malathion</td>
<td>0.001</td>
<td>0.02</td>
</tr>
<tr>
<td>Ethyl sulfotep</td>
<td>0.0002</td>
<td>0.02</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.04</td>
<td>0.7</td>
</tr>
<tr>
<td>Amino parathion</td>
<td>1</td>
<td>130</td>
</tr>
<tr>
<td>p-nitrophenol</td>
<td>2</td>
<td>40</td>
</tr>
<tr>
<td>EP2-acid</td>
<td>4</td>
<td>420</td>
</tr>
<tr>
<td>MP2-acid</td>
<td>20</td>
<td>290</td>
</tr>
<tr>
<td>4-chloro-o-cresol</td>
<td>5</td>
<td>6</td>
</tr>
</tbody>
</table>
The use of annual average values for the mixing zone is suitable for the continuous contaminant discharge from the site. The maximum allowable concentrations can be relevant in connection with a pulse release of contaminants in connection with storm flushing. However, these events are harder to monitor.

The determination of the environmental quality standards has been based on generally accepted procedures. Available data on the environmental fate and toxicity from several sources are utilised and the procedure of the European Chemicals Bureau Technical Guidance Document on Risk Assessment /37/ is followed. The largest uncertainties are related to the available ecotoxicity data for the different compounds, which for some of the compounds are very scarce (e.g. ethyl sulfotep). The scarcity of toxicity data has resulted in high assessment factors for some of the compounds. However, for most of the very toxic organophosphate parent compounds ecotoxicity data are available for both short and long term tests, for both salt and fresh water species and for species of different taxonomic groups /38/.

### 3.2 Remediation by in situ alkaline hydrolysis

The mass and distribution of the contaminants will change as the remediation at the site is carried out. The planned remediation technology is *in situ* alkaline hydrolysis, which is a new technology. The technology is currently used for the pilot scale remediation project at the site. The goal of the remediation is to achieve a significant mass reduction in the source area in order to reduce any adverse impacts on the North Sea when the sheet pile barrier has deteriorated.

*In situ* alkaline hydrolysis utilises infiltration of NaOH, which result in hydrolysis of the contaminants upon contact. After the reaction, the majority of the formed hydrolysis products are removed by drainage of the infiltrated fluid. For the parent compounds, the remediation with *in situ* alkaline hydrolysis is expected to result in the following processes /39/:

- Ethyl parathion → EP2-acid + p-nitrophenol
- Methyl parathion → MP2-acid + p-nitrophenol
- Malathion → MP2-acid + diethyl mercaptosuccinate (or sodium variety)
- Ethyl sulfotep → 2 EP2-acid
- Amino parathion → EP2-acid + p-aminophenol

For all these compounds, the hydrolysis products are assessed to be less toxic than the parent compounds /38, 40/. A significant toxicity reduction is thereby expected following successful remediation. The hydrolysis products will most likely be present as soluble sodium salts varieties /39/.
The chlorinated aromatics (e.g. MCPA and cresols), benzine and BTEX are not expected to undergo hydrolysis. However, the alkaline hydrolysis may result in the formation of sodium salts of e.g. MCPA /39/.

The remediation with *in situ* alkaline hydrolysis is planned to be implemented in the upper secondary aquifer (down to the silt layer). The water in the pilot scale area will be drained and NaOH will be infiltrated to the area. The cycles of draining and infiltration can be run until the contamination levels live up to the remediation stop criteria.

No remedial actions are currently planned for the silt layer and the lower secondary aquifer. Upon corrosion of the sheet pile barrier, the contamination situation in these layers will be similar to the situation before the installation of the sheet pile barrier. While the remediation will change the composition of the leachate from the upper secondary aquifer, the leachate from the lower secondary aquifer is expected to have a similar composition as before the sheet pile barrier was installed. The focus compounds will therefore be a combination of relevant contaminants both before and after alkaline hydrolysis.

### 3.3 Focus compounds

With the complex mixture of contaminants at the site, it is not possible to include them all in the risk assessment. A group of up to ten focus compounds will therefore be selected based on the expected risk posed by the individual contaminants. The suggestion of focus compounds is partly based on earlier estimated risk quotients for around 50 of the contaminants found at the site /34/. These estimates have been based on the environmental quality standards (equal to PNEC) and predicted (modelled) environmental concentrations (PEC) in the North Sea. The resulting risk quotients were above one for 35 of the compounds, and above one hundred for 21 of the compounds.

Before the installation of the sheet pile barrier (2004), seven of the compounds with a high risk quotient were identified as focus compounds /2, 34/. The identified compounds included the ones with the highest estimated risk quotients and mercury (cf. Table 4). The environmental quality standards have been adjusted since the previous selection of focus compounds. However, the previous selection of focus compounds is still a good starting point.

The contaminant composition of the mixture will change as a result of the remediation in the upper secondary aquifer. However, hydrolysis is a natural occurring process at the site. After removal of the majority of the organophosphates and the water soluble alkaline hydrolysis products, any remaining contaminants are likely to undergo further hydrolysis. Hydrolysis products may thereby still be of importance, although concentrations will be reduced compared to earlier estimates. The risk quotients of Table 4 will thereby be significantly reduced.
Table 4. The seven focus compounds identified before the installation of the sheet pile barrier in 2006 /34/. The predicted concentrations and environmental standards are given in µg/L, while the risk quotient represents the needed dilution for each contaminant.

<table>
<thead>
<tr>
<th>Compound</th>
<th>PEC¹</th>
<th>PNEC²</th>
<th>Risk quotient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl parathion</td>
<td>1,200</td>
<td>0.003</td>
<td>400,000</td>
</tr>
<tr>
<td>Methyl parathion</td>
<td>350</td>
<td>0.009</td>
<td>39,000</td>
</tr>
<tr>
<td>Ethyl sulfotep</td>
<td>28</td>
<td>0.0002</td>
<td>140,000</td>
</tr>
<tr>
<td>Malathion</td>
<td>270</td>
<td>0.006</td>
<td>45,000</td>
</tr>
<tr>
<td>EP1</td>
<td>15,000</td>
<td>0.5</td>
<td>30,000</td>
</tr>
<tr>
<td>EP2-acid</td>
<td>135,000</td>
<td>40</td>
<td>3,400</td>
</tr>
<tr>
<td>Mercury</td>
<td>72</td>
<td>0.3</td>
<td>240</td>
</tr>
</tbody>
</table>

¹PEC is calculated as the average leachate concentration before remediation based on estimates from 2003, so the PEC is not the concentration in the North Sea but an estimated concentration before dilution.

²The predicted no effect concentrations have since been updated for all the contaminants except methyl parathion and ethyl sulfotep (cf. Table 3). This has resulted in higher dilution demands for all the contaminants except for EP1 /36/.

3.3.1 Parent compounds (organophosphates)

The previously selected focus compounds are primarily parent compounds. Before remediation ethyl parathion, methyl parathion, sulfotep and malathion are the compounds with the highest risk quotients. After remediation the risk related to the parent compounds will be reduced as they are hydrolysed upon contact with NaOH. However, the compounds remain important from a risk assessment point of view. This is partly due to the fact that the ecotoxicity of the parent compounds are several orders in magnitude higher than the hydrolysis products (cf. Table 3), whereby even small quantities of untreated parent compounds can have a great effect on the potential risk. Also, the untreated parent compounds in and below the silt layer are expected to have a great impact on the long-term effects in the North Sea. Ethyl parathion, methyl parathion, sulfotep and malathion should therefore be included as the most important focus compounds. Especially, the inclusion of ethyl parathion and ethyl sulfotep is important as these are the overall most toxic compounds and the most prevalent parent compounds at the foreshore.
3.3.2 Degradation compounds

With regard to the degradation products, the previous selection included EP1 and EP2-acid. It is suggested that EP1 is no longer included as a focus compound, while EP2-acid is still included.

It is suggested that EP1 is excluded since it is not a main degradation compound from alkaline hydrolysis. Also, the current environmental quality standard allows for higher concentrations than previously. EP1 is not found in large quantities at the site (<1 ton /4/), it has not been detected in the North Sea (<40 µg/L) and it is not one of the most prevalent diesters at the foreshore (<6 mg/L).

The *in situ* alkaline hydrolysis at the source area will lead to significantly increased concentrations of EP2-acid, since it is a main hydrolysis product of several of the main contaminants at the site. The majority of the formed mobile hydrolysis products are removed for further treatment during the draining cycles of the remedial method. Based on the remediation concept, the EP2-acid concentrations are not expected to be significantly elevated after the remediation. After the remediation, formation of EP2-acid may be ongoing as any remaining mass of the parent compounds is hydrolysed. The inclusion of EP2-acid as a focus compound can also be used to access the needed efficiency of the removal during the draining cycles.

Additional focus compounds can be included; however, all the more mobile degradation products are expected to be largely removed during the draining cycles. Degradation of the parent compounds also result in the production of MP2-acid (methyl parathion, malathion) and *p*-nitrophenol (parathion). The production of MP2-acid is expected to be limited compared to the production of EP2-acid. The production of *p*-nitrophenol is expected to be significant, since it is a hydrolysis product of both methyl and ethyl parathion. The environmental quality standards for *p*-nitrophenol are lower than for the diesters, which may result in a potential risk following the alkaline hydrolysis. MP2-acid and *p*-nitrophenol may be included as focus compounds, but could be substituted if other more interesting focus compounds are identified during the later phase of the risk assessment (2012-2013).

While several of the diesters are produced by hydrolysis of the organophosphate parent compounds, the triesters are not expected to be produced in significant amounts. The triesters EOOSPS, EOOSPO and EOOOPS have been detected at both the foreshore and in the North Sea. However, without any additional production the triesters are not expected to pose any significant risks, since the concentrations are low and the environmental quality standards are high.

The highest measured concentrations in the North Sea both before and after the installation of the sheet pile barrier are of amino parathion. Amino parathion is produced by the reduction of ethyl parathion under anaerobic conditions. The process is naturally occurring at the site and amino parathion is expected to be produced continuously from any remaining ethyl parathion in the area (e.g. in and below the silt...
layer). Amino parathion is significantly less toxic than the parent compound, but it still has relatively low environmental quality standards (cf. Table 3). The combination of relatively high baseline concentrations, expected continuous production and relatively low environmental quality standards make the inclusion of amino parathion as a focus compound desirable.

### 3.3.3 Metals

Mercury has a significantly lower risk quotient than the other six of the previously selected focus compounds (cf. Table 4). Mercury is highly toxic, but the predicted environmental concentrations are relatively low compared to the other compounds. The inclusion of mercury as a focus compound is highly depended on the effect of alkaline hydrolysis on mercury.

Since the removal of most of the contamination in 1981, investigations have shown a decrease in the concentration of mercury of the blue mussels in the area. Concentrations around 0.05 mg/kg DW are found, which is close to the background level and below a national threshold level of 0.3 mg/kg DW /41/. Investigations in the North Sea show that the concentrations are below the background level for mercury (10 ng/L /42/) and the hydraulic isolation of the source area has not resulted in a change /27-28/. The measured concentrations in the North Sea are around 1-2 ng/L both before and after the installation of the sheet pile barrier, and the same concentration levels are found at groyne 39-40 and 44-45. The mercury at the source area is therefore expected to be strongly bound without much potential impact on the North Sea.

However, investigations indicate that the increased pH from alkaline hydrolysis may mobilise the mercury. The relationship between mercury in the water phase and the increased pH from addition of NaOH is not presently clear. The prediction of this relationship is difficult, since it is unknown how mercury is bound and therefore how easily the bonds are broken. It is therefore suggested, that mercury is not included in the risk assessment unless the pilot test confirms any mobilisation. In the same connection, it could be worthwhile to consider possible arsenic mobilisation as well. The metals are only assessed to pose a potential risk in connection with the upper secondary aquifer, where mobilisation due to the remediation may occur.

### 3.3.4 Chlorinated compounds

The chlorinated herbicide MCPA and related cresols are present in significant amounts /1/. Although they are significantly less toxic than the organophosphate insecticides, they still have risk quotients above one /34/. High concentrations of especially 4-chloro-\textit{o}-cresol have been detected in the North Sea; however, the environmental quality standards are also relatively high. The compounds are not expected to undergo hydrolysis and they could be included in the risk assessment,
although they are not expected to pose the greatest risks in the North Sea. The inclusion of 4-chloro-o-cresol as a focus compound is preferred relative to MCPA, due to the higher concentrations and lower environmental quality standards.

3.3.5 Preliminary selection

The selected focus compounds are based on the above observations in connection with the quantity, the toxicity and the expected degradation pathway of contaminants at the site. The focus compounds aim at representing the most toxic compounds along with some of the degradations compounds that are expected to be most prevalent. The inclusion of both natural degradation compounds and expected hydrolysis products from the remediation has been prioritised to represent both the changed contamination situation after the remediation and the long term development of the situation at the site. Even with the expected high removal efficiency for the formed hydrolysis products during the remediation, the hydrolysis products may still be interesting as hydrolysis is a natural occurring process at the site.

The suggested focus compounds are presented in Table 5 along with an array of physiochemical properties with relevance for the environmental fate. Mercury can be included as a focus compound if the pilot scale remediation shows significant metal mobilisation at the high pH.

Table 5. Physiochemical information on the ten focus compounds of the risk assessment. All data are obtained from /38/ and given at 20 ºC unless otherwise mentioned.

<table>
<thead>
<tr>
<th>Compound</th>
<th>CAS</th>
<th>M_w</th>
<th>log K_{ow}</th>
<th>S_w</th>
<th>P_l</th>
<th>ρ</th>
<th>pK_a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[g/mole]</td>
<td>[-]</td>
<td>[mg/L]</td>
<td>[Pa]</td>
<td>[kg/L]</td>
<td>[-]</td>
<td></td>
</tr>
<tr>
<td>Ethyl parathion</td>
<td>56-38-2</td>
<td>291.26</td>
<td>3.83</td>
<td>11</td>
<td>9×10^{-4}</td>
<td>1.26</td>
<td>-</td>
</tr>
<tr>
<td>Methyl parathion</td>
<td>298-00-0</td>
<td>263.21</td>
<td>2.86</td>
<td>55</td>
<td>2×10^{-4}</td>
<td>1.36</td>
<td>-</td>
</tr>
<tr>
<td>Malathion</td>
<td>121-75-5</td>
<td>330.36</td>
<td>2.36</td>
<td>145</td>
<td>1×10^{-2}</td>
<td>1.23</td>
<td>-</td>
</tr>
<tr>
<td>Ethyl sulfotep</td>
<td>3689-24-5</td>
<td>322.32</td>
<td>3.99</td>
<td>30</td>
<td>1×10^{-2}</td>
<td>1.20</td>
<td>-</td>
</tr>
<tr>
<td>Amino parathion</td>
<td>3735-01-1</td>
<td>261.28</td>
<td>2.60</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>EP2-acid</td>
<td>5871-17-0</td>
<td>170.17</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MP2-acid</td>
<td>112-77-8</td>
<td>142.11</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>p-nitrophenol</td>
<td>100-02-7</td>
<td>139.11</td>
<td>1.91</td>
<td>1000</td>
<td>1×10^{-2}</td>
<td>1.27</td>
<td>1.715</td>
</tr>
<tr>
<td>4-chloro-o-cresol</td>
<td>1570-64-5</td>
<td>142.58</td>
<td>2.78</td>
<td>100</td>
<td>1.3</td>
<td>1.20</td>
<td>3.971</td>
</tr>
<tr>
<td>Mercury</td>
<td>7439-97-6</td>
<td>200.59</td>
<td>-</td>
<td>0.06</td>
<td>0.27</td>
<td>13.5</td>
<td>-</td>
</tr>
</tbody>
</table>

125ºC; 215ºC; 3Unknown temperature; 4The properties will depend on the form of mercury, the values are given for metallic mercury.
4 Risk assessment

This chapter includes an introduction to the remediation stop criteria, the risk assessment approach and points of compliance. The planned risk assessment approach is presented including the individual steps for determination of the relationship between the concentrations in the source area and the concentrations in the North Sea down-gradient of the source.

4.1 Remediation criteria and risk assessment approach

The remediation criteria related to the risk assessment can be split in two different types: absolute criteria and functional criteria. The absolute criteria describe the overall objectives of the remediation, while the functional criteria are means by which the absolute criteria are achieved. Absolute criteria generally represent social values achieved through the remediation e.g. the protection of human health, ecosystem health or groundwater resources /43/. The absolute criterion at the contaminated site is the protection of the North Sea ecosystem health.

The absolute criteria are generally not easily quantifiable. Functional criteria are therefore introduced to obtain quantifiable goals of the remediation. The quantifiable performance metrics that accompany the functional criteria are important to ensure that compliance with the criteria can be measured. Common functional criteria include the reduction of contaminant concentrations below a threshold level, removal of a certain fraction of the contaminant mass from the source area or reduction of the mass flux leaving the source area /43/.

In order to relate the concentration in the source area and the concentration in the North Sea, the risk assessment operates with two types of functional criteria: the long-term criteria to ensure good ecosystem health and the short-term criteria (the remediation stop criteria) to ensure sufficient remediation in the source zone to achieve the long-term criteria. The two criteria are included as the source area remediation will not necessarily result in a rapid reduction of the contaminant concentrations in the North Sea. However, the remediation stop criteria should ensure that the required concentration reduction will eventually be achieved. The two criteria at each their points of compliance (North Sea and source) can be linked via the dilution occurring between the two points, whereby the long-term criteria can be transformed into the remediation stop criteria at the source area /44/.

The approach is called a reverse risk assessment approach. The transformation of the long-term criteria for the North Sea into acceptable contaminant levels at the source is reversed compared to the traditional risk assessment, where the impact on the North Sea would be determined based on existing concentrations leaching from the source.
The approach includes the definition of the acceptable impact on the North Sea and a combination of several models (e.g. leaching, transport and dilution).

4.2 Leaching and transport from the source to the North Sea

The transport of contaminants between the source area and the North Sea will be modelled by a modified FEFLOW model developed by Aarhus University, which can include densities in the modelling. The current numerical model has been developed to simulate groundwater flow and seawater inundation of the beach. The vertical plane 2D FEFLOW model operates with a large area that horizontally stretches from 250 m inland to 65 m of the coastline and vertically from the clay layer (-9 m) up into the unsaturated zone (2.8 m). It does not include the sandy sludge layer in the unsaturated zone, but it includes the four saturated geological layers in the source area (cf. Figure 2). Due to the larger model area there are some discrepancies with regard to the thickness, elevation and properties of the layers. The model operates with four boundaries: an inland boundary (specific head), the clay bottom (no flow), the sea and the surface. Dynamic boundary conditions are created using time-series from 2008 on recharge, sea level and salinity.

The leaching of contaminants and the transport of contaminants from the source to the North Sea will greatly depend on the condition of the sheet pile barrier and the efficiency of the remediation technology. Several model scenarios can be established to ensure the best risk assessment for the complex situation. Further modification of the FEFLOW model is needed to adequately represent the different scenarios. The different scenarios are presented along with the purpose of the individual scenarios and the needs to be fulfilled by the model to answer the questions related to the risk assessment. The actually model development will be done in cooperation with Aarhus University prior to the second project phase (phase B).

Based on the conceptual model and the planned remediation at the site, it is suggested that the risk assessment includes six scenarios. The scenarios reflect the temporal and spatial variations in the hydraulic conditions (sheet pile barrier and cover membrane) and the contaminant mass (remediation). The six suggested scenarios for the risk assessment are:

A) Baseline situation: The scenario represents the current situation before the impermeable barriers starts to deteriorate. The entire flow is directed around the source area and the remediation has not yet been initialised. Hence, heavy contamination still exists but is isolated from the flow. The contamination situation is represented by the baseline situation, where the North Sea is only affected by leaching from the low levels of contamination left outside the source area (cf. Figure 6).

B1) Uniform deterioration (intact membrane cover): The scenario represents the situation, where uniform deterioration of the sheet pile barrier has resulted in
leakage from the source area. The source area is bypassed by most of the groundwater flow, but a minor portion flows through the source area (e.g. 20 % water penetration). The membrane cover is still intact as it is expected to have a longer life-time than the sheet pile barrier. The remediation has been finalised above the silt layer. It is assumed that the majority of the contamination in the upper secondary aquifer is removed, while the situation in the other geological layers is unchanged compared to the current situation (cf. Figure 7).

B2) Uniform deterioration (deteriorated membrane cover): With the exception of the condition of the membrane cover, this scenario is identical to scenario B1. The membrane cover has been deteriorating with the same rate as the sheet piling (e.g. 20 % water penetration of all barriers), whereby the flow through the source area is greater (cf. Figure 8).

C1) No barriers (short term): The scenario represents the situation, where the sheet pile barrier and the membrane cover are removed immediately after the remediation. The water flows unhindered through the source area and the hydraulic conditions are equal to the situation before the barriers were installed. The contamination situation is the same as in scenarios B, where the remediation has been finalised above the silt layer (cf. Figure 9).

C2) No barriers (long term): The scenario represents the long-term situation, where the impermeable barriers are completely deteriorated. Like scenario C1, the flow patterns are back to the situation before the barriers were installed. The difference between the two scenarios (C1 and C2) is the initial contaminant situation. During the deterioration of the barriers, the contamination has been partly removed from all the layers and the initial contaminant concentrations are somewhat reduced (cf. Figure 10).

D) Long-term situation (no remediation): The scenario represents a situation, where no remediation has been carried out before the barriers are completely deteriorated. The contaminant situation is like the current situation, while the hydraulic conditions are like the situation before the barriers were installed (cf. Figure 11). The scenario can serve as a worst case scenario.

The main purpose of including several scenarios is to determine the dilution factors between the source area (POCsource) and the down-gradient discharge point to the North Sea (POCdowngr.) under different flow and contamination conditions. The points of compliance are described in more detail in chapter 4.5.
Figure 6. Model scenario A: the baseline situation. The barriers are still impermeable and the flow is bypassing the source area. Remediation has not yet been implemented at the source area, but the area is hydraulic isolated from the North Sea. The concentrations in the North Sea are the result of the lower levels of contamination left outside the sheet pile barrier. Points of compliance for the short- and long-term functional criteria (solute concentration) are indicated with purple circles; the remediation stop criteria for the source area does not yet apply in the baseline scenario (before remediation). (a) The horizontal plane showing an aerial view of the contaminated site; (b) The vertical plane showing a cross-sectional view through the secondary aquifers.
Figure 7. Model scenario B1: uniform deterioration of the sheet pile barrier (intact cover membrane). The sheet pile barrier has started to leak and the remediation of the source area above the silt layer has been finalised. Points of compliance for the short- and long-term functional criteria (solute concentration) are indicated with purple circles. (a) The horizontal plane showing an aerial view of the contaminated site; (b) The vertical plane showing a cross-sectional view through the secondary aquifers.
Figure 8. Model scenario B2: uniform deterioration of the sheet pile barrier (deteriorated cover membrane). The sheet pile barrier and the membrane cover have started to leak and the remediation of the source area above the silt layer has been finalised. Points of compliance for the short- and long-term functional criteria (solute concentration) are indicated with purple circles. (a) The horizontal plane showing an aerial view of the contaminated site; (b) The vertical plane showing a cross-sectional view through the secondary aquifers.
Figure 9. Model scenario C1: no barriers (short term). After the remediation of the source area has been finalised, the barriers (sheet pile and membrane cover) are immediately removed. Points of compliance for the short- and long-term functional criteria (solute concentration) are indicated with purple circles. (a) The horizontal plane showing an aerial view of the contaminated site; (b) The vertical plane showing a cross-sectional view through the secondary aquifers.
Figure 10. Model scenario C2: no barriers (long term). The sheet pile barrier and the membrane cover have completely deteriorated. During the slow process of barrier deterioration, a major part of the contamination has been removed from the source area (leaching). Contamination remains in all the layers, especially the lower permeable silt layer, whereby back diffusion can start to play a significant role. Points of compliance for the short- and long-term functional criteria are indicated with purple circles. (a) The horizontal plane showing an aerial view of the contaminated site; (b) The vertical plane showing a cross-sectional view through the secondary aquifers.
Figure 11. Model scenario D: no remediation (long-term). The situation in case no remediation had been carried out at the time the barriers have completely deteriorated. The contamination is at the current level, while the hydraulic conditions are the same as before the barriers were installed. Points of compliance for the short- and long-term functional criteria (solute concentration) are indicated with purple circles. (a) The horizontal plane showing an aerial view of the contaminated site; (b) The vertical plane showing a cross-sectional view through the secondary aquifers.
4.2.1 Baseline situation: Scenario A

Scenario A is designed to represent the baseline situation, where both the contamination and flow situation are similar to the current situation. The baseline is of interest in connection with the assessment of the North Sea, as the baseline concentrations in the North Sea will have to be subtracted from the environmental quality standards before the allowable additional leaching from the source area can be determined. Current measurements exist for the concentration levels at the foreshore and in the North Sea. However, these only represent a relatively short time period (four years) after the isolation from the source area and a limited statistical foundation (annual measurements), whereby the current baseline concentrations may not yet depict representative concentrations.

Scenario A ideally requires a 3D numerical model for adequate representation of the conditions. The sheet pile barrier complicates the situation. The inclusion of the horizontal plane in the modelling is necessary in order to adequately describe the flow patterns around the barrier. The vertical plane is necessary to represent the entire geological sequence and the interaction between the aquifers.

The input data for the numerical model will be based on the available data on geology and hydrogeology for the current conceptual model. The initial mass of contaminants in the individual layers of the model can be based on existing measurement. Input data can potentially be supplemented with additional measurements to improve the conceptual model.

The flow boundary conditions will be similar to those of the current FEFLOW model. The surface boundary will be slightly different, as the surface of the source area will be impermeable to recharge (membrane cover). No flow boundary conditions will apply to the sides (north, south and west) and the bottom of the model area. The boundaries around the source area will be represented by cells with a very low permeability preventing flow through the source area.

The concentration boundary conditions will be represented by zero concentrations at all the boundaries except for the down-gradient boundary to the North Sea, where a zero concentration gradient will be applied.

The leaching of contaminants from the area outside the sheet piled source area will depend on the remaining mass in the saturated zone and will be controlled by advection. Degradation could be included as a factor affecting the dilution, but the information (e.g. half-lives) on the degradation of the focus compounds is either very limited or highly uncertain, also it varies based on the relatively unknown redox conditions /46-47/.
4.2.2 Uniform deterioration: Scenarios B

Scenarios B1 and B2 are designed to represent a situation where the impermeable barriers have partly deteriorated (uniformly) and the contaminants have started to leach from the source area. For scenario B1 only the sheet pile barrier has deteriorated, while for scenario B2 the weather conditions have also weakened the membrane cover. Apart from this distinction the scenarios are identical.

The remediation of the source zone has been implemented and the contamination situation improved significantly compared to the current situation. However, the situation has only been improved for the upper secondary aquifer. The situation in the other less contaminated layers is the same as the current situation with high concentrations or even DNAPL. In scenario B2 the deterioration of the cover membrane has resulted in infiltration through the unsaturated zone and thereby through the sandy sludge layer, where contaminants will start to leach into the upper secondary aquifer.

The extent to which the contaminated leachate from the source zone is mixed with the relatively clean water bypassing the source area is of interest from a risk assessment point of view as the dilution factor will depend on this. This will be investigated along with the effect of the additional contaminated leachate entering the upper aquifer from the unsaturated zone (scenario B2).

The requirements for the model will be similar to scenario A and ideally the same 3D numerical model should be used. The outer boundary conditions are the same, while the boundaries around the source area have changed. The permeability of the sheet pile barrier is increased uniformly by increasing the hydraulic conductivity in all the low permeability boundary cells. For scenario B2 an altered surface boundary also applies, where a fraction of the recharge is allowed to enter the unsaturated zone above the source area.

The input data for the contamination situation in the source area will be based on available data on the initial mass of contaminants in the individual layers; this includes both the estimates for the current conceptual model and additional information obtained in connection with the pilot scale remediation. To prevent a significant adverse impact on the North Sea, the initial mass and concentrations in the upper secondary aquifer can be adjusted to comply with the remediation stop criteria, which will eventually be determined through the risk assessment.

The leaching from the source area will depend on the initial source mass in the individual geological layers. The leaching from the upper secondary aquifer will depend on the remaining mass after the remediation and will be controlled by advection. The leaching from the lower secondary aquifer will also be controlled by advection, while the presence of DNAPL will result in DNAPL dissolution with high solute concentrations. For the silt layer the leaching will be slow and controlled by diffusion. The contribution from the unsaturated sandy sludge layer will depend on
the infiltration through the cover membrane. Based on the estimated initial source mass and the hydraulic conditions, simple leaching calculations can be carried out in order to determine the dissolution of DNAPL and removal with time.

4.2.3 No barriers: Scenarios C

Scenarios C1 and C2 are designed to represent a situation, where the impermeable barriers have been completely removed. In scenario C1 the removal of the barriers occurs immediately after the remediation, while in scenario C2 the removal is the result of a slow deterioration. This difference between the two scenarios will effect the initial contaminant concentrations. The initial contamination situation in scenario C1 is equal to that of scenarios B. In scenario C2, a new situation with lower contaminant levels has developed. The hydraulic conditions resulting from the removal of the barriers are the same for both scenarios C, where the flow conditions have returned to the situation before the installation of the barriers.

Compared to scenarios B, these scenarios examine the dilution factor of the leachate from the source zone, when the hydraulic conditions are not affected by the barriers. Compared to scenario C1, scenario C2 focuses on the compliance with the environmental quality standards on the longer term.

Unlike the previous scenarios, scenarios C can be represented adequately by a 2D numerical model in the vertical plane like the current FEFLOW model. Representation in the horizontal plane is no longer necessary with the removal of the impermeable barriers. However, since the 3D numerical model will already be developed, it can be used for all the scenarios. Compared to scenarios B, the change to the numerical model is that no special boundary conditions apply to the source area as the impermeable barriers are gone. Only the outer boundary conditions apply.

The input data for the contamination situation in the source area for scenario C1 is the same as for scenarios B, while the initial situation is different for scenario C2. The extent of the additional removal after the finalisation of the remediation can be varied from a relatively limited additional removal to an almost complete removal. The governing processes will depend on the extent of the removal.

With extensive removal of the contaminant mass in the source area, the main source of contamination can be back-diffusion from the low permeable silt layer, which may constitute a significant long-term source /48/. The organic silt layer in the source area will initially be saturated by DNAPL. As the DNAPL in the silt layer dissolves, the contaminant flux out of the silt layer will be diffusion controlled and driven by a linear concentration gradient. The diffusive flux can be described using Fick’s first law. The distance from the surface of the DNAPL to the surface of the silt layer will increase with time until the DNAPL is completely dissolved. Two contaminant fluxes of equal size will be directed at the sandy layer above the silt layer and the sandy layer below the silt layer. The contaminant flux out of the silt layer will be diluted as it
mixes with the clean up-gradient groundwater flowing along the surfaces of the silt layer. Hence, the scenario can be used to examine the long-term effect on the dilution factor from the continuous back-diffusion into the two aquifers.

4.2.4 No remediation (long-term): Scenario D

Scenario D has been designed to represent a situation, where no remediation has been achieved. The initial contaminant situation is assumed to be unchanged compared to the current situation (similar to scenario A), while the hydraulic conditions has changed back to the situation before the barriers were installed (like scenarios C).

Scenario D can be considered as a worst-case scenario, which can be the result of either a failed remediation attempt or a decision not to implement any remedial actions. The outcome of the modelling can be used to describe the impact on the North Sea if no effort is made to adjust the contaminant mass and concentrations to comply with the remediation stop criteria.

Scenario D can be modelled in a similar way as scenarios C. The 3D numerical model will be used, although the scenario could be adequately represented by a 2D numerical model in the vertical plane. The hydraulic conditions (no barriers) are also the same for scenario D and scenarios C.

The input data for the contamination situation in the source area is the same as for scenario A. While the initial mass was of little importance in scenario A as the source area was confined by the hydraulic barriers, the initial mass is of great importance for scenario D.

4.3 Dilution in the North Sea

The attenuation of contaminants in aquifers is generally relatively small /44/, the dilution in the North Sea is therefore expected to be the primary contributor to the overall dilution factor. A significant dilution can be achieved, when the relatively small volume of leachate from the source area is mixed with the sea water upon discharge to the North Sea. This dilution in the mixing zone depends on conditions such as the local inshore bathymetry, currents and waves. The dilution in the North Sea is relatively independent of the risk assessment scenarios.

The dilution in the surf along the Danish coastline has been estimated in the Dashboard project done by DHI for the Danish EPA /49/. For the grid around the contaminated site, the Dashboard model estimates an average dilution of 82,600 times, a minimum dilution (5 % quantile) of 9,400 times and an absolute minimum dilution of 5,200 times. The dilution occurs in a 55 m mixing zone with a depth of 2.7 m. However, the 3D numerical model has a relatively low resolution (6 km grid), and it uses a standardised discharge of leachate (0.1 l/s) from a point source on the
shoreline. With a relatively small volume of leachate the dilution is inversely proportional with the discharge, which makes a correction possible /49/.

The Dashboard project mentions a local model for the contaminated site. The local model has a higher resolution (100 m grid) and was developed by DHI in 2004 /19/. The 2D depth integrated numerical model (MIKE21) combines a wave model (MIKE 21 NSW), a 2D hydrodynamic model (MIKE 21 HD) and a model for spreading and dilution (MIKE 21 AD).

The concentration input to the model is a number of point sources along the shoreline (300 m). It is assessed that the transport and dilution in the area is mainly controlled by tidal effects, regional weather systems and local wind condition. In the surf zone the transport is further affected by waves. These processes have been included in the local model (approximately 10 km along the coast and 3 km wide), which has been developed as a combined hydrodynamic and advection-dispersion model /19/. The model results are expected to be used in the risk assessment without further adjustment. In case there is a great difference in the modelled volumes of leachate from the FEFLOW model and the DHI model (discharge around 1 l/s) a simple correction of the dilution factor can be applied.

The model does not include all ten focus compounds. The compounds included in the model are: ethyl parathion, EP1, EP2-acid, mercury and formaldehyde. It is assumed that only mercury has a baseline concentration in the North Sea (2.5 ng/L). Degradation half-lives are given for parathion, EP2-acid and formaldehyde, but formaldehyde is the only compound where first order degradation has been included in the model /19/. Hence, the data on the other compounds can be used for a conservative estimate of the dilution in the North Sea for all the organic focus compounds.

The model gives estimates of the yearly mean and maximum concentrations. As the input concentrations are known, the 2D maps with the contaminant concentrations in the sea are translatable to dilution factors. An example of the 2D maps from the model is shown in Figure 12.

Based on the maps, the average dilution factors in the area closest to the source (approximate 400 m x 100 m mixing zone between groyne 42 and groyne 43) appears to be around 3000-8500 times for the yearly average situation. This correlates relatively well with expectations based on the Dashboard model. With the inverse proportionality, the dilution should be around 10 times lower than predicted with the Dashboard model, so around 8,200 times on average. In peak situation the dilution factor is generally less than 1000 times, which also correlates well with the Dashboard prediction (around 520 times). For more detailed information on the dilution, the data behind the maps should be obtained.
While the dilution in the North Sea is relatively independent of the risk assessment scenarios, it is likely to depend on the point of discharge. The initial dilution is expected to be larger, when the leachate is discharge from the seabed at a greater depth compared to the shallow water at the shoreline. This is due to the greater volume of the receiving water, where a turbulent vertical mixing is expected depending on the buoyancy of the discharge water compared to the sea water /50/.

The local DHI model found around ten times higher dilution at Cheminova’s wastewater pipeline 500 m of the coast (8 m depth) compared to the dilution of the of the contaminants from the source area /19, 49/.

The two secondary aquifers are likely to have different discharge zones at the seabed. The upper secondary aquifer is expected to primarily discharge into the shallow
mixing zone between the groynes (42-43), while the discharge zone of the lower secondary aquifer is more uncertain.

If assumed that the discharge from the lower secondary aquifer occurs at depths equivalent to the silt layer, then based on the bathymetry in the area /19/ the discharge will occur somewhere around the outer reach of the groynes (100 m of the coast). Considering the uncertainty of the discharge zone from the lower secondary aquifer, the dilution factors for both secondary aquifers will be based on the local DHI’s model with discharge at the shoreline.

4.4 Assessment of the North Sea water quality

In connection with the determination of acceptable contaminant levels in the North Sea different approaches have been considered including a tiered approach. The use of environmental quality standards, leachate toxicity bioassays and a species biodiversity survey were all considered.

4.4.1 Environmental quality standards

In connection with the assessment of the North Sea, the existing data on the determination of the environmental quality standards have been reviewed /22, 34-36/. From the documents, it is clear that recognised methods have been used to determine the environmental quality standards of the individual compounds. The European Chemicals Bureau’s Technical Guidance Document on Risk Assessment (TGD /37/) has been used. Toxicity data have been collected from multiple sources hereunder toxicity tests carried out for Cheminova or the former Ringkjøbing County and several databases (e.g. TOXNET, IUCLID, Ecotox, PAN) with information on toxicity towards both fresh water and salt water species. With regard to the assessment factors, it is clear that they have been updated to the marine assessment factors after the TGD was updated in 2003, and that the assessment factors for adverse long-term effects have been included. The determination of environmental quality standards for the individual compounds is therefore assessed to be sound and adjustments are not necessary unless new, and different, data on the toxicity, bioaccumulation or persistency emerge.

The measurements from the North Sea show that the environmental quality standards (cf. Table 3) have been complied with or are likely to have been complied with for all the focus compounds since 2009 /28/. However, some of the detection limits are higher than the environmental quality standards (around 10 times) and the statistical foundation for determination of the baseline concentrations is limited. The contribution from the baseline concentrations should be kept in mind. With high baseline concentrations the allowable additional contribution from the source area leachate is significantly limited.
The concentrations in the North Sea are expected to increase as the sheet pile barrier starts to deteriorate. It would be ideal if the leaching from the source area at this time did not cause the long term environmental quality standards to be exceeded at any time. However, it may be necessary to accept a higher impact on the North Sea for an intermediate period.

The environmental quality standards are based on the toxicity data of the individual contaminants. This does not consider the possible toxicity interaction between the individual contaminants in the mixture. Since several of the organophosphates have the same mode of action (acetylcholinesterase inhibitors) a cocktail effect may be likely, whereby an additive approach to the toxicity of the mixture of the focus compounds would be reasonable. The overall needed dilution factor (DF) between POC\textsubscript{source} and POC\textsubscript{rec} can be determined based on the solute concentration of the contaminants in the source (C\textsubscript{i}), the environmental quality standards that applies down-gradient in the North Sea (EQS\textsubscript{i}) and the baseline concentrations already present in the North Sea (C\textsubscript{base, i}):

\[
DF = \sum \frac{C_i}{EQS_i - C_{base, i}}
\]

The risk assessment for the North Sea will be based on the existing environmental quality standards. In case the risk assessment shows, that the remediation stop criteria will be difficult to obtain for a few compounds (e.g. ethyl sulfotep), the environmental quality standards could be adjusted through additional toxicity tests with those individual compounds in order to try to reduce any assessment factors that are high due to the scarcity of data. However, a lowered toxicity is not necessarily the outcome of additional testing, but it will add to the certainty of the risk assessment.

### 4.4.2 Leachate toxicity bioassays

The use of site specific toxicity testing of the contaminant leachate as an assessment tool for water quality and a parameter for the remediation stop criteria has primarily been considered due to the possible cocktail effects of the mixture.

The use of alkaline hydrolysis will most likely greatly reduce the toxicity of the contaminated water. The identified hydrolysis products are less toxic than the hydrolysed parent compounds, and they are largely removed during the draining cycles of the method. However, in a mixture as complex as the one at the site the prediction of the changed toxicity following remediation will be somewhat uncertain. Minor amounts of toxic degradation compounds may remain after the final drainage, and the changed condition in the source area may affect the availability of all the remaining compounds (e.g. dissociating or metal mobility). If too many of the compounds in the final mixture are not accounted for among the focus compounds,
good chemical conditions might be achieved without this necessarily resulting in good ecological conditions.

Toxicity bioassays with a test battery of different marine organisms could be a mean to ensure that the overall toxicity declines as expected following the remediation /51/. An acceptable toxicity of the leachate from the source area after implementation of in situ alkaline hydrolysis could be included in the remediation stop criteria. Toxicity tests have previously been used at Kærgård Plantation in connection with the assessment of the needed dilution factor between the source area and the sea /52-53/.

The problem with a site specific toxicity test as a remediation stop criterion is that it traditionally does not have any inbuilt assessment factors like the environmental quality standards. However, an approach utilising assessment factors could be applied. This has been done in connection with waste water effluents /54/, and a similar approach using the marine assessment factor for the environmental quality standards /37/ could be applied.

Bench-scale studies with site material could be carried out to observe the change in toxicity due to alkaline hydrolysis. Chemical analysis could be used to relate the toxicity results to the concentration of focus compound to ensure a reasonable correlation with the environmental quality standard. The comparison could be eased by the use of the toxic unit (TU) concept, where the toxicity bioassay based toxic unit (TU_B) can be expressed as:

\[
TU_B = \frac{1000 \ mL/L}{\text{Sample toxicity (e.g. } EC_{50} \ \text{in mL/L)}}
\]

and the theoretical chemical based toxic unit (TU_C) as:

\[
TU_C = \sum_i TU_i = \sum_i \frac{C_i}{EQS_i}
\]

The toxic units express the ratio between the environmental exposure concentration and the toxicological endpoint /54/ or, in other words, how many times a sample needs to be diluted to reach the base for the toxic unit (e.g. EC_{50}). Toxic units are already used as part of the criteria for the temporary discharge permit for treated groundwater and drain water at the site /36/.

The additive approach (TU_C) used in connection with the environmental quality standards for the single components of the mixture may not necessary correctly depict the interaction between the contaminants. Also, it is not likely to include all the single components of the entire mixture of contaminants at the site. Hence, the two toxic units may be significantly different. Bench-scale studies with site material has been used in connection with the assessment of other remediation technologies targeting the organophosphate parent compounds /31-33/. These studies have shown that the chemically unexplained toxicity of the sample is larger after remediation than before.
While the chemical composition is relatively well-known before remediation, the same is not the case after remediation. This may also be the case for alkaline hydrolysis, where the focus compounds does not fully describe the overall toxicity.

4.4.3 Species biodiversity survey

The use of a type of biological biodiversity survey has been considered. The survey should ideally be used to compare the actual biological conditions in the North Sea down-gradient of the source area with an unaffected reference. However, a number of issues with this type of investigation have been noted.

A problem with using species diversity as an indicator for the ecosystem health is that the method only considers the presence of a species and not the condition of the species; severely affected species may still be present and count towards a higher biodiversity /55/. Also, the biodiversity survey does not consider long-term effects of species that periodically migrate through the affected area, which for a large open system like the North Sea could be a significant number of species.

The species diversity in the North Sea may not only be affected by the leaching contaminants. Natural fluctuation due to e.g. local variation in the preferred habitats (structural variation in sediments, density of seagrasses, etc.) and seasonal variations could also affect the biodiversity.

Finally, the leaching of contaminants occurs over a relatively large surface. The detection of changes in biodiversity from a more widespread source may be difficult compared to more concentrated outlet of effluents (e.g. pipeline).

4.5 Compliance points

The risk assessment and determination of remediation stop criteria should be coupled with the determination of appropriate points of compliance. These are important for proper monitoring of the short- and long-term fulfilment of the environmental quality standard. Points of compliance should be determined for both the source area and down-gradient of the source area. These points can be supplemented with calculation points to support the reverse risk assessment.

The risk assessment will operate with three fundamental types of points of compliance (POC): the POCsource in the source area, where the remediation stop criteria should be complied with; the POCrec in the North Sea, where the long-term criteria should be complied with; and the POCdowngr at the discharge point from the aquifer to the North Sea, which is primarily a calculation point.

The calculation point, POCdowngr, is used as a transition point between the dilution in the aquifer and the dilution in the North Sea, which are calculated in different ways. The dilution in the aquifer, from POCsource to POCdowngr, will use the described leaching and solute transport modelling, while the dilution in the North Sea, from
POC$_{\text{downgr}}$ to POC$_{\text{rec}}$, will use the described modelling of the spreading in the North Sea. A down-gradient calculation point can also be used as a warning point in case the concentrations at this point do not live up to the needed dilution before discharge to the marine mixing zone.

4.5.1 Placement of the compliance points

At least two sets of compliance and calculation points will be included: the first set for the sandy layer right above the silt layer and the second set for the sandy layer right below the silt layer. Two sets of compliance points have been chosen, since the temporal development at the site will be significantly different for the upper secondary aquifer and the lower secondary aquifer. The contribution from both layers will be considered for the long term effect on the ecological condition in the North Sea (only one POC$_{\text{rec}}$). The points should be placed close to the silt layer, where the contamination levels are highest. The effect of insufficient remediation or back-diffusion is expected to be most significant close to the silt layer. The currently suggested placement of the points of compliance were presented in Figure 6-Figure 11.

4.5.2 Sampling matrix and parameters

It is suggested that the solute concentrations of the focus compounds are measured at the points of compliance (or conversion of total concentrations in the source area). A consistent use of solute concentration is considered to be the easiest solution for all the points of compliance. It is also suggested that pH is measured. During the remediation the pH-value can give an indication of the extent of alkaline hydrolysis at the points of compliance. Following the remediation, additional measurements outside the sheet pile barrier may give an indication of the possible leaching from the source area (shorter-term) or the interaction between the source area leachate and the bypassing water and/or seawater (longer-term).

The placement of the points of compliance in the source area will be used to document the fulfilment of the determined remediation stop criteria. These criteria should be complied with before the in situ alkaline hydrolysis is finalised and any significant deterioration of the impermeable barriers has occurred. The lack of flow within the borders of the sheet pile barrier at this time hinders the use of flux criteria as remediation stop criteria. This is the reason for suggesting the use solute concentrations at POC$_{\text{source}}$.

The long-term criteria, to ensure good ecosystem health, should be fulfilled at POC$_{\text{res}}$ in the North Sea. As earlier mentioned the environmental quality standards are designed to ensure that compliance in the North Sea provides adequate protection for all compartments of the water environment. The use of solute concentrations in the North Sea thereby seems most reasonable.
4.5.3 Sampling frequency and magnitude

The risk assessment modelling will be based on simplified relatively homogeneous conditions. The points of compliance in the model can therefore be represented by a few points.

In reality, the source area is both large and heterogeneous. Great concentrations differences have been seen over relatively short distances and this will be reflected in the need for sampling points to determine whether the remediation stop criteria are fulfilled. Although water samples are generally more homogeneous than soil samples several monitoring points will still be needed in the source area.

As a starting point the needed number of sampling points should be similar to the needed number of sampling points in connection with the characterisation of the site /44/. The effect of *in situ* alkaline hydrolysis, with the repeated cycles of draining and infiltration, on the distribution of contaminants is generally unknown. Experiences with the initial and final characterisation of the pilot scale remediation area may contribute to a better estimation of the needed sampling points in the source area (*POC*<sub>source</sub>).

Due to the significant mixing in the North Sea, the condition should be more homogeneous and the needed numbers of sampling points significantly lower than for the source zone. The previous measurements in the North Sea do show significant differences at the three sampling points close to the site, whereby several points along the coast should be included.

The sampling frequency at the source area should be closely linked with the cycles of the *in situ* alkaline hydrolysis. The cycles should be continued until the remediation stop criteria are reached within the source area. For the initial cycles a less extensive monitoring program can be implemented until the solute concentrations are close to the compliance concentrations.

After determination of the baseline conditions in the North Sea, frequent sampling down-gradient of the sheet pile barrier is not necessary. The sheet pile barrier is expected to have a long life-time and annual measurement similar to the current ones should be sufficient initially. The monitoring program can then be intensified once/if the concentrations starts increasing due to deterioration of the sheet pile barrier.
5 Summary and recommendations

5.1 The conceptual model

A conceptual model for the contaminated site has been determined based on the review of the existing data available for the site. The conceptual model will be used in connection with the risk assessment. In summary the conceptual model consists of the following geology, hydrogeology and initial contamination:

- The geology at the site can be represented with a simplified geological sequence consisting of four continuous uniform layers and a fifth layer only present in part of the hotspot area. The four continuous layers are: an upper aquifer (medium sand), a thin organic silt layer, a lower aquifer (silty sand), and a downwards delineating clay layer. The fifth layer is a thin sandy sludge layer in the unsaturated zone.

- The hydrogeology at the site is strongly affected by the fluctuating conditions in the North Sea, which results in temporal variation in the flow direction and the interaction between the two secondary aquifers. The hydrogeology is further affected by the impermeable barriers at the site (cover membrane and sheet piles), which results in complex flow and recharge patterns.

- The distribution of contaminants can be divided into several horizontal zones: a peripheral area outside the sheet pile barrier with low contaminant concentrations, which results in a baseline contamination of the North Sea; the source area bordered by the sheet pile barrier, where the contaminant concentrations are high, but no DNAPL is present (15,000 m²); and a hotspot area where residual and mobile DNAPL is present (6,000 m²). In part of the hotspot area additional contamination is present in the unsaturated zone.

- The majority of the contamination is found in the upper aquifer, while significant levels of contamination is also found in the lower aquifer, the organic silt layer and the unsaturated sandy sludge layer.

The review of the existing data has shown that there are significant conceptual uncertainties connected with the organic silt layer, the lower aquifer and the sandy sludge layer. The investigations have generally been focus on the most contaminated upper aquifer, which is the layer designated for remediation. After the remediation the other layer will be a significant source to the overall contaminant flux to the North Sea.

It is recommended that additional data are collected for the layers with the highest uncertainty. This is especially valid for the newly discovered sandy sludge layer, where data are very limited. Since *in situ* alkaline hydrolysis is not applied to these layers additional data on the initial contaminant mass are especially desirable. The
reevaluation of the initial contaminant mass for all the selected focus compounds may be partly based on the data collected in connection with the different \textit{in situ} alkaline hydrolysis pilot tests in the area. In case the conceptual model is not updated, the suggested estimates in the report will be used in the risk assessment.

\section*{5.2 Risk assessment}

The risk assessment will be carried out using a reversed risk assessment approach to relate the acceptable down-gradient concentrations in the North Sea to remediation stop criteria in the source area. The relationship is based on modelling of the dilution factors.

The planned risk assessment will include several elements. The dilution between the source area and the discharge point to the North Sea will be determined using a modified version of the FEFLOW model and simple leaching calculation. Ideally the modelling should be done in 3D to properly represent both the flow patterns around the sheet pile barrier (horizontal plane) and the development in the contamination situation in the different geological layers (vertical plane). The model development should be carried out in cooperation with Aarhus University during the intermediate period (2012).

It is suggested that the modelling includes six scenarios with different hydraulic conditions and contamination situations. The six scenarios are:

A) Baseline situation (one scenario): The current situation, where contaminants are leaching to the North Sea from the area outside the sheet pile barrier. If the baseline concentrations are high, the additional contribution from source area leachate after deterioration of the sheet pile barrier will be limited.

B) Uniform deterioration of the impermeable barriers (two scenarios): One scenario represents a situation where only the sheet pile barrier deteriorates; the other scenario represents a situation where both the sheet pile barrier and the membrane cover deteriorate. For both the scenarios the contaminants are released with a uniform flow through the source area, while the majority of the flow is bypassing the barrier.

C) No barriers (two scenarios): One scenario represents a situation where the impermeable barriers are removed immediately after the remediation; the other scenario represents a situation where the barriers have been slowly deteriorated leaving less contamination behind at the time the barriers are gone. The hydraulic conditions are back to the situation before the sheet pile barrier was installed.

D) No remediation (one scenario): The situation in case the sheet pile barrier is removed without any remediation carried out. Similar to the situation before the
The same 3D model is used for all the scenarios, these can relatively easy be adjusted if any changes in the conceptual model suggests that another combination of the hydraulic and contaminant condition would be more desirable.

The dilution after discharge of the leachate to the North Sea will be determined based on a local 2D depth integrated numerical model (MIKE21) developed by DHI. The model considers tidal effects, regional weather systems and local wind condition in the determination of contaminant spreading in the North Sea. The model results are used without further adjustment unless the discharge volume of leachate from the FEFLOW modelling differs greatly from the modelled volume (around 1 l/s). Also, the dilution factor will be assumed to be the same for the discharge from the upper aquifer and the lower aquifer. The model data is obtained from DHI by the Central Region during the intermediate period (2012).

The assessment of ecosystem health in the North Sea will focus on nine selected compounds. The focus compounds have been based on previous selected focus compounds, observation on compound toxicity and prevalence, along with the expected degradation pathways at the site (alkaline hydrolysis and natural degradation). The nine suggested focus compounds are:

- Ethyl parathion
- Methyl parathion
- Malathion
- Ethyl sulfotep
- Amino parathion
- EP2-acid
- MP2-acid
- \( p \)-nitrophenol
- 4-chloro-\( o \)-cresol

Mercury can be added to the list of focus compounds in case the pilot scale remediation shows that the increased pH results in significant metal mobilisation.

It is suggested that the assessment of the North Sea is based on the already existing environmental quality standards as these are based on recognised methods. Supplementary toxicity testing of the leachate could be applied. This could be beneficial in connection with the range of contaminants not included among the focus compounds and unexpected adverse impacts of the changed environmental conditions due to NaOH addition. However, it is not a standard approach and some method development may be needed.
Appropriate points of compliance should be placed in order to determine the short- and long-term fulfilment of the environmental quality standards. Placement of two sets of compliance points are suggested: one set above the organic silt layer and one below the organic silt layer. The use of two sets of compliance points reflects that the expected development of the contaminant flux is significantly different the two aquifers. This distinction between the contributions from the two secondary aquifers will not be applied after discharge to the North Sea, since the location of the discharge zones for the aquifers is unclear and the mixing is significant.

It is suggested that solute concentrations of the focus compounds and pH are measured at the points of compliance. The sampling frequency will initially be related to the in situ alkaline hydrolysis cycles. The long-term monitoring program after the remediation should be based on the condition of the sheet pile barrier; the most frequent sampling campaigns should be after indications of sheet pile barrier deterioration have been observed. The sampling density will be an important issue in connection with the determination of compliance with the remediation stop criteria. Initially, it is suggested that this is examined further in connection with the current pilot-scale remediation project, since the variation in the concentrations after addition of NaOH is of great importance for the needed sampling density.

5.3 Activities in 2012

Based on the uncertainty of the available data and the model needs of the risk assessment it is suggested that a number of tasks are carried out in the intermediate period (2012) before phase B. An outline of the tasks is presented in Table 6.
Table 6. Outline of tasks to be carried out in the intermediate period (2012), and the assignment of responsibility for initialising and/or performing the task.

<table>
<thead>
<tr>
<th>Task</th>
<th>Responsible</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Conceptual model:</strong></td>
<td></td>
</tr>
<tr>
<td>Characterisation of the sandy sludge layer (extent, properties) for</td>
<td>Central Region</td>
</tr>
<tr>
<td>determination of leaching from the unsaturated zone</td>
<td></td>
</tr>
<tr>
<td>Reevaluation of the initial mass in all geological layers (focus</td>
<td>Central Region</td>
</tr>
<tr>
<td>compounds)</td>
<td></td>
</tr>
<tr>
<td><strong>Focus compounds:</strong></td>
<td></td>
</tr>
<tr>
<td>Assessment of the mobilisation of mercury by alkaline hydrolysis</td>
<td>Central Region (COWI)</td>
</tr>
<tr>
<td>(risk potential)</td>
<td></td>
</tr>
<tr>
<td><strong>Solute transport (dilution from source area to North Sea):</strong></td>
<td></td>
</tr>
<tr>
<td>Set-up of 3D numerical model for the focus area</td>
<td>Aarhus University</td>
</tr>
<tr>
<td>Input for 3D numerical model</td>
<td>DTU Environment</td>
</tr>
<tr>
<td>Additional hydraulic data (e.g. head measurements) for model set-up</td>
<td>Central Region</td>
</tr>
<tr>
<td>Final determination of model scenarios</td>
<td>Central Region/DTU</td>
</tr>
<tr>
<td><strong>Dilution in North Sea:</strong></td>
<td></td>
</tr>
<tr>
<td>Data acquisition (DHI model)</td>
<td>Central Region</td>
</tr>
<tr>
<td><strong>Assessment of the North Sea water quality:</strong></td>
<td></td>
</tr>
<tr>
<td>Additional measurements for baseline levels of the two focus</td>
<td>Central Region</td>
</tr>
<tr>
<td>compounds close to EQS (ethyl sulfotep, ethyl amino parathion)</td>
<td></td>
</tr>
<tr>
<td>*Approach for supplementary toxicity based remediation criteria</td>
<td>DTU Environment</td>
</tr>
<tr>
<td>*Bench-scale toxicity studies (site material and alkaline hydrolysis)</td>
<td>Central Region</td>
</tr>
<tr>
<td><strong>Compliance points:</strong></td>
<td></td>
</tr>
<tr>
<td>Needed sampling density for characterisation of the pilot scale</td>
<td>Central Region (COWI)</td>
</tr>
<tr>
<td>remediation (spatial variation after <em>in situ</em> alkaline hydrolysis)</td>
<td></td>
</tr>
</tbody>
</table>

*Depending of the desire for using this supplementary approach.
6 References


/23/ Analysis of DNAPL from Groyne 42 (2011), data from the Central Region.


/27/ Concentrations at the foreshore (2007-2010), database from the Central Region.

/28/ Concentrations in the North Sea (2004-2010), database from the Central Region.


/38/ TOXNET (2011). Hazardous Substances Data Bank (HSDB) at the TOXicology Data NETwork. Toxicology and Environmental Health Information Program (TEHIP) in the Division of Specialized Information Services (SIS) of the National Library of Medicine (NLM).


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