Technical University of Denmark

DTU

NorthPestClean

Remediation Stop Criteria

Fjordbøge, Annika Sidelmann; Bjerg, Poul Løgstrup; Binning, Philip John; Poulsen, Søren E.

Publication date:
2014

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):
Fjordbøge, A. S., Bjerg, P. L., Binning, P. J., & Poulsen, S. E. (2014). NorthPestClean: Remediation Stop Criteria. Kgs. Lyngby: Technical University of Denmark (DTU).
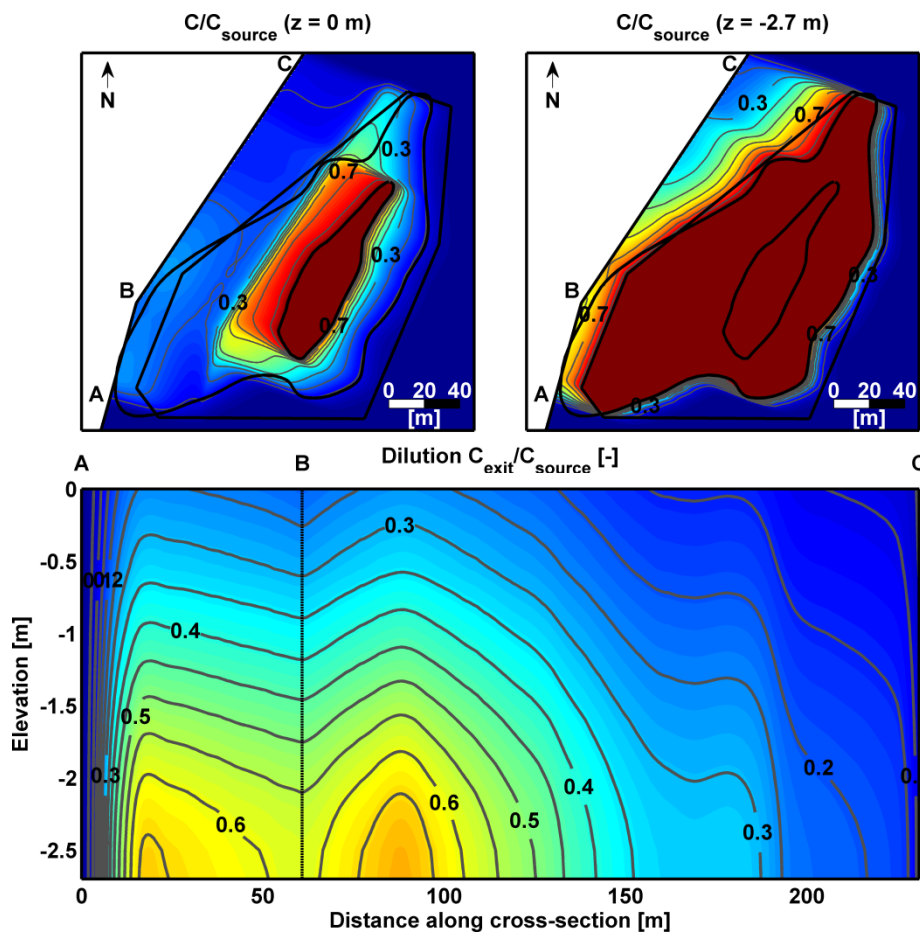
DTU Library
Technical Information Center of Denmark

NorthPestClean: Remediation Stop Criteria

Prepared by:

DTU Environment: Annika S. Fjordbøge, Poul L. Bjerg, and Philip J. Binning

Department of Earth Sciences, Aarhus University: Søren E. Poulsen

June 2014

Project no.: Life09/ENV/DK368

Preface

The focus of this report is the remediation stop criteria needed to achieve the existing environmental quality standards in the North Sea downstream of the Groyne 42 site. This work is done as a part of the EU Life project NorthPestClean (NPC).

The reported remediation criteria are partly based on existing data related to the conceptual model for the site. This data was collected by the Central Denmark Region and the consultant consortium associated with the NPC project.

The risk assessment modelling and the final remediation stop criteria are determined by DTU Environment in collaboration with the Department of Earth Sciences, Aarhus University. This work was started in August 2011 and finalized in May 2014. The majority of the work was done in two phases: an initial phase (2011) with conceptual development and identification of data needs (cf. Appendix A); and a final phase (2013) with risk assessment modelling resulting in the determination of remediation stop criteria and suggestions for remediation compliance points.

In the initial phase ten focus compounds (ethyl parathion, methyl parathion, malathion, ethyl sulfotep, EP2-acid, MP2-acid, *p*-nitrophenol, ethyl aminoparathion, 4-chloro-*o*-cresol and mercury) were selected and six different model scenarios were suggested (cf. Appendix A). Additional data has been collected in the intermediate period (2012); as a result, the conceptual model and the final model scenarios have been adjusted. However, the elements of the reverse risk assessment approach remain the same. The main changes to the conceptual model are presented in chapter 2, while the new model scenarios are presented in chapter 3.

Summary

The Remediation Stop Criteria (RSC) project is part of the EU Life project, NorthPestClean (NPC). The NPC project assesses the efficacy of *in situ* alkaline hydrolysis for remediation of organophosphate insecticides at a DNAPL (Dense Non-Aqueous Phase Liquid) contaminated site, Groyne 42 (Høfde 42). This report is the final outcome of the RCS project.

Remediation stop criteria were determined based on risk assessment modelling and points of compliance were suggested. The remediation stop criteria were determined for ten focus compounds: ethyl parathion, methyl parathion, malathion, ethyl sulfotep, aminoparathion, *p*-nitrophenol, EP2-acid, MP2-acid, 4-chloro-*o*-cresol and mercury (total species).

The risk assessment modelling was based on a reverse risk assessment approach, where the long-term criteria for the North Sea (marine environmental quality standards) are transformed to acceptable contaminant levels at the source area (remediation stop criteria). The dilution in the upper secondary aquifer (source area to sea) was determined by FEFLOW 3D modelling with steady-state confined groundwater flow and conservative solute transport. The mixing based dilution in the North Sea was determined by the DHI Dashboard model for the Danish coastline. The dilution in the secondary upper aquifer was determined for the following scenarios: contamination of the entire area (natural flow conditions and limited flow conditions with and without infiltration), contamination of the central infiltration area and contamination of the peripheral area.

The remediation stop criteria strongly depended on the extent of the contaminated peripheral area. In case of heavy contamination in the peripheral area, remediation of the central infiltration area alone would have almost no impact on the marine contaminant levels. In case the contamination in the peripheral area was negligible, the remediation stop criteria were one order of magnitude higher than when the entire area was significantly contaminated. Hence, the proximity of the source area to the North Sea was of great importance; a shorter transportation path from the source to the North Sea allowed for significantly less dilution from recharge and overtopping of seawater. A very high efficiency (>99 %) will be required of the remediation technology to reduce the most challenging compounds (ethyl parathion, methyl parathion and malathion) to the remediation stop criteria. Compliance with the remediation stop criteria will reduce the mass discharge of parathion to the North Sea to <1 kg/year.

The fulfilment of the remediation stop criteria should be documented at a set of compliance points in the source area. Based on the current conceptual model, an even distribution of compliance points in the source area was recommended. Also, ongoing monitoring (snapshot checking) should take place during remediation, ultimately followed by a full monitoring campaign (solute and/or total concentrations).

Table of content

1   Introduction

1.1 Background

The Remediation Stop Criteria (RSC) project is part of the EU Life project NorthPestClean (NPC) in which pilot scale testing of *in situ* alkaline hydrolysis is conducted at the Groyne 42 site (Høfde 42). The NPC project should demonstrate the efficacy of *in situ* alkaline hydrolysis and provide the knowledge required to design a full scale site remediation.

The Groyne 42 site is located at the Danish West Coast. The site was used to deposit various chemicals in the 1950's and 1960's. The primary contaminants are organophosphate insecticides produced at the nearby chemical plant, which had permission to deposit waste water and solid waste at the site. In 1981, the majority of the contamination was removed by excavation of the unsaturated zone /1/. However, the remaining contamination has resulted in continued contaminant discharge to the North Sea. Therefore, the source area was encased by a sheet pile barrier in 2006. At the same time different remediation technologies were screened and *in situ* alkaline hydrolysis was chosen for pilot scale remediation /2/.

The RSC project should determine the remediation stop criteria for any chosen remediation technology. Two different types of remediation criteria can be defined: the absolute criteria and the 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 /3/. The absolute criterion at the Groyne 42 site has been defined as the protection of the North Sea ecosystem health (cf. Appendix A), whereby compliance with the criterion should prevent any further adverse ecological impacts in the North Sea. Since the absolute criterion is not easily quantifiable, the functional criteria are introduced to obtain quantifiable goals for the remediation. For the Groyne 42 site the functional criteria have been defined as the reduction of contaminant concentrations below a threshold level at the compliance points (locations and times at which to monitor remediation outcomes) in the source area (cf. Appendix A).

1.2 Project aim

The main project aim was to develop functional remediation stop criteria for the remediation of the Groyne 42 site based on risk assessment. The risk assessment included:

- an assessment of the post remediation contaminant discharge from the source area to the North Sea on the basis of 3D modelling with steady-state confined groundwater flow and conservative solute transport

- an assessment of the mixing in the North Sea based on the existing Dashboard model for the Danish coastline

- an ecological assessment based on existing marine environmental quality standards (EQS) developed on the basis of the PNEC (Predicted No Effect Concentration) values for the North Sea

Remediation stop criteria were recommended based on the outcome of the risk assessment and modelling. The stop criteria are to be controlled at an appropriate set of compliance points for remediation monitoring and long-term monitoring after the remediation; these were developed in the project.

2   Method

This chapter presents the overall approach for the risk assessment modelling and the resulting remediation stop criteria and points of compliance. Also, the updated conceptual model is presented along with the deliberations that led to the conceptual changes. The conceptual model has been updated with better understanding of the hydraulic conditions at the site through additional modelling in this RSC project, while the updates relating to the contamination distribution were done by the consultant consortium behind the pilot scale testing /4/.

2.1   Approach

The risk assessment was based on a reverse risk assessment approach (cf. Figure 2.1). To relate the concentration in the source area and the concentration in the North Sea the risk assessment operated with two types of functional criteria: the long-term criteria to ensure good ecosystem health in the North Sea (marine EQS) and the short-term criteria (remediation stop criteria) to ensure remediation in the source area is sufficient to achieve the long-term criteria. Due to the solute transport time there will be a delay between the source area remediation and the reduction in the contaminant concentrations in the North Sea. The two types of functional criteria, at each point of compliance (North Sea and source), were linked via the dilution occurring between the two points. The approach is called a reverse risk assessment approach as 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 area.

The approach included the definition of the acceptable environmental impacts on the North Sea and a combination of models to determine the contaminant dilution from the source area to the North Sea. The dilution between the source area and the discharge point to the North Sea was determined using a 3D model (FEFLOW) with steady-state confined groundwater flow and conservative solute transport (cf. Appendix B). The dilution in the North Sea was determined based on the DHI Dashboard model /5/; the Dashboard model was found to be in good agreement with a more detailed local DHI MIKE21 model /6/ (cf. Appendix A). The acceptable environmental impacts were established through already existing EQS; these were found to be determined by recognised methods for marine EQS (cf. section 3.4) /7/. Further details on the approach and the findings in the initial phase of the project can be found in Appendix A.
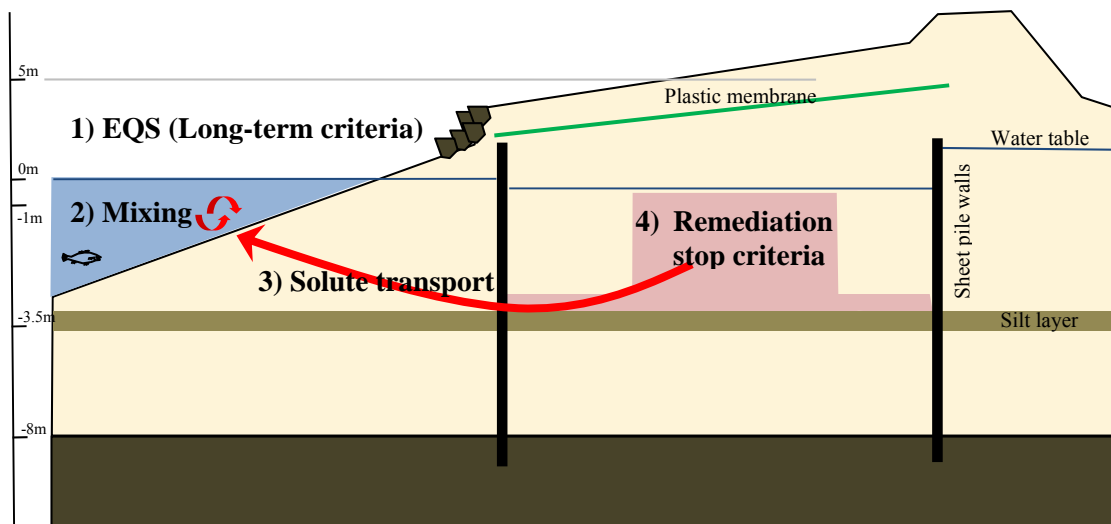
Figure 2.1. Schematic cross section of the site showing the steps of the reverse risk assessment to get to the final remediation stop criteria: 1) specified long-term criteria for compliance in form of the marine EQS; 2) dilution by mixing in the North Sea (Dashboard); 3) dilution during solute transport from the source area to the North Sea (FEFLOW); and 4) the final specified remediation stop criteria.

2.2 Data interpretation

In the initial phase of the project a simplified conceptual model was introduced based on the available data on geology, hydrology and contaminant distribution (Appendix A). The hydraulic interaction between the upper and the lower secondary aquifer has since been investigated through modelling (cf. Appendix D). Also, additional characterization of the source area has led to a revised conceptual model of contaminant distribution made by the consultant consortium behind the pilot scale testing /4/.

2.2.1 Hydraulic interaction

In the initial phase of the project, the information on the hydraulic interaction between the upper and the lower secondary aquifer was found to be limited (Appendix A). The difference in hydraulic head was small between the two aquifers and the direction of the hydraulic gradient seemed to depend on the specific location and the conditions in the North Sea.

A 2D numerical model (FEFLOW) simulating density-dependent flow was set up to test the leakage from the upper to the lower secondary aquifer through the thin silt layer separating the two aquifers. The calculated salinity distributions (with and without leakage) were compared to the observed salinity at groyne 41, 42 and 44. The best fit was achieved when assuming negligible leakage to the lower aquifer (cf. Appendix D). Hence indicating that it is reasonable to simulate the upper and lower secondary aquifer separately.

The negligible leakage to the lower aquifer also indicates that the convective transport of contaminants from the upper to the lower aquifer will be very limited. Based on conservative calculation the Central Denmark Region has concluded that both the convective and the diffusive transport of contaminant from the upper to the lower aquifer and the resulting mass discharge to the North Sea is negligible (around 1 kg/year for parathion) compared to the mass discharge from the upper aquifer (cf. Appendix E).

2.2.2 Contaminant distribution and concentrations

The horizontal (Figure 2.2) and vertical (Figure 2.3) distribution of the contaminants have been re-evaluated by the consultant consortium behind the pilot scale testing /4/. The extent of the central infiltration area, characterized by heavy contamination in the full depth of the upper secondary aquifer (elevation +1.5 m to -2.8 m), was smaller than previously assumed. In the surrounding peripheral area the contamination was primarily found at the first 0.5 m right above the silt layer. It was also found that the silt layer was only slightly contaminated.

Figure 2.2. The conceptual horizontal distribution of the contaminants as given by the consultant consortium /4/. The site has been divided into three areas: the central infiltration area (zone 1-2; red), the peripheral area (zone 3-6; yellow) and a lightly contaminated outer area (green); whereas the different borehole colors/symbols indicate different sampling years. Only the areas within the sheet pile barrier were included in the mass calculations /4/.
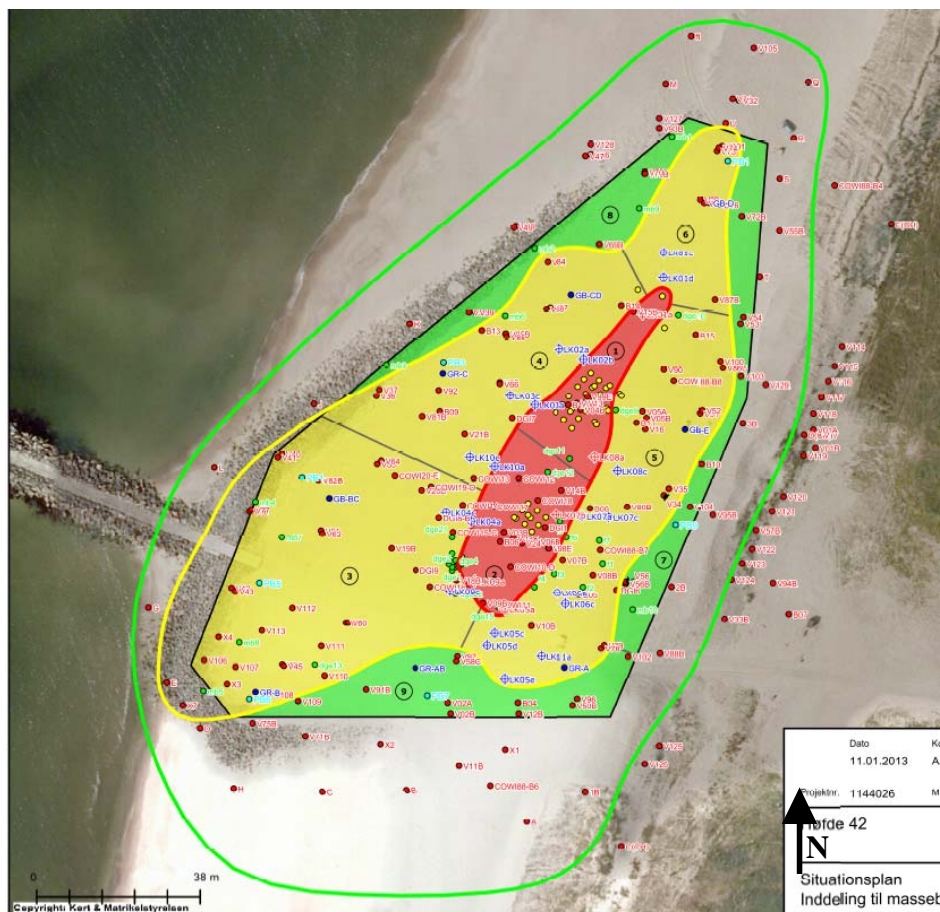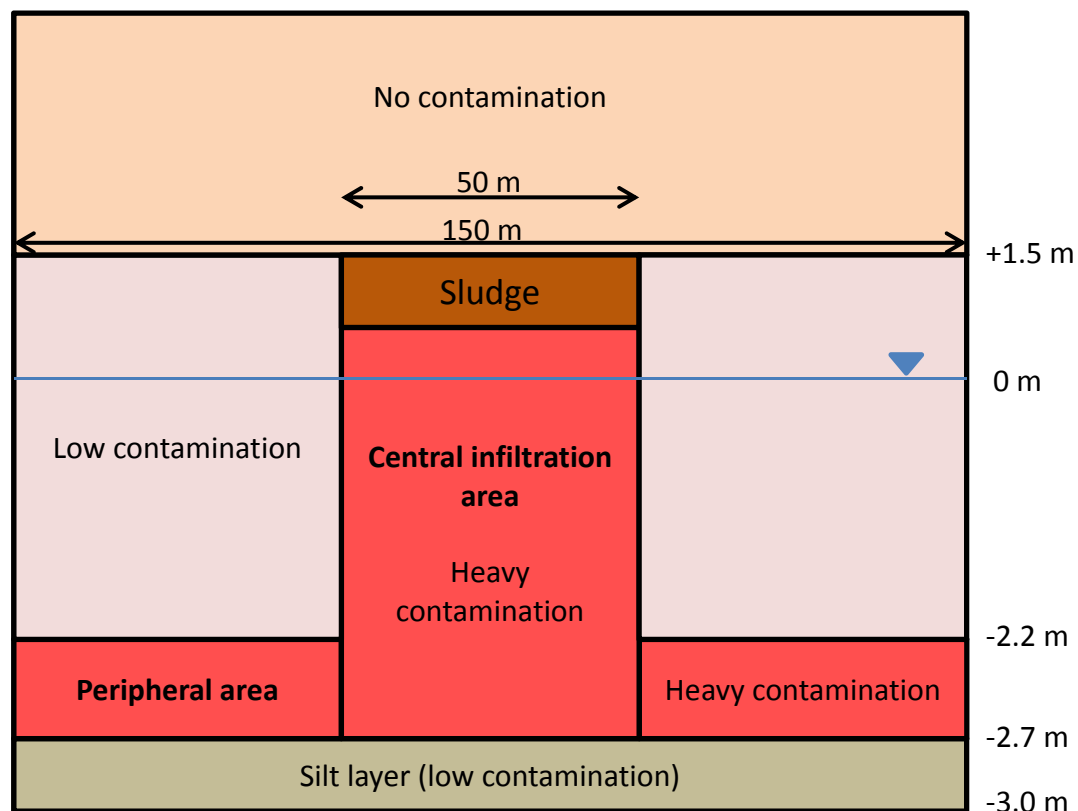
Figure 2.3. The conceptual vertical distribution of the contaminants given by the consultant consortium /4/. The site has been divided into two areas: the central infiltration area (contamination over the full depth) and the peripheral area (contamination only right above the silt layer). "Low" concentrations have been assigned to the silt layer and the upper sand in the peripheral area, which were therefore not included in the mass calculation or risk assessment.

Since the re-evaluation was focused on delineation of the central infiltration area, the extent of this area is well-defined. However, the extent of the peripheral area is more uncertain, especially towards the North Sea (western direction).

Additionally, the contaminant mass in the source area was estimated by the consultant consortium based on simple average concentrations in the subzones (Table 2.1) i.e. with no weighting of sample density in specific areas.

Table 2.1. Average soil concentrations (mg/kg) of seven focus compounds in: the central infiltration area (zone 1-2), the bottom 0.5 m of the peripheral area (zone 3-6) and their combined total area (zone 1-6) /4/. The median concentrations (mg/kg) are given in parentheses.

Area	Ethyl parathion (mg/kg)	Methyl parathion (mg/kg)	Malathion (mg/kg)	Ethyl sulfotep (mg/kg)	Mercury (mg/kg)	Amino-parathion (mg/kg)	4-Cl-*o*-cresol (mg/kg)
Infiltration	1888 (1083)	346 (81)	157 (20)	70 (9.2)	186 (110)	14 (3.0)	15 (2.6)
Peripheral	3895 (1400)	525 (91)	119 (11)	418 (95)	70 (12)	124 (6.0)	319 (46)
Total	2178 (1098)	367 (81)	152 (19)	111 (11)	157 (79)	27 (3.1)	35 (2.9)

The data show that the average concentration levels in the bottom of the peripheral area are generally at least as high as the average concentration levels in the infiltration area (cf. Table 2.1). Only the malathion and mercury concentrations are estimated to be lower in the peripheral are than in the infiltration area. The high concentrations in the peripheral area may be an indication of the poorer characterization of this area (few high concentration samples).

Statistical processing of the data shows a positively skewed concentration distribution (cf. Figure 2.4); as a result the average concentrations are up to one order of magnitude higher than the median concentrations (up to two orders in magnitude when only considering the peripheral area, cf. Appendix F). Hence, the use of average concentrations gives additional weight to the high concentration outliers.
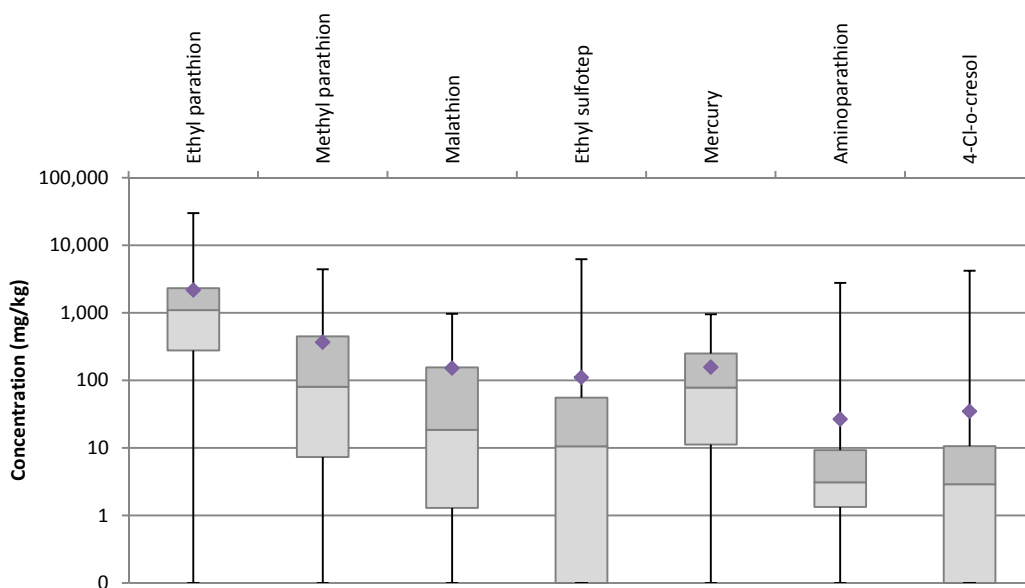
Figure 2.4. The average concentration (diamond) of seven focus compounds in the total area shown on a logarithmic scale. Additionally, the box plot shows the median, the interquartile range (box) and the extremes (whiskers).

Given that the characteristics of the porous media are similar to those at Groyne 44 (a porosity of 0.3, a bulk density of 1.86 kg/L and an organic carbon content of 0.5 %), the average concentrations in both the infiltration area and the peripheral area indicate the presence of DNAPL for the organophosphate insecticides (ethyl parathion, methyl parathion and malathion). The conceptual understanding of the contaminant distribution would therefore benefit from an assessment of the DNAPL distribution at the site in the form of visual observations and calculations of DNAPL saturation.

Based on the concentration of individual samples, 72-77 % of the sample locations in the infiltration area are likely to contain DNAPL (ethyl parathion).

In contrast, none (e.g. borehole V40, V76 and V85) or very little (e.g. V36) DNAPL is present in the peripheral area closest to the North Sea (cf. Appendix G**Error!**

Reference source not found., in Danish). Earlier measurements of aqueous concentrations also indicate that the area close to the North Sea is not heavily DNAPL contaminated, since most aqueous concentrations are less than 1% of the water solubility /8/. Both the DNAPL saturations and the sample densities vary significantly within the peripheral area. Also, the samples assigned to the peripheral area (contaminated lower 0.5 m) vary significantly in elevation (-1.09 m to -3.77 m). The calculations for the peripheral area are thereby rather uncertain and might benefit from weighing of the measured concentration data based on sample density.

2.3 The conceptual model

The conceptual model is presented in Figure 2.5.
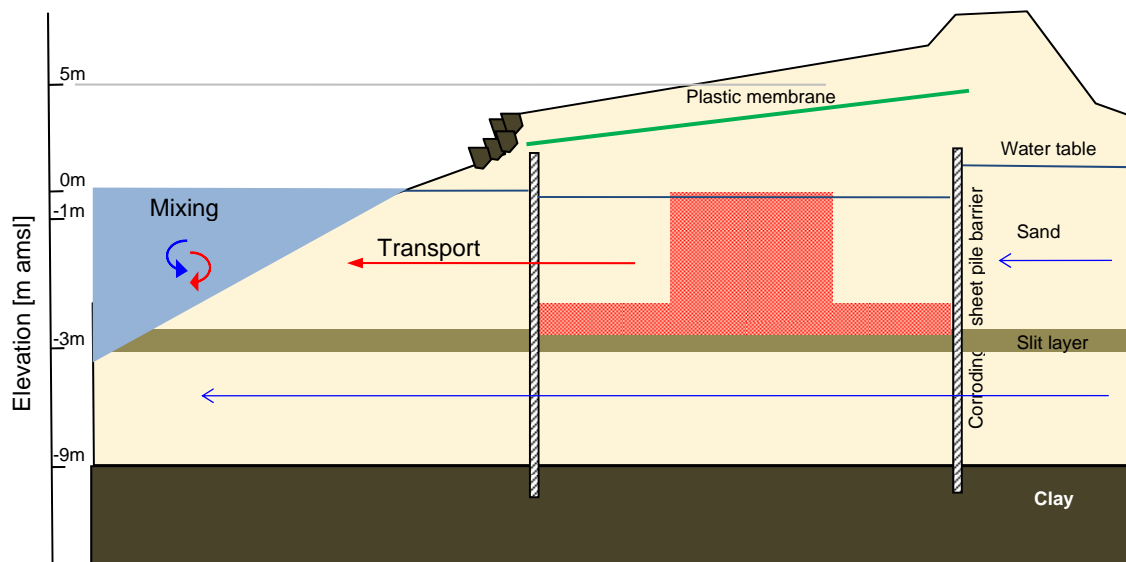
Figure 2.5. The conceptual model shows the current understanding of the contaminant distribution and the hydraulic and geological conditions at the contaminated site.

In connection with the risk assessment, the following simplifications/assumptions apply to the conceptual model:

- The geological sequence is assumed to be represented by four homogeneous layers: an upper sandy aquifer (2.7 m), a low permeable organic silt layer (0.3 m), 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.

- There is no significant contamination in the lower secondary aquifer, since the silt layer has low contaminant concentrations and there is no hydraulic interaction between the upper and the lower secondary aquifer.

- After the remediation there is assumed to be no significant contamination in the unsaturated zone (treated or excavated).

- Inside the sheet pile barrier the high contaminant concentrations are present in the entire central infiltration area and in the first 0.5 m above the silt layer in the entire peripheral area. In the remaining area the contamination is negligible; this is also the case for the entire area outside the sheet pile barrier.

If the situation differs significantly from the above mentioned it may have an impact on the validity of the remediation stop criteria determined by the risk assessment modelling. In particular, the possible presence of significant amounts of contaminants below the silt layer and outside the sheet pile barrier (i.e. the extent of the peripheral area) are worth mentioning as possible sources of error.

3 Risk assessment modelling

This chapter briefly presents the individual steps of the risk assessment modelling and the final model scenarios. The discharge from the source to the North Sea (FEFLOW model), the mixing in the North Sea (Dashboard model) and the marine EQS for compliance are presented.

3.1 Model scenarios

The updated conceptual understanding of the contaminant distribution has led to a new set of model scenarios. The final scenarios are:

A. Baseline situation: The scenario represents the current situation before the impermeable barriers starts to deteriorate, where the contamination is isolated from the flow. The scenario is only used to set up the model hydraulics e.g. to narrow the model domain to the currently used domain.

B. Partly deteriorated sheet pile barrier: The scenario represents a situation where groundwater no longer is prevented from flowing through the source area. Since the barrier is only partially deteriorated, the groundwater flow is less than under natural conditions. The scenario includes two different infiltration situations:

   B1) Intact cover membrane (no infiltration)

   B2) No cover membrane (full infiltration)

Contamination levels are the same for the infiltration area and the peripheral area (bottom 0.5 m).

These scenarios are used to determine the importance of a partial flow through the source area with and without infiltration.

C. Fully deteriorated sheet pile barrier (partial remediation): The scenario represents a situation where the flow through the source area is the same as under natural conditions. The scenario includes two different contamination situations:

   C1) Only the peripheral area is contaminated

   C2) Only the infiltration area is contaminated

These scenarios are used to determine the importance of which areas are included in the remediation.

D. Fully deteriorated sheet pile barrier (full remediation): The scenario is the same as scenario C with regard to the flow conditions; however, both the infiltration and the peripheral area are contaminated as in scenario B.

The main purpose of including several scenarios is to determine the dilution under different flow and remediation conditions.

3.2 Discharge from the source area to the North Sea

The contaminant discharge from the source area has been modelled for the different scenarios using a FEFLOW 3D model with steady-state confined groundwater flow and conservative solute transport. The model only includes the upper secondary aquifer as the hydraulic interaction with the lower secondary aquifer through the silt layer is negligible.

The results of the model simulations of baseline scenario A (cf. Appendix C) illustrates the impact on the flow from the sheet pile barrier (cf. Figure 3.1).
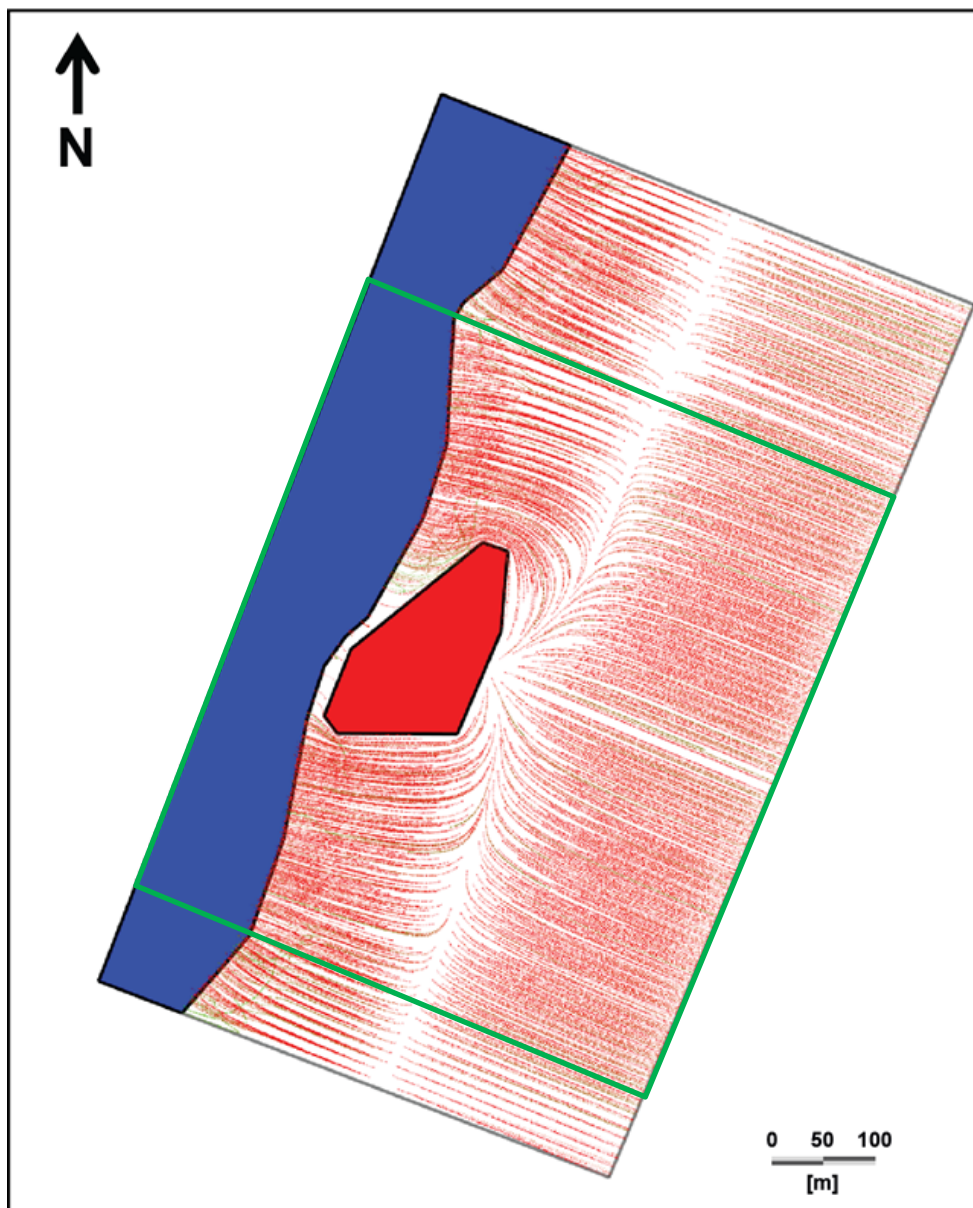
Figure 3.1. The effect on the flow by the sheet pile barrier is illustrated by stream lines in the FEFLOW model area (scenario A). A water divide is located a short distance east of the repository. The reduced model domain (green square) for the other scenarios is illustrated.

A reduced model domain was used for the other scenarios, since the flow outside this area was not affected by the sheet pile barrier. The final model domain and boundary conditions are presented in Figure 3.2, further details can be found in Appendix B.
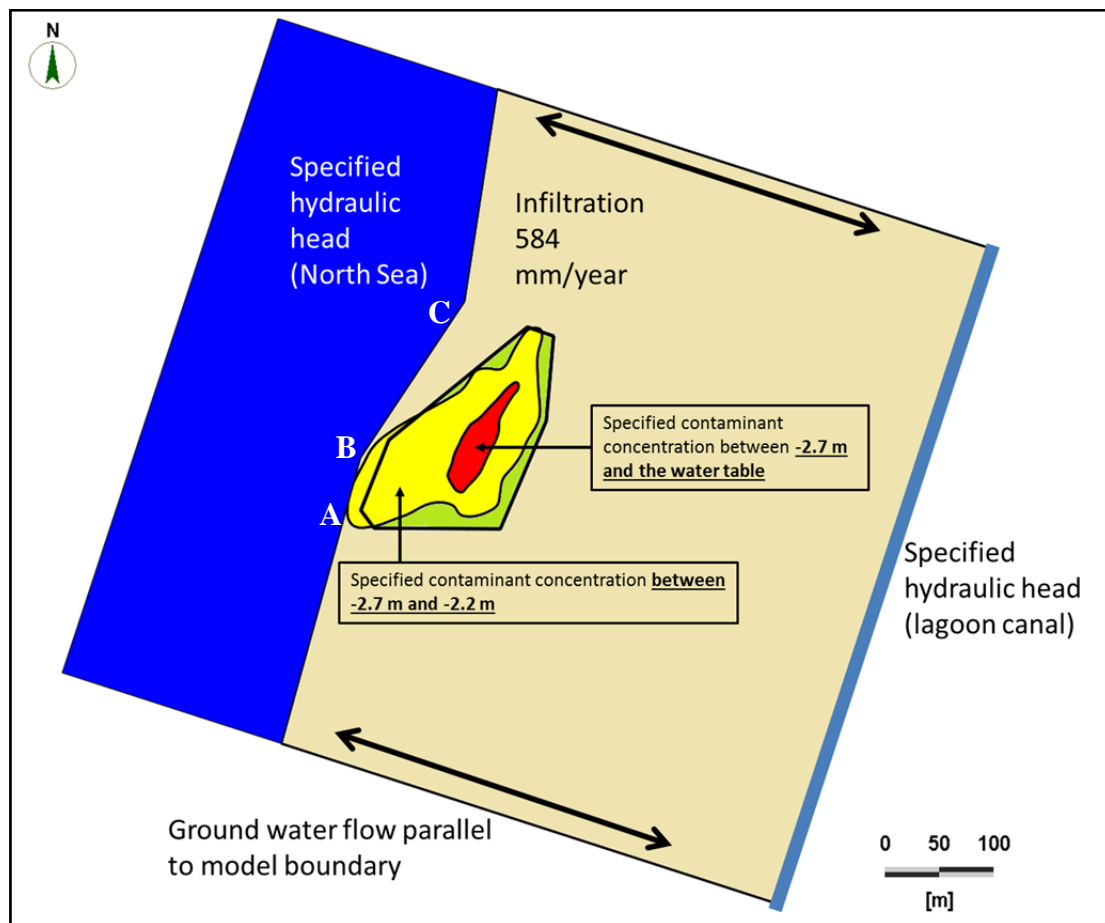
Figure 3.2. The illustrated model domain and boundary conditions were used for the FEFLOW model. The contamination is only specified for the infiltration area (red) and the peripheral area (yellow) inside the sheet pile barrier. The contamination does not extend outside the confines of the sheet pile barrier (as otherwise indicated). The letters A, B and C indicate where vertical contour maps of the normalized contaminant concentration at the discharge area to the North Sea have been generated by the FEFLOW model.

The results of the model simulations of the contaminant transport (scenarios B-D) are illustrated by horizontal and vertical contour maps of the normalized contaminant concentration, where the normalized solute source concentration has a specified value of one.

The vertical contour maps are similar for most scenarios (cf. Appendix B), only scenario C2 shows a contour map that is very different from the other scenarios. Contour maps of the normalized contaminant concentration at the vertical coastline profile and horizontal planes are presented for scenario C2 (Figure 3.3) and scenario D (Figure 3.4).
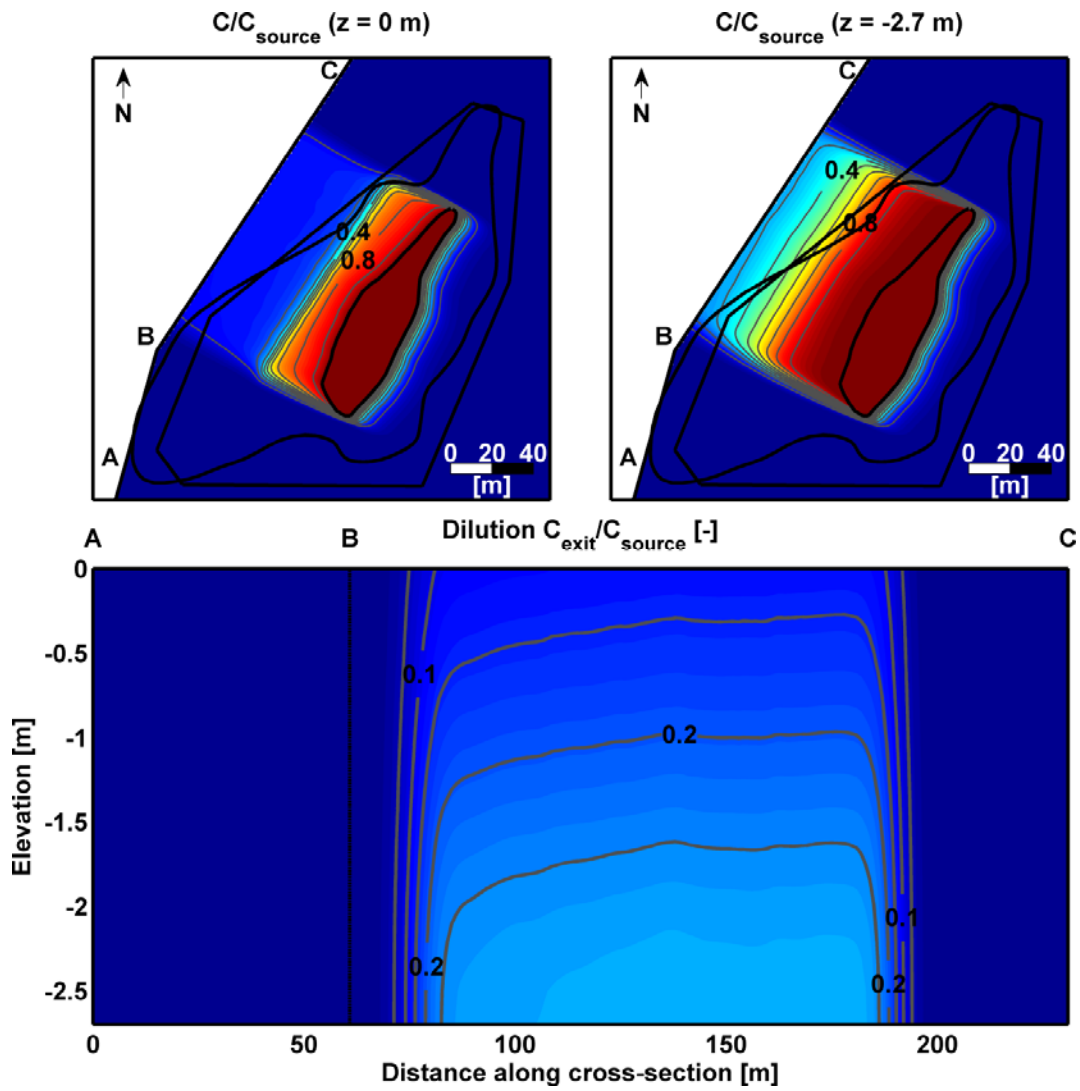
Figure 3.3. Normalized contaminant concentration for scenario C2 at: 0 m (top left) and the top of the silt layer -2.7 m (top right). Contaminant exit concentration (C_{exit}) relative to the source concentration (C_{source}) along the vertical coastline cross-section (south to north) indicated by ABC in the top left and right figures (bottom figure). Equidistance = 0.1 (top figures) and 0.05 (bottom figure). Aspect ratio is 40:1 in the bottom figure.
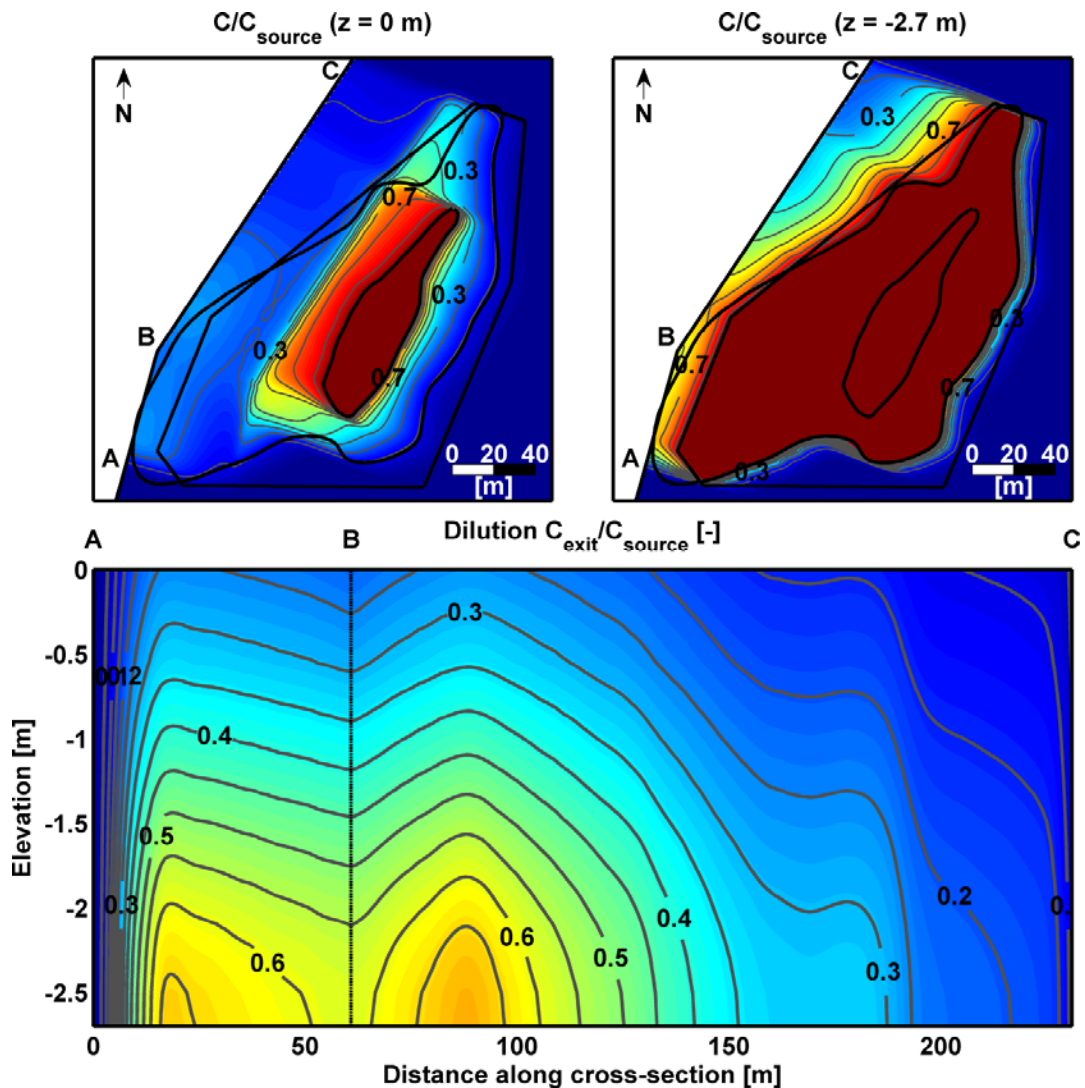
Figure 3.4: Normalized contaminant concentration for scenario D at: 0 m (top left) and the top of the silt layer -2.7 m (top right). Contaminant exit concentration (C_{exit}) relative to the source concentration (C_{source}) along the vertical coastline cross-section (south to north) indicated by ABC in the top left and right figures (bottom figure). Equidistance = 0.1 (top figures) and 0.05 (bottom figure). Aspect ratio is 40:1 in the bottom figure.

Since the FEFLOW model uses conservative solute transport, the dilution is only obtained from recharge and overtopping of seawater. This dilution results in relatively low concentrations in the shallow part of the aquifer. The concentrations increase with depth due to the relatively large extent of the peripheral contamination area (except scenario C2), where the largest concentrations are found just above the silt layer. The concentrations are generally lower in the northern part of the vertical cross-section due to a greater distance between the source area and the North Sea. One local concentration maximum is found for scenario C2, while two local concentration maxima are found for all the other scenarios. The positions of these maxima are controlled by the geometry of the source area.

Statistics of the measures for the contaminant discharge concentrations are presented in Table 3.1 in the form of average dilution and contaminant discharge (L/s).

14

Table 3.1. The average dilution and the contaminant discharge (L/s) from the source area to the North Sea are given for the different scenarios.

	Scenario B1	Scenario B2	Scenario C1	Scenario C2	Scenario D
Average dilution	4.8	4.4	3.1	9.3	3.0
Contaminant discharge (L/s)	0.35	0.44	1.2	0.41	1.2

Scenario B shows an effect of the hampered flow (groundwater and recharge) through the source area, this yields 1.5-1.6 times more dilution than scenario D with natural flow conditions. The difference in infiltration/recharge has a relatively small effect on the average dilution (B1 relative to B2) compared to the reduction of the groundwater flow (B relative to D). Since the flow through the source area is reduced, the contaminant discharge volume is also reduced.

A comparison of scenario C and D shows that the extent of the contaminant distribution is of great importance. Given that the contamination concentrations are the same in the infiltration area and the peripheral area, remediation of the peripheral area has a much greater impact on the contaminant dilution than remediation of the infiltration area. The extent of the peripheral area is significantly larger than the infiltration area and also much closer to the North Sea; the shorter transportation path from the source to the North Sea allows for significantly less dilution. As a result scenario C1 is almost identical to D. Since the source area is smaller in scenario C2, the contaminant discharge volume is also smaller.

The model is associated with some uncertainty of which the conceptual uncertainty is thought to be the greatest. With regard to processes affecting the transport and dilution of the contaminants, then the model does not include sorption and degradation. Since it is a steady-state model with a fixed source concentration the sorption will only delay the contaminant transport, while the lack of degradation may result in overestimation of the parent compounds and underestimation of the degradation compounds. However, since the model operates with a fast pore velocity (~200 m/year) and the distance from the boundaries of the source to the sea is short (~20 m in scenario D), the effect of degradation is expected to be limited. Degradation half-lives of 6-25 days under anaerobic conditions have been indicated by previous studies /9-10/, while the actual redox conditions in specific areas of the site are relatively unknown /11/.

3.3   Mixing in the North Sea

The attenuation of the contaminants in the aquifer was generally relatively small; the dilution in the North Sea is therefore the primary contributor to the overall dilution factor. Significant dilution can be achieved since the discharged volume from the

source area is relatively small compared to the volume of sea water it is mixed with upon discharge to the North Sea.

Two possible models can be used to determine the dilution due to mixing in the North Sea: a site specific 2D depth integrated numerical model /6/ or the Dashboard model for the entire Danish coastline /5/. In the initial phase of the project it was found that the dilution factors in the shallower water near the coastline were similar for the two models (Appendix A). Since there is no contaminant discharge from the lower secondary aquifer (assumed uncontaminated) most of the contaminants will be discharge to the shallower region of the seabed; it has therefore been decided to use the more available Dashboard model.

For the grid around Groyne 42, Dashboard estimates an average dilution of 82,600 times, a minimum dilution (0.05 quantile) of 9,400 times and an absolute minimum dilution of 5,200 times in a 55 m surf zone with a depth of 2.7 m. The Dashboard model uses a standardised discharge of 0.1 L/s from a point source on the shoreline. A relatively small discharge volume is inversely proportional with the dilution, whereby a simple correction is possible using the discharge volumes found by the FEFLOW model (cf. Table 3.1). The resulting dilution is presented in Table 3.2.

Table 3.2. The average and minimum (0.05 quantile and absolute) dilution due to mixing in the North Sea for the different scenarios.

Dilution	Scenario B1	Scenario B2	Scenario C1	Scenario C2	Scenario D
Average	23600	18800	6760	20200	6630
Minimum (0.05 quantile)	2690	2150	772	2300	758
Minimum (absolute)	1480	1180	423	1260	415

One limitation of the Dashboard model is that it cannot be used to illustrate how the dilution increases in the North Sea with distance to the source, the more detailed local model is needed for this. However, this is not necessary for determining the remediation stop criteria, since these are based on compliance with the marine EQS close to the coastline.

3.4   Environmental quality standards

The most important focus compounds are the highly toxic organophosphate parent compounds (ethyl parathion, methyl parathion, malathion and ethyl sulfotep). Ethyl parathion is of special interest, since it is the main parent compound (main constituent of the DNAPL) and has very low marine EQS.

Additional focus compounds include: mercury species; the very water soluble main hydrolysis products (EP2-acid, MP2-acid and *p*-nitrophenol); the degradation compound under reduced conditions ethyl aminoparathion; and 4-chloro-*o*-cresol.

With regard to mercury, the risk involved strongly depends on the actual mercury species present at the site and the site conditions (redox, pH and water chemistry). While elemental mercury and e.g. mercuric chloride species have relatively high water solubility compared to other species, mercuric sulphide (i.e. cinnabar, HgS) has a very low solubility and is practically immobile. Due to the low pH values at the site cinnabar is likely to be present under reduced conditions in the source area /12/. However, the exact distribution of mercury species is unknown and may change following the remediation e.g. due to changes in redox and pH). The mercury speciation is too complex and uncertain to include in this risk assessment; the assessment will therefore be based on elemental mercury with relatively high water solubility. It should be mentioned that the mercury measurements in the North Sea before the sheet pile barrier was installed did not exceed the marine EQS or even the normal background concentration of mercury in coastal seawater (cf. Appendix A). Also, the instalment of the sheet pile barrier did not significantly reduce the mercury concentration in the North Sea, whereby mercury is expected to be present in the source area as poorly soluble species. Hence, mercury is not expected to cause a problem unless the remediation results in a shift to more soluble/mobile mercury species.

EQS have previously been determined by the authorities (cf. Table **3.3**) following the European Chemicals Bureaus Technical Guidance Document on Risk Assessment /7/. Inclusion of more compounds can easily be done due to the conservative nature of the modelling.

Table 3.3. Environmental quality standards in μg/L for the ten focus compounds determined by the authorities (former Ringkjøbing Amt) /13/.

Compound	Annual average (AA-EQS in μg/L)	Maximum allowable concentrations (MAC-EQS in μg/L)
Ethyl parathion	0.0003	0.03
Methyl parathion	0.009	0.03
Malathion	0.001	0.02
Ethyl sulfotep	0.0002	0.02
Mercury (total species)	0.04	0.7
Aminoparathion	1	130
p-nitrophenol	2	40
EP2-acid	4	420
MP2-acid	20	290
4-chloro-o-cresol	5	6

The marine AA-EQS for the organophosphate parent compounds are very strict e.g. seven orders in magnitude between the solubility and the AA-EQS for parathion. These are based on either a good toxicological data set (several trophic levels, marine species and long-term testing) with a very low NOEC (No Observed Effect Concentration) towards crustaceans or, in the case of ethyl sulfotep, a high assessment factor due to a poor data set. The other compounds generally have intermediate toxicological data sets and corresponding assessment factors. The EQS for mercury is based on the water frame directive /13/.

4   Compliance points

In this chapter suitable compliance points for the remediation stop criteria are suggested. This includes the placement of the points, the matrix and parameters to sample, how many samples to collect and how frequently monitoring should take place.

4.1   Placement of the compliance points

Measurement at the points of compliance in the source area should document the fulfilment of the determined remediation stop criteria. The placement will depend on the specific area (infiltration or peripheral). In the infiltration area the contamination is assumed to be uniform in the full depth of the upper secondary area, therefore an even distribution of compliance points to cover the entire area and depth is recommended. In the peripheral area the contamination is only present in the first 0.5 m just above the silt layer, therefore an even areal distribution of compliance points at a single depth right above the silt layer (without puncturing of the layer) is one possibility. Another possibility is to increase the number of compliance points in specific subarea of greater importance. A subarea of greater importance could be the western part of the peripheral area (close to the North Sea) since the proximity of the contamination to the North Sea is of great importance for the remediation stop criteria. Other subareas of importance could be areas where DNAPL has been observed or DNAPL saturation calculations indicate high levels of DNAPL.

With regard to long-term points of compliance, which should document the long-term fulfilment of the marine EQS in the North Sea, these can be placed based on the modelled exit concentrations along the vertical coastline cross-section (cf. Figure 3.3-Figure 3.4). For most of the scenarios, the largest mass discharge can be found within 50 m on either side of groyne 42 (point B, Figure 3.2). For scenario C2 (infiltration area) the largest mass discharge is found north of groyne 42 (between point B and C, Figure 3.2). Also, the sampling density should be largest right above the silt layer, since the mass discharge is largest at the silt layer and 1-1.5 m above it.

4.2   Sampling matrix and parameters

Since the source area is encased by the sheet pile barrier during the remediation, there will be no flow through the source area during the site remediation. The lack of contaminant mass discharge during the remediation makes this parameter unsuitable as a remediation stop criteria. Instead concentrations (solute and/or conversion to total concentrations) of the focus compounds can be used for the remediation stop criteria. Additional parameters specific to the chosen remediation technology could be included (e.g. pH for alkaline hydrolysis or temperature for thermal remediation).

4.3   Sampling frequency

In general, it is recommended that less extensive monitoring be conducted during the remediation (snapshot with fewer samples). When the sampling indicates that the remediation can be finalized, a more extensive monitoring campaign should be carried out to check that the remediation stop criteria are met in the entire area. However, the specific sampling frequency to document the fulfilment of the remediation stop criteria will be closely linked with the remediation technology and the expected timeframe for remediation with the specific technology. For some remediation technologies there will be natural intervals for snapshot monitoring (e.g. each injection/draining cycle for alkaline hydrolysis), while other remediation technologies will have a more steady removal of contaminants whereby snapshot monitoring every few months (depending on expected total timeframe for the remediation) will be applicable. The specific sampling frequency and total length of the monitoring programme will have to be determined; however, this may best be done in parallel with the specific remediation designed after a technology has been chosen.

While the monitoring of the remediation stop criteria are closely linked with the remediation technology, the long-term monitoring in the North Sea will be the same for all technologies, since the sheet pile barrier will be in place for several years following the remediation. Extensive monitoring is not needed as long as the sheet pile barrier remains intact. The current frequency of once per year will be sufficient to monitor the continued encasement of the source area. The sampling frequency in the sea can be intensified once/if the concentrations start increasing.

4.4   Sampling magnitude

4.4.1 Soil samples

Since the risk assessment modelling has been based on uniform contaminant concentrations in the source area, the model results are not used to estimate the needed sampling magnitude. Instead, the recommendations will be based on the characterization data collected at the site.

The Danish EPA recommends that the minimal documentation for *in situ* remediation is that required for an excavation of the source /14/. To estimate the numbers of samples needed to verify the fulfilment of the remediation stop criteria it is suggested to consider the sample density used for characterization of the source area.

The current sampling densities in the infiltration area, the peripheral area and the total area are: one soil sample per 17, 91 and 28 m^3, respectively. The sampling density for the peripheral area is somewhat uncertain, since it is calculated based on a depth of 0.5 m. However, samples with an elevation span of 2.7 m have been assigned to this area (cf. section 2.2.2), whereby the "true" density may be as low as one per 446 m^3.

The areal borehole densities for the same areas are: one borehole per 32, 182 and 107 m^2, respectively. In the peripheral area, the area furthest from the North Sea (zone 5) has the best borehole density (one per 122 m^2), while the area north of the infiltration area (zone 6) has the lowest borehole density (one per 323 m^2).

The infiltration area is considered to be well characterized, while the characterization of the peripheral area seems insufficient as statistical dispersion is larger on the concentration data in this area (cf. Appendix F). The densities can be used as an indicator of how many samples are needed for a proper characterization after the remediation.

To test the robustness of the characterization data, average and median concentrations were calculated from a set of five random selections of 90 %, 80%, 70 % and 60 % of the full data set. For the infiltration area a difference of ≥10 % in the average concentrations was not observed before the data set was reduced to 60 % of the original set. For the peripheral area this difference was found already at 90 % of the original data set, while for the total area the same difference was found at 80 % of the original data set.

Hence, in case of the same heterogeneity before and after remediation, one soil sample per 25-30 m^3 should be sufficient to document the fulfilment of the remediation stop criteria at the completion of the remediation. If the remediation technology decreases the degree of heterogeneity in the source area this number may be lowered.

4.4.2 Water samples

The remediation stop criteria are initially determined as solute concentrations. Hence, the use of solute concentrations will not be affected by the limited knowledge on the organic carbon content (f_{oc}) at the site and the actual partitioning coefficients (K_d) of the compounds as is the case for conversion to total concentrations (via Abdul's equation). The solute concentrations are also more suitable as remediation stop criteria for the very water soluble compounds (i.e. MP2- and EP2-acid).

The remediation wells (e.g. injection/extraction wells) may be used to monitor the ongoing remedial progress. However, these wells should not be used as the only documentation for post-remediation fulfilment of the remediation stop criteria. A separate set of monitoring wells (unaffected by remediation operational processes) should be established to account for site heterogeneities.

Based on the characterization data, one soil sample per 25-30 m^3 was recommended to document the fulfilment of the remediation stop criteria. Since water samples generally show less heterogeneity than soil samples fewer sampling points are needed for documentation when using solute concentrations. However, the data for the solute concentrations have not been collected and scrutinized in the same way as the data for

the soil concentrations. Therefore, it has not been possible to do the same robustness analysis as for the soil data.

Based on the conceptual model, it is suggested that nested (multilevel) monitoring wells are installed in the infiltration area covering the whole depth of the aquifer (e.g. five nested wells of each 5 screens) and that the monitoring wells in the peripheral area are focused on a single depth right above the silt layer (e.g. one well per 400 m^2 as for the infiltration area). For the peripheral area too long screens should be avoided to prevent dilution with less contaminated overlaying water (screens of <1 m is recommended). For the infiltration area too long distances between the top and bottom of each multilevel sampling screen should be avoided to better represent the whole depth (e.g. 0.3 m screens with 0.5 m between). Special attention should be given to the area between the infiltration and peripheral area.

With regard to long-term points of compliance in the North Sea, then the conditions in the sea are relatively homogeneous due to the extensive mixing. Only a few sampling points would be needed.

5   Remediation stop criteria

In this chapter the remediation stop criteria are determined for three contamination scenarios: full area contamination (incl. limited flow), peripheral area contamination and infiltration area contamination (cf. Figure 5.1). The determination of the remediation stop criteria is based on the assumption that contaminant levels are uniform throughout the area. The current conceptual model is represented by the full area (scenario D) contamination.

| Full area (Scenario D) | Peripheral area (Scenario C1) | Infiltration area (Scenario C2) |
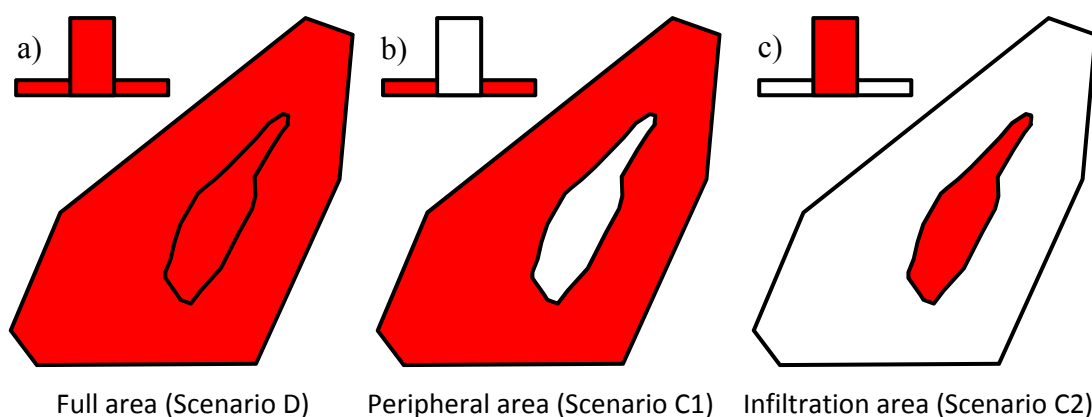
Figure 5.1. The three contamination scenarios (D, C1 and C2) considered for the remediation stop criteria. The presence of contamination, for which the remediation stop criteria apply, is indicated by red coloration in both the vertical plane and the horizontal plane. The surrounding areas are assumed to be uncontaminated.

In addition to the three contamination/remediation scenarios, different dilution levels can be applied. The groundwater dilution in the aquifer is only represented by a steady-state average dilution. Additional dilution from the inundation of the beach during storm surges is included as an additional average daily recharge of the inundated section of the beach (cf. Appendix B). However, the dilution in the North Sea is represented by both the average and the minimum (0.05 quantile) dilution. The minimum dilution (0.05 quantile) is often used for risk assessment, since this gives a conservative "worst-case" assessment and ensures that the most critical situations are considered /5/. Under the assumption that the most critical situation mainly causes issues with acute toxicity, while the average situation is the main contributor to the chronic toxicity, the MAC-EQS have been linked with the minimum dilution (0.05 quantile) and the AA-EQS have been linked with the average dilution.

Since the minimum dilution (0.05 quantile) is approximately one order of magnitude lower than the average dilution (cf. Table 3.2), while the MAC-EQS generally are more than one order of magnitude higher than the AA-EQS (cf. Table 3.3), the average values will be controlling for the remediation stop criteria. The remediation stop criteria presented in this chapter will therefore mainly be based on the average situation (cf. Table 5.1). However, this is not the case for methyl parathion and 4-chloro-*o*-cresol, where the MAC-EQS are only 3.3 and 1.2 times, respectively, higher

than the AA-EQS. The results for the minimum dilution (0.05 quantile) and the MAC-EQS are presented in Appendix H.

In addition to the model scenarios the "measured" dilution is given for parathion (cf. Appendix H for other focus compounds). The dilution is based on the assumptions that: the concentration in the source area is equal to the solubility of parathion (11 mg/L); the concentration measurements for parathion in 2005 in monitoring wells on the beach along 300 m of the coastline /11/ are representative for the concentrations discharging to the North Sea (weighted average concentration of 0.24 mg/L); and that the concentrations of parathion measured in the North Sea in 2004-2005 before the sheet pile barrier was emplaced are representative for the concentrations in the North Sea (average concentration of 0.02 µg/L).

Table 5.1. Average dilution from transport from the source area to the North Sea and mixing within the North Sea along with the overall dilution for the different scenarios. Actual average measurements for parathion before the sheet pile barrier was emplaced are also presented.

Dilution	Scenario B1	Scenario B2	Scenario C1	Scenario C2	Scenario D	Measured (parathion)
Source to sea	4.8	4.4	3.1	9.3	3.0	46
Sea	23600	18800	6760	20200	6630	12600
Overall	113000	82800	20900	187000	19900	579000

The dilution in the sea appears to the well represented by the mixing model (Dashboard), while the conservative solute transport (FEFLOW) from the source to the sea may underestimate the dilution of a degradable contaminant e.g. one order of magnitude for parathion. A more detailed comparison of measured and modelled concentrations is presented later in the chapter (5.4.2).

The remediation stop criteria are given as both the solute water concentration in the source area and the converted total concentration based on the site parameters (porosity, bulk density and organic carbon) mentioned in chapter 2.2.2, the compound specific physiochemical parameters (Table 5.2) and Abdul's equation. For the very water soluble hydrolysis products, MP2-acid and EP2-acid, the log K_{ow} values are unknown; therefore, conversion to total concentrations has not been performed. The accuracy of the converted total concentrations depends on the quality of the parameters used for conversion. For mercury the K_d value ($K_d = 52$ L/kg) is based on values for elemental mercury at a neutral pH given by the US EPA /15/.

Table 5.2. Physiochemical information on the nine focus compounds of the risk assessment. All data are obtained from /16/ and given at 20 ºC unless otherwise mentioned.

Compound	M_w (g/mole)	log K_{ow} (-)	S_w (mg/L)	ρ (kg/L)	pKa (-)
Ethyl parathion	291.26	3.83	11	1.26	-
Methyl parathion	263.21	2.86	55	1.36	-
Malathion	330.36	2.36	145	1.23	-
Ethyl sulfotep	322.32	3.99	30	1.20	-
Mercury[4]	200.59	0.62	0.06[1]	13.5[1]	-
Aminoparathion	261.28	2.60	-	-	-
p-nitrophenol	139.11	1.91	10000[2]	1.27	7.15[1]
EP2-acid	170.17	-	-	-	-
MP2-acid	142.11	-	-	-	-
4-chloro-*o*-cresol	142.58	2.78	4000[1]	1.20	9.71[3]

[1]25ºC; [2]15ºC; [3]Unknown temperature; [4]The properties will depend on the form of mercury, the values are given for elemental mercury.

5.1 Full area

The remediation stop criteria for the full area (cf. Figure 5.1a) include three scenarios: D, B1 and B2. Scenario B1 and B2 are very similar; therefore, only B2 (full infiltration) has been compared to scenario D. The determined remediation stop criteria are given in Table 5.3.

Table 5.3. Remediation stop criteria for the full area (scenario D) are given for both the water phase (mg/L) and the total matrix (mg/kg). The total matrix stop criteria are also given with a limited flow though the source area (scenario B2).

Compound	Water concentration	Total concentration	Total concentration (limited flow)
	(mg/L)	(mg/kg)	(mg/kg)
Ethyl parathion	0.006	0.04	0.18
Methyl parathion	0.18	0.15	0.63
Malathion	0.02	0.01	0.03
Ethyl sulfotep	0.004	0.04	0.17
Mercury (total species)	0.80[1]	-	-
Aminoparathion	20	10	44
p-nitrophenol	40	9.2	38
EP2-acid	80	-	-
MP2-acid	398	-	-
4-chloro-o-cresol	99	72	300

[1]The solute concentration is higher than the water solubility of the given compounds, whereby the remediation stop criteria has not been converted to the total concentration.

The higher remediation stop criterion with the limited flow (1 % of natural conditions) through the source area shows that the groundwater flow is of importance. The limited flow though the source area reduces the amount of contaminant discharge to the North Sea, whereby the stop criteria can be higher. However, the criteria cannot be applied as there is no direct control of the sheet pile barrier deterioration. Limited flow can also be caused by heavy DNAPL contamination saturating the porous media and thereby blocking water flow. However, after remediation all DNAPL should be removed to comply with the stop criteria.

For mercury the solute remediation stop criteria is higher than the solubility of elemental mercury (cf. Table 5.2). Mercury will thereby not cause a problem unless species with significantly higher water solubility are present.

5.2 Peripheral area

A set of remediation stop criteria for contaminants in the peripheral area (cf. Figure 5.1b) have been determined (cf. Table 5.4). The remediation stop criteria in the peripheral area are very similar (almost identical) to the criteria for the full area. In case of a heavy contamination in the peripheral area (as indicated by the current mass

calculation) even complete remediation of the central area would have almost no impact on the concentration levels arriving at the North Sea.

Table 5.4. Remediation stop criteria for the peripheral area (scenario C1) in case the infiltration area is completely remediated are given for both the water phase (mg/L) and the total matrix (mg/kg).

Compound	Water concentration (mg/L)	Total concentration (mg/kg)
Ethyl parathion	0.006	0.04
Methyl parathion	0.19	0.16
Malathion	0.02	0.01
Ethyl sulfotep	0.004	0.04
Mercury (total species)	0.84[1]	-
Aminoparathion	21	11
p-nitrophenol	42	9.7
EP2-acid	84	-
MP2-acid	419	-
4-chloro-*o*-cresol	105	76

[1]The solute concentration is higher than the water solubility of the given compounds, whereby the remediation stop criteria has not been converted to the total concentration.

5.3 Infiltration area

A set of remediation stop criteria for the contaminants in the infiltration area (cf. Figure 5.1c) have been determined (cf. Table 5.5). The remediation stop criteria for the infiltration area are one order of magnitude higher than the remediation stop criteria for the total area (cf. Table 5.3) and the peripheral area (cf. Table 5.4).

Table 5.5. Remediation stop criteria for the infiltration area (scenario C2) in case the peripheral area is completely remediated are given for both the water phase (mg/L) and the total matrix (mg/kg).

Compound	Water concentration (mg/L)	Total concentration (mg/kg)
Ethyl parathion	0.06	0.40
Methyl parathion	1.7	1.4
Malathion	0.19	0.07
Ethyl sulfotep	0.04	0.39
Mercury (total species)	7.5[1]	-
Aminoparathion	187	99
p-nitrophenol	375	87
EP2-acid	750	-
MP2-acid	3750	-
4-chloro-o-cresol	937	679

[1]The solute concentration is higher than the water solubility of the given compounds, whereby the remediation stop criteria has not been converted to the total concentration.

5.4   Contaminant levels in the North Sea

The contaminant levels in the North Sea can be used to get an impression of background concentrations levels currently existing at the site. In the conceptual model, it is assumed that no contaminants are present outside the sheet pile barrier. Actual measurements can be used to evaluate how close this is to reality. The actual measurements in the North Sea and in the aquifer where it discharges to the sea can also be used to assess how well the conservative model represents the actual conditions.

5.4.1 Background contamination

The contaminant concentrations in the North Sea have been measured before and after the emplacement of the sheet pile barrier (Table 5.6).

Table 5.6. Average concentrations (µg/L) of the ten focus compounds in the North Sea before and after emplacement of the sheet pile barrier in 2006 /17/. Median concentrations are also given for the North Sea before the emplacement of the sheet pile barrier; these values are given in parentheses.

Compound	Before (2004-2005) (µg/L)	After (2007-2012) (µg/L)
Ethyl parathion	0.019 (0.006)	<0.005
Methyl parathion	0.084 (0.022)	<0.005
Malathion	0.006 (<0.005)	<0.005
Ethyl sulfotep	0.030 (0.010)	0.010
Mercury (total species)	0.002 (0.002)	0.001
Aminoparathion	3.71 (0.97)	0.564
p-nitrophenol	-	<0.010
EP2-acid	43 (<40)	<50
MP2-acid	<20 (<20)	<100
4-chloro-o-cresol	0.313 (0.135)	<0.050

The background concentrations (2007-2012) are generally below the detection levels, so there is no apparent reason to include them in the calculation of the remediation stop criteria. For mercury the background levels are within normal marine background levels (0.010 µg/L) /18/. However, measurable background levels are found for ethyl sulfotep and aminoparathion. For ethyl parathion the background level is already 50 times higher than the AA-EQS (0.0002 µg/L), while the background level for aminoparathion is 56 % of the AA-EQS (1 µg/L).

It is worth mentioning that the concentrations (2007-2012) are measured during an annual "worst-case" situation and thereby do not represent the annual average situation (MAC-EQS are not exceeded). Also, the remediation removal efficiency required for ethyl sulfotep is very high even without background concentrations (cf. section 5.5), while the concentrations of aminoparathion in many cases are already below the remediation stop criteria. The aminoparathion remediation stop criteria could be reduced by 56 % if these background levels were considered.

The assessment of the importance of the background concentrations is challenged by the fact that the measured concentrations represent the annual "worst-case" situation, actual annual average concentrations would be desirable in case of background level inclusion in the remediation stop criteria. Also, the high detections limits (compared to the EQS) are problematic when assessing the actual background situation in the North Sea.

5.4.2 Comparison of measured and modelled concentrations

To determine the applicability of the risk assessment modelling approach the measured concentrations in the North Sea (2004-2005, without sheet piling) have been compared to the modelled values. The modelled values are determined based on the estimated source concentrations (cf. Table 2.1), which have been converted to aqueous concentrations and diluted according to the specific scenario (full area and infiltrations area scenarios are included). The discrepancies between the modelled and measured North Sea average concentrations are also given in Table 5.7.

Table 5.7. Modelled and measured contaminant average concentrations (µg/L) in the North Sea before remediation based on the scenario specific dilution. The discrepancy between the modelled and measured concentrations in the North Sea before remediation (2004-2005) is given in percentages. **Bold values** indicate values within the same order of magnitude.

Compound	Full area (scenario D)			Infiltration area (scenario C2)		
	Modelled	Measured	Discrepancy	Modelled	Measured	Discrepancy
	(µg/L)	(µg/L)	(%)	(µg/L)	(µg/L)	(%)
Ethyl parathion	0.55[1]	0.02	2810	**0.06[1]**	**0.02**	**209**
Methyl parathion[1]	2.8[1]	0.08	3190	**0.29[1]**	**0.08**	**249**
Malathion	6.0	0.006	100000	0.66	0.006	10900
Ethyl sulfotep	**0.16**	**0.03**	**418**	**0.01**	**0.03**	**-65**
Mercury	0.04	0.002	2820	**0.005**	**0.002**	**266**
Aminoparathion	**0.74**	**3.7**	**-80**	0.04	3.7	-99
4-Cl-*o*-cresol[1]	**0.70**	**0.31**	**123**	0.03	0.31	-90

[1]The values are based on the solubility of the compounds, since the average soil concentrations indicate DNAPL and direct conversion would result in concentrations above the solubility.

Comparison between the modelled and the actual measured concentrations in the North Sea shows that the agreement between the modelled and the measured concentrations are generally better with scenario C2 (infiltration area) than with scenario D (full area). The exceptions are aminoparathion and 4-cl-*o*-cresol, where the best agreement is found for the full area scenario. Similar results can be found for median concentrations (cf. Appendix H).

Generally, relatively good agreements can be found between the modelled and the measured concentrations for all the compounds except malathion, which is significantly overestimated in the model.

For the other parent compounds relatively good agreements with values within the same order of magnitude (similar to variations caused by uncertainties in the source concentration, cf. Figure 2.4) can be found for scenario C2. This may indicate that the

concentrations in the peripheral area are overestimated, whereby the conceptual distribution of heavy contamination may be better represented by scenario C2 than scenario D. Another reason for overestimation of the parent compounds can be the lack of degradation in the conservative solute transport model. This may also explain why especially aminoparathion is underestimated by the model. Remediation stop criteria based on the observed dilution can be found for some of the focus compounds in Appendix H.

Since mercury shows the same trend in the difference between the modelled and measured concentrations, the overestimation is likely due to the simplified conceptual model for the entire source area (i.e. the concentrations close to the sea in scenario D may be significantly overestimated). Degradation processes may still explain some of the more compound specific differences (e.g. underestimation of aminoparathion).

5.5 Estimation of required removal efficiencies

Based on the remediation stop criteria for the scenarios and the current contamination levels (cf. Table 2.1), the removal efficiencies required of the remediation technology have been estimated for the full area (scenario D) and the infiltration area (scenario C2). The estimation has been done on the basis of both average source concentrations (Table 5.8) and median source concentrations (Table 5.9).

Table 5.8. Estimated removal efficiencies (%) required of the remediation technology considering the full area (scenario D) and the infiltration area (scenario C2). The estimations are based on the average source area total concentrations (mg/kg) and the modelled based remediation stop criteria (mg/kg).

Compound	Full area (scenario D)			Infiltration area (scenario C2)		
	Initial concentration	Remediation stop criteria	Needed removal	Initial concentration	Remediation stop criteria	Needed removal
	(mg/kg)	(mg/kg)	(%)	(mg/kg)	(mg/kg)	(%)
Ethyl parathion	2178	0.04	>99.99	1888	0.40	99.98
Methyl parathion[1]	367	0.06	99.98	346	0.54	99.8
Malathion	152	0.01	>99.99	157	0.07	99.96
Ethyl sulfotep	111	0.04	99.96	70	0.39	99.4
Mercury	157	-[2]	0	186	-[2]	0
Aminoparathion	27	10	60.8	14	99	0
4-Cl-*o*-cresol[1]	35	9.9	71.7	15	93	0

[1]The remediation stop criteria are based on the minimum dilution and MAC-EQS (cf. Appendix H).

[2]The solute remediation stop criteria are higher than the water solubility of mercury, whereby no conversion to total concentration is made.

Based on the average source concentrations the needed removal efficiencies of the organophosphate insecticides (ethyl parathion, methyl parathion, malathion and ethyl sulfotep) are very high for both the full area scenario (>99.9 %) and the infiltration area scenario (>99 %). Since the remediation stop criteria are generally one order of magnitude lower for the full area, the removal is required to be one order of magnitude more efficient.

Since the solubility of mercury is lower than the solute remediation stop criteria, no removal of mercury is needed, unless more water soluble species are present.

For the other focus compounds (aminoparathion and 4-cl-o-cresol) the scenario is of great importance for the removal efficiencies; for the full area scenario 61-72 % removal is needed, while no removal is needed for the infiltration area scenario.

Table 5.9. Estimated removal efficiencies (%) required of the remediation technology considering the full area (scenario D) and the infiltration area (scenario C2). The estimations are based on the median source area total concentrations (mg/kg) and the modelled based remediation stop criteria (mg/kg).

Compound	Full area (scenario D)			Infiltration area (scenario C2)		
	Initial concentration	Remediation stop criteria	Needed removal	Initial concentration	Remediation stop criteria	Needed removal
	(mg/kg)	(mg/kg)	(%)	(mg/kg)	(mg/kg)	(%)
Ethyl parathion	1098	0.04	>99.99	1083	0.40	99.96
Methyl parathion[1]	81	0.06	99.93	81	0.54	99.3
Malathion	19	0.01	99.96	20	0.07	99.7
Ethyl sulfotep	11	0.04	99.6	9.2	0.39	95.8
Mercury	79	-[2]	0	110	-[2]	0
Aminoparathion	3.1	10	0	3.0	99	0
4-Cl-o-cresol[1]	2.9	9.9	0	2.6	93	0

[1]The remediation stop criteria are based on the minimum dilution and MAC-EQS (cf. Appendix H).

[2]The solute remediation stop criteria are higher than the water solubility of mercury, whereby no conversion to total concentration is made.

Based on the median source concentrations the needed removal efficiencies of the organophosphate insecticides (ethyl parathion, methyl parathion, malathion and ethyl sulfotep) are still above 99 % for both the full area scenario and the infiltration area scenario; the exception being ethyl sulfotep in the infiltration area scenario (>95 %). For the other focus compounds (mercury, aminoparathion and 4-cl-o-cresol) no removal is needed for either scenario.

The best case scenario for the main contaminant, parathion, would be that the total dilution is equal to the 579000 times observed based on the concentration measurements from 2005 (cf. Table 5.1) and that the median initial source concentration (~1100 mg/kg) is representative for the source area. However, even then a removal efficiency of more than 99 % would be needed (cf. Appendix H)

The given removal efficiencies are very dependent on the actual initial concentrations. When using the lower median concentrations instead of the average concentrations, the needed removal efficiencies are reduced by up to one order of magnitude. Since the characterization of the peripheral area is somewhat limited, better characterization may reduce the needed removal efficiencies for the full area in case an overestimation has occurred.

6 Conclusions

6.1 Compliance points

Post-remediation fulfilment of the remediation stop criteria can be measured at a set of compliance points in the source area. The determined remediation stop criteria should be documented at these points before the remediation can be finalized. Based on the current conceptual model, it is recommended to use an even spatial distribution of compliance points to cover the entire area and depth of the infiltration area, and an even areal distribution of compliance points in a single depth right above the silt layer in the peripheral area.

The sampling frequency will be closely link with the remediation technology (e.g. each injection cycle for alkaline hydrolysis). It is recommended that less extensive monitoring is carried out during the remediation (snapshot checking with fewer samples), while an extensive monitoring campaign is ultimately required to check that the remediation stop criteria are met in the entire area. The specific sampling frequency may best be determined in parallel with the remediation design after a specific technology has been chosen.

Solute and/or total concentrations should be used to document the remediation stop criteria. For solute concentrations it is recommended that the concentrations in the infiltration area are measured in nested (multilevel) monitoring wells covering the entire depth of the aquifer, while single depth monitoring wells screened right above the silt layer can be used in the peripheral area (approximately one per 400 m^2). For the total concentrations it is recommended that documentation is done by one soil sample per 25-30 m^3. The actual monitoring program may vary from these recommendations based on the specific combination of solute and total concentrations, changes in source heterogeneity based on the remediation technology and other experiences gained as the remediation proceeds.

6.2 Remediation stop criteria

Based on risk assessment modelling the average groundwater dilution in the secondary upper aquifer was determined along with the average and the minimum dilution (0.05 quantile) in the North Sea. The determined dilution factors were combined with the marine EQS for the ten focus compounds to back-calculate the solute remediation stop criteria for two different remediation scenarios based on the current conceptual model (cf. Table 6.1). Comparison shows that the agreement between the modelled and the measured concentrations is generally better with scenario C2 (infiltration area), which allows more remaining contamination after the remediation.

Table 6.1. Remediation stop criteria (mg/L) for the ten focus compounds determined for two different remediation scenarios incl. remediation stop criteria for the full area (D) and the infiltration area (C2). The remediation stop criteria do not consider background levels of the contaminants.

Compound	Full area (D) (mg/L)	Infiltration area (C2) (mg/L)
Ethyl parathion	0.006	0.06
Methyl parathion	0.07	0.64
Malathion	0.02	0.19
Ethyl sulfotep	0.004	0.04
Mercury (total species)	0.80	7.5
Aminoparathion	20	187
p-nitrophenol	40	375
EP2-acid	80	750
MP2-acid	398	3750
4-chloro-*o*-cresol	14	129

The remediation stop criteria are conservative estimates, which may be less strict for the natural degradable compounds. However, the measured concentrations in the North Sea indicate that the dilution is in the right order of magnitude. Increasing the remediation stop criteria by more than one order of magnitude is therefore not recommendable unless more detailed information on the degradation of all the relevant focus compounds is obtained. Compliance with the given remediation stop criteria should reduce the contaminant mass discharge of parathion to the North Sea to <1 kg/year.

The most challenging compounds to remediate will be the organophosphate parent compounds (ethyl parathion, methyl parathion, malathion and ethyl sulfotep), which for all the scenarios have needed reduction levels of more than 95 % (in most cases more than 99 %). The demands placed on the chosen remediation technology are thereby high. Alternatively, the extent of a larger exemption zone (e.g. only fulfilment of MAC-EQS, cf. Appendix H) could be considered.

6.3 Uncertainties

The remediation stop criteria are associated with conceptual, model and measurement uncertainties.

The remediation stop criteria are very dependent on the extent of the contaminated peripheral area. If the contamination in the peripheral area is negligible, the remediation stop criteria are around one order of magnitude higher than in the case

where the entire area is significantly contaminated. This is linked to the proximity to the North Sea; a shorter transportation path from the source to the North Sea allows for significantly less dilution from recharge and overtopping of seawater. Better characterization of the contaminant distribution between the infiltration area and the North Sea could significantly improve the certainty of the remediation stop criteria.

Since the model utilizes conservative solute transport there is a risk of overestimation for the degradable compounds and underestimation of the degradation compounds. Since the highest remediation efficiencies are required for the parent compounds, the overestimation of these seems of greater importance than underestimation of the less toxic degradation compounds. Further modelling with detailed information on the degradation of the compounds could increase the certainty of the remediation stop criteria.

The background levels for most of the focus compounds were determined to be of no apparent importance (below detection limits) for the remediation stop criteria. However, for two of the compounds (ethyl sulfotep and aminoparathion) significant background levels have been observed. In case of ethyl parathion the background level already significantly exceeds the AA-EQS, while for aminoparathion the background level is already 56 % of the AA-EQS. Since these values are based on an annual (2007-2012) "worst-case" situation, it is difficult to directly include them in the remediation stop criteria; to do so it would be relevant to measure the concentrations in the North Sea under normal (average) conditions and adjust the remediation stop criteria accordingly.

7 References

/1/ Ringkjøbing Amt, Teknik- og Miljøområdet (2001). Høfde 42: Undersøgelse af forureningssituationen ved høfde 42 og "Cheminovahullet" på Harboøre Tange.

/2/ Kirkegaard, C., Ramsay, L., Jørgensen, C. (2008). Skitseprojekt, Høfde 42. UDKAST Demonstration af basisk hydrolyse & biologisk nedbrydning: Skitseprojekt. DGE/Alectia/DHI.

/3/ ITRC (2008). In-situ Bioremediation of Chlorinated Ethane: DNAPL Source Zones. The Interstate Technology & Regulatory Council.

/4/ COWI/Rambøll/Geosyntec/Kogsgaard (2013). Høfde 42 Afgrænsning af nedsivningsområde.

/5/ Jacobsen, F., Petersen, O. (2006). Fortynding langs danske kyster. DHI, Institut for Vand og Miljø. (http://www2.mst.dk/fortynding).

/6/ Uhrenholdt, T., Zyserman, J.A. (2004). CHEMINOVA UDLEDNINGER, Spredningsberegninger for Vesterhavet. DHI, Institut for Vand og Miljø.

/7/ TGD (2003). Technical Guidance Document on Risk Assessment, Part II. Institute for Health and Consumer Protection, European Chemicals Bureau. European Commission, Joint Research Centre.

/8/ NIRAS (2004). Høfde 42, Harboøre Tange: Supplerende forureningsundersøgelser. Ringkjøbing Amt.

/9/ AKTOR Innovation (2004). Litteraturundersøgelse og modelbeskrivelse af naturlig nedbrydning af parathion. Miljøstyrelsen.

/10/ DHI (2005). Anaerob omdannelse af parathion i sediment fra Høfde 42. Ringkjøbing Amt.

/11/ Niras (2005). Estimering af udsivning til Vesterhavet. Ringkjøbing Amt.

/12/ Hansen, M.S. (2012). Kviksølv mobilisering og speciering i forurenet jord - med udgangspunkt i forsøg med basisk hydrolyse ved Høfde 42. MSc. Thesis, Institut for Geoscience, Aarhus universitet.

/13/ Kimø, L. (2006). Midlertidig tilladelse til udledning af renset grundvand fra Høfde 42, Harboøre Tange samt drænvand fra det afskærende dræn langs havdiget øst for høfde 42 til Vesterhavet. Ringkjøbing Amt, Teknik og Miljø.

/14/ Loll, P., Larsen, C. (2008). Anbefalinger til sagsforløb ved in situ oprensning af jordforurening. Miljøprojekt nr. 1255, Miljøstyrelsen.

/15/ US EPA (2001). Supplemental Guidance for Developing Soil Screening Levels for Superfund Sites. Report OSWER 9355.4-24, Solid Waste and

Emergency Response, US Environmental Protection Agency, Washington, DC.

/16/ 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).

/17/ Concentrations in the North Sea (2004-2012), database from the Central Region.

/18/ Förster, U., Wittman, G.T.W. (1979). Metal Pollution in the Aquatic Environment. Springer-Verlag, Berlin Heidelberg, New York.

8   Appendices

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

Appendix B: FEFLOW: The numerical model.

Appendix C: FEFLOW: Extended model domain

Appendix D: FEFLOW: Leakage from the upper to the lower aquifer

Appendix E: Note on the contaminant mass discharge from the lower secondary aquifer at Groyne 42 (in Danish)

Appendix F: Concentration distribution (statistics)

Appendix G: Note on the considerations in connection with the contaminant distribution, February 25th 2013 (in Danish)

Appendix H: Remediation stop criteria with minimum dilution (0.05 quantile)

Appendix A

NorthPestClean: Remediation Stop Criteria

Phase A: Conceptual development and identification of data needs

Annika S. Fjordbøge, Poul L. Bjerg, K. Ole Kusk and Philip J. Binning

DTU Environment

March 2012

NorthPestClean: Remediation Stop Criteria

Phase A: Conceptual development and identification of data needs

Prepared by:

Annika S. Fjordbøge, Poul L. Bjerg, Kresten Ole Kusk and Philip J. Binning

DTU Environment

March 2012

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.

Table of content

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/.

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.
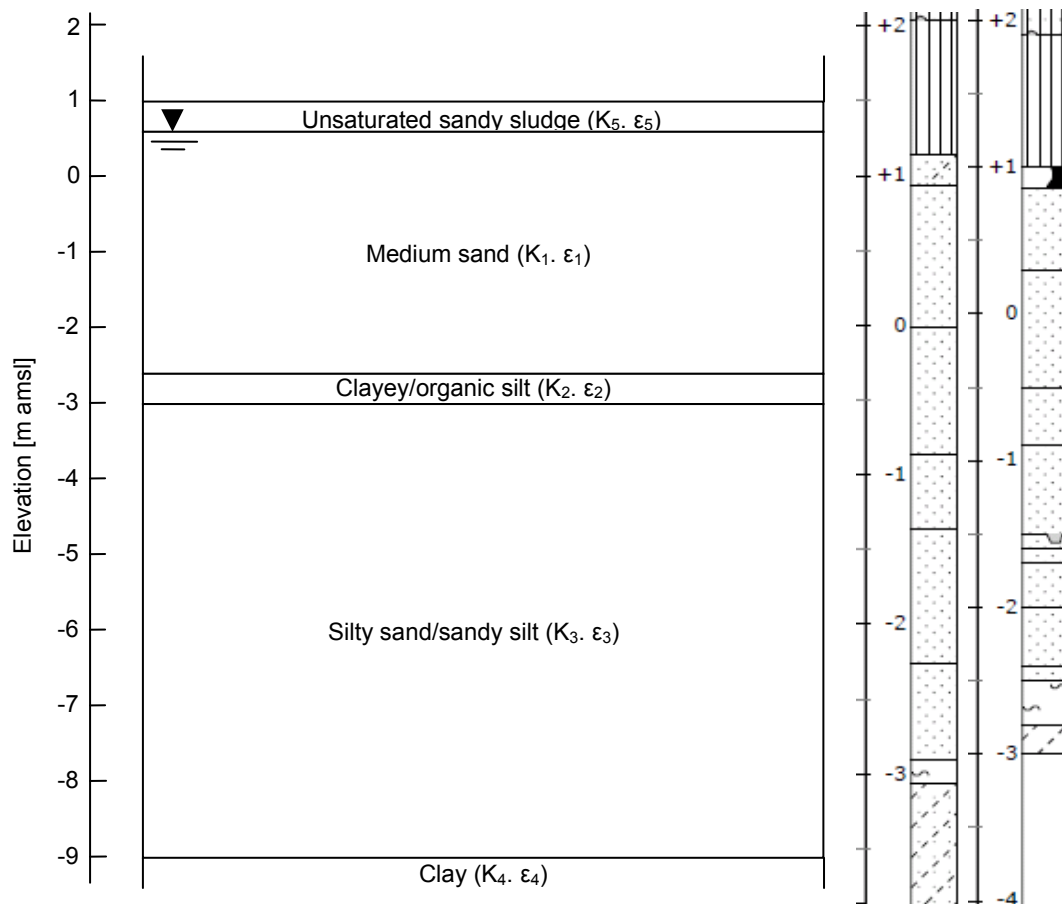
Figure 2. Left) The simplified geological sequence of the marine deposits at the site (source area) /3, 10-11/; and right) examples of borehole profiles (TC1-1 and TC3-3) down to -4 m amsl from the pilot scale remediation area /8/. Note that the scales are different.

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.

5

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 1. Hydraulic parameters for the layers in the geological sequence at the site.

Layer	Parameter	Unit	Value	Reference
1: Medium sand	K_1	[m/s]	4×10^{-4}	/10/
	ε_1	[-]	0.44	/15/
2: Organic silt	$K_{2,\,vertical}$	[m/s]	4×10^{-6}	/15/
	ε_2	[-]	0.39	/15/
3: Sandy silt	K_3	[m/s]	1×10^{-4}	/10/
	ε_3	[-]	0.39	/15/
4: Clay	K_4	[m/s]	8×10^{-10}	/14/
	ε_4	[-]	0.40	(estimate)
5: Sandy sludge	K_4	[m/s]	-	-
	ε_4	[-]	-	-

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 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.

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

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 m^2 resulting in an estimated DNAPL area of 6000 m^2. 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 m^2) 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/.
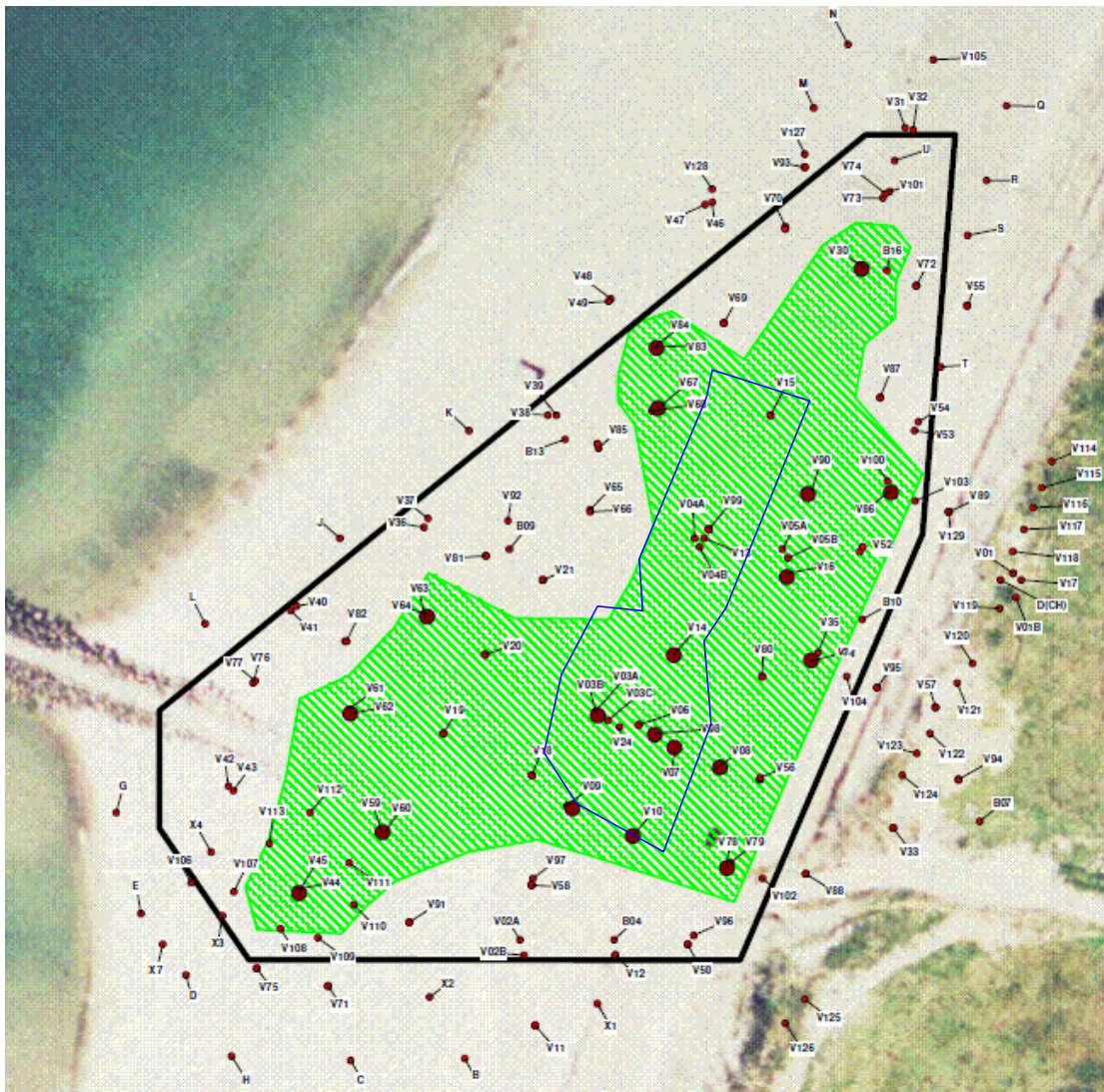
Figure 3. The possible extent of the DNAPL area (shaded green); DNAPL detection is indicated by larger red dots /4/. The blue area indicates the old chemical depot and percolation area. The sheet pile barrier is indicated by the thicker black line.

Based on the estimated distribution of DNAPL, all the DNAPL should be within the 21,000 m^2 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 m^2) 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 m^2). 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 m^2) 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 preformed. 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/.

Figure 4. Placement of the monitoring wells (MB1-5) at the foreshore immediately down-gradient of the sheet pile barrier. Also, the approximate location of the most frequent sampling point in the North Sea.

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.
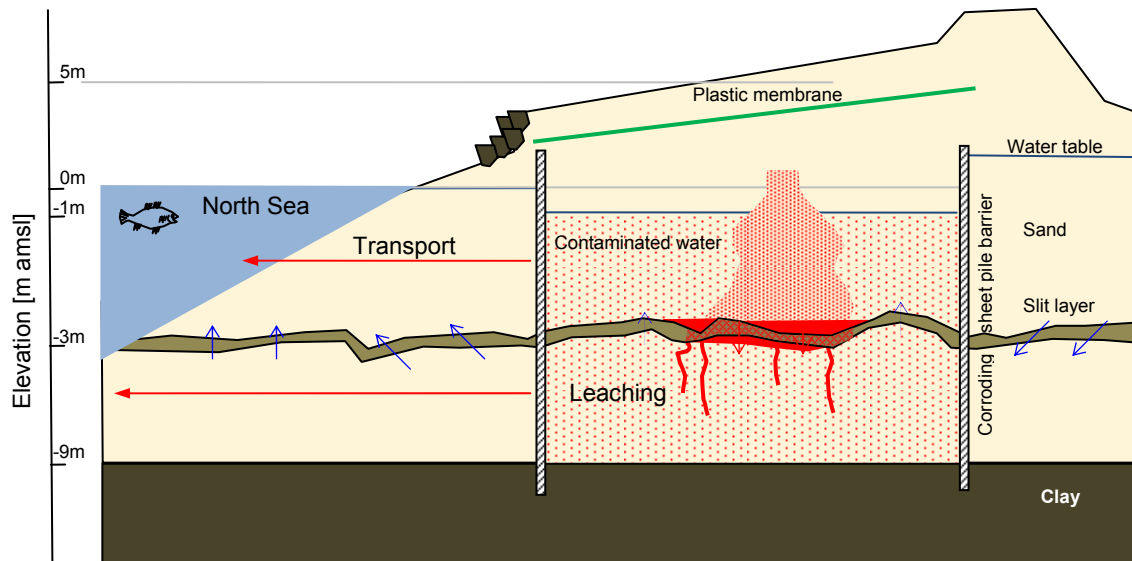

Figure 5. Conceptual model for the situation at the contaminated site.

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 m^2) can be divided into a heavily contaminated hotspot area with both residual and mobile DNAPL (6000 m^2) 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 m^2).

- 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 3. Environmental quality standards in µg/L for selected contaminants /36/ based on the calculation of predicted no effect concentrations done by the former County by use of the European Chemicals Bureaus Technical Guidance Document on Risk Assessment.

Compound	Annual average (AA-EQS)	Maximum allowable concentrations (MAC-EQS)
Ethyl parathion	0.0003	0.03
Methyl parathion	0.009	0.03
Malathion	0.001	0.02
Ethyl sulfotep	0.0002	0.02
Mercury	0.04	0.7
Amino parathion	1	130
p-nitrophenol	2	40
EP2-acid	4	420
MP2-acid	20	290
4-chloro-*o*-cresol	5	6

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 Bureaus 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.

Compound	PEC[1]	PNEC[2]	Risk quotient
Ethyl parathion	1,200	0.003	400,000
Methyl parathion	350	0.009	39,000
Ethyl sulfotep	28	0.0002	140,000
Malathion	270	0.006	45,000
EP1	15,000	0.5	30,000
EP2-acid	135,000	40	3,400
Mercury	72	0.3	240

[1]PEC 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.

[2]The 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-*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.

Compound	CAS	M_w	log K_{ow}	S_w	P_i	ρ	pK_a
		[g/mole]	[-]	[mg/L]	[Pa]	[kg/L]	[-]
Ethyl parathion	56-38-2	291.26	3.83	11	9×10^{-4}	1.26	-
Methyl parathion	298-00-0	263.21	2.86	55	2×10^{-4}	1.36	-
Malathion	121-75-5	330.36	2.36	145	[1]2×10^{-2}	1.23	-
Ethyl sulfotep	3689-24-5	322.32	3.99	30	1×10^{-2}	1.20	-
Amino parathion	3735-01-1	261.28	2.60	-	-	-	-
EP2-acid	5871-17-0	170.17	-	-	-	-	-
MP2-acid	112-77-8	142.11	-	-	-	-	-
p-nitrophenol	100-02-7	139.11	1.91	[2]10000	1×10^{-2}	1.27	[1]7.15
4-chloro-*o*-cresol	1570-64-5	142.58	2.78	[1]4000	[1]3.2	1.20	[3]9.71
Mercury[4]	7439-97-6	200.59	-	0.06[1]	0.27[1]	13.5[1]	-

[1]25ºC; [2]15ºC; [3]Unknown temperature; [4]The 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

area /44/. 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 /45/. 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 (POC_{source}) and the down-gradient discharge point to the North Sea ($POC_{downgr.}$) under different flow and contamination conditions. The points of compliance are described in more detail in chapter 4.5.
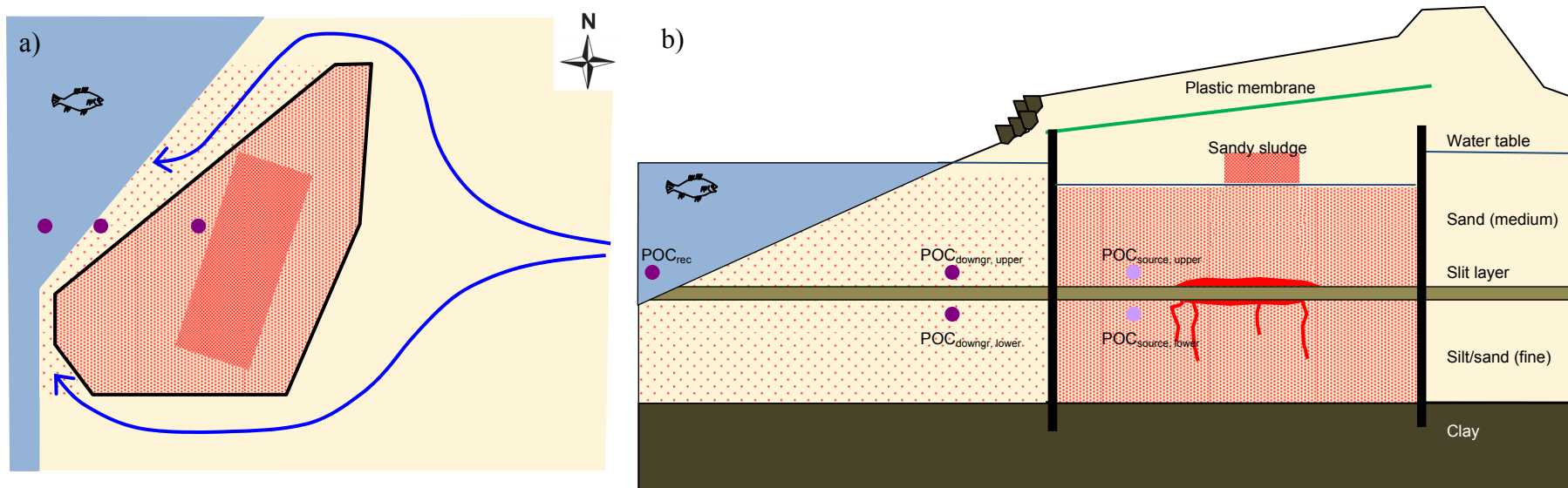
Figure 6. Model scenario A: the baseline situation. The barriers are still impermeable and the flow is bypassing the source area. Remediation has not yet been implemented at the source area, but the area is hydraulic isolated from the North Sea. The concentrations in the North Sea are the result of the 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.
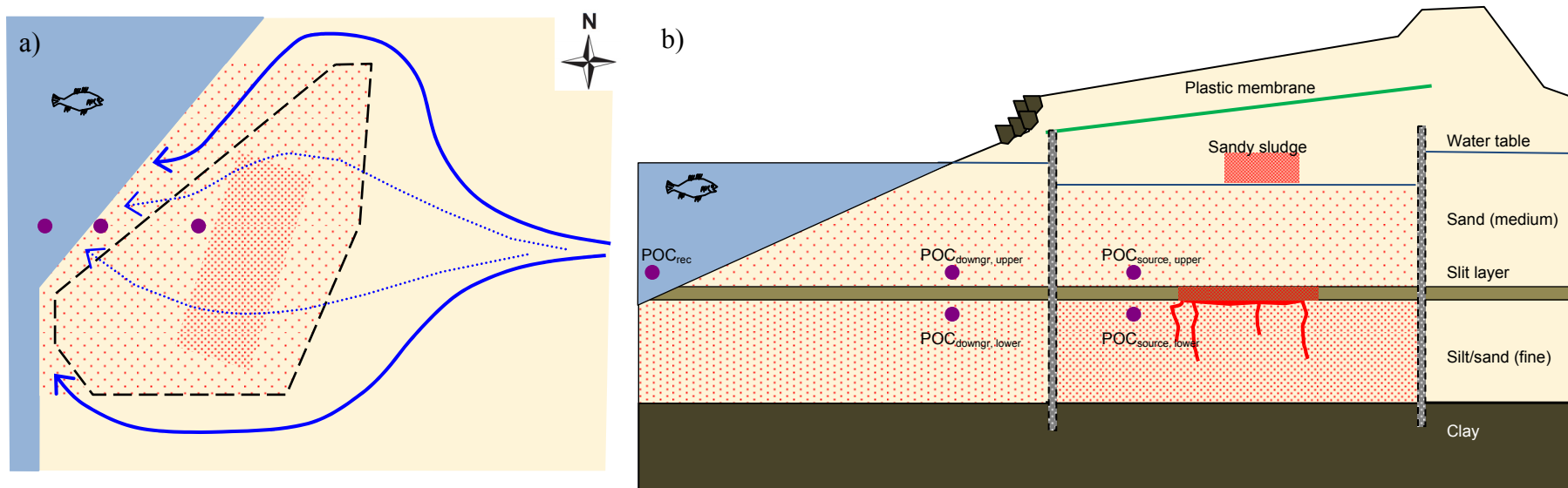
Figure 7. Model scenario B1: uniform deterioration of the sheet pile barrier (intact cover membrane). The sheet pile barrier has started to leak and the remediation of the source area above the silt layer has been finalised. Points of compliance for the short- and long-term functional criteria (solute 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.
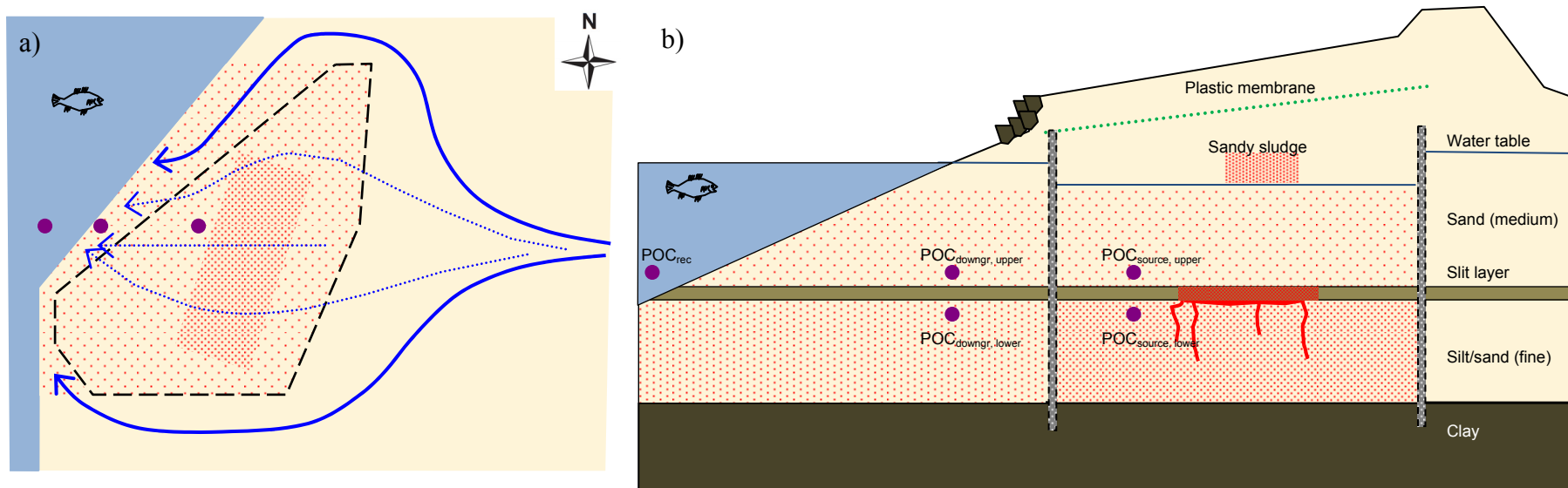
Figure 8. Model scenario B2: uniform deterioration of the sheet pile barrier (deteriorated cover membrane). The sheet pile barrier and the membrane cover have started to leak and the remediation of the source area above the silt layer has been finalised. Points of compliance for the short- and long-term 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.
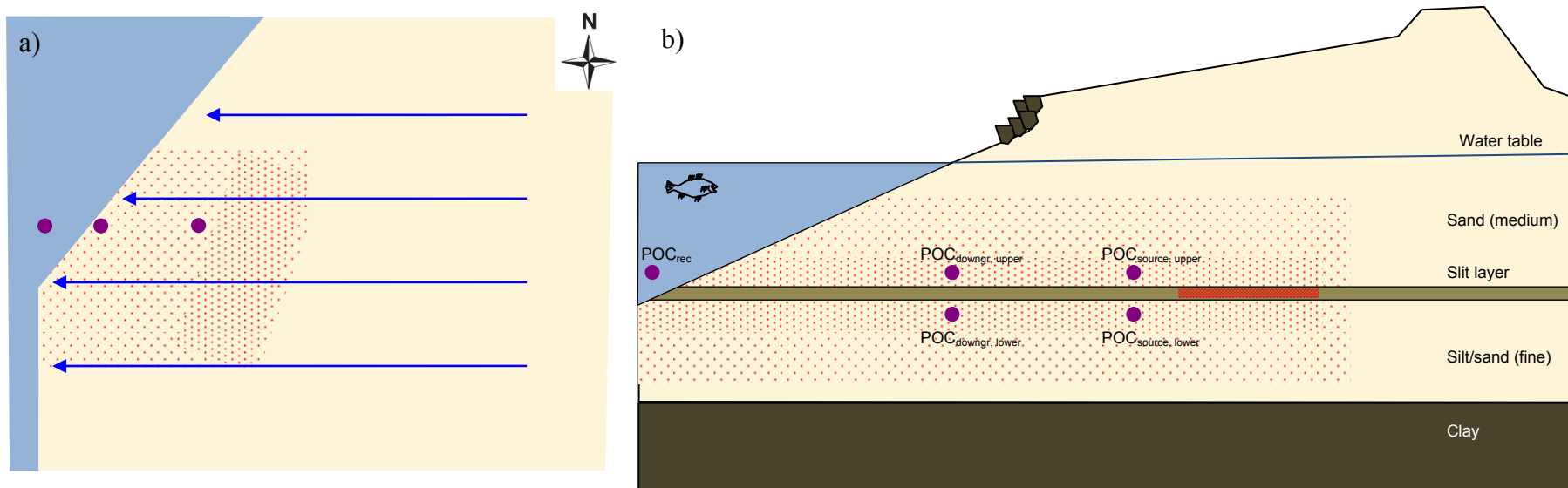
Figure 10. Model scenario C2: no barriers (long term). The sheet pile barrier and the membrane cover have completely deteriorated. During the slow process of barrier deterioration, a major part of the contamination has been removed from the source area (leaching). Contamination remains in all the layers, 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.
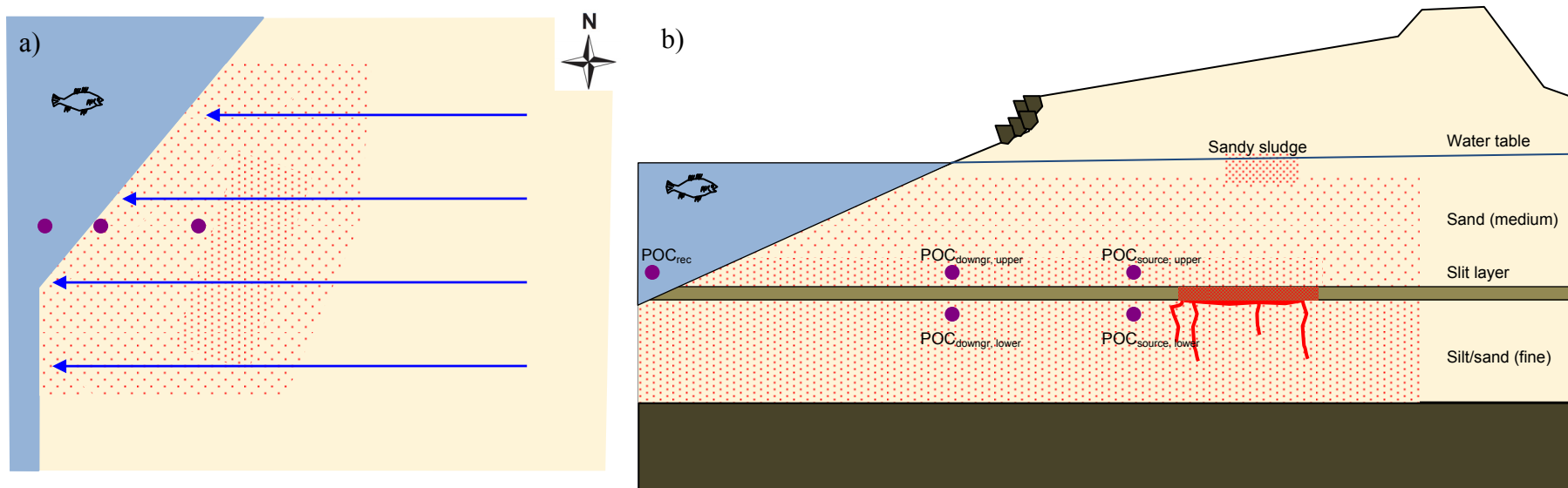
Figure 11. Model scenario D: no remediation (long-term). The situation in case no remediation had been carried out at the time the barriers have completely deteriorated. The contamination is at the current level, while the hydraulic conditions are the same as before the barriers where installed. Points 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.
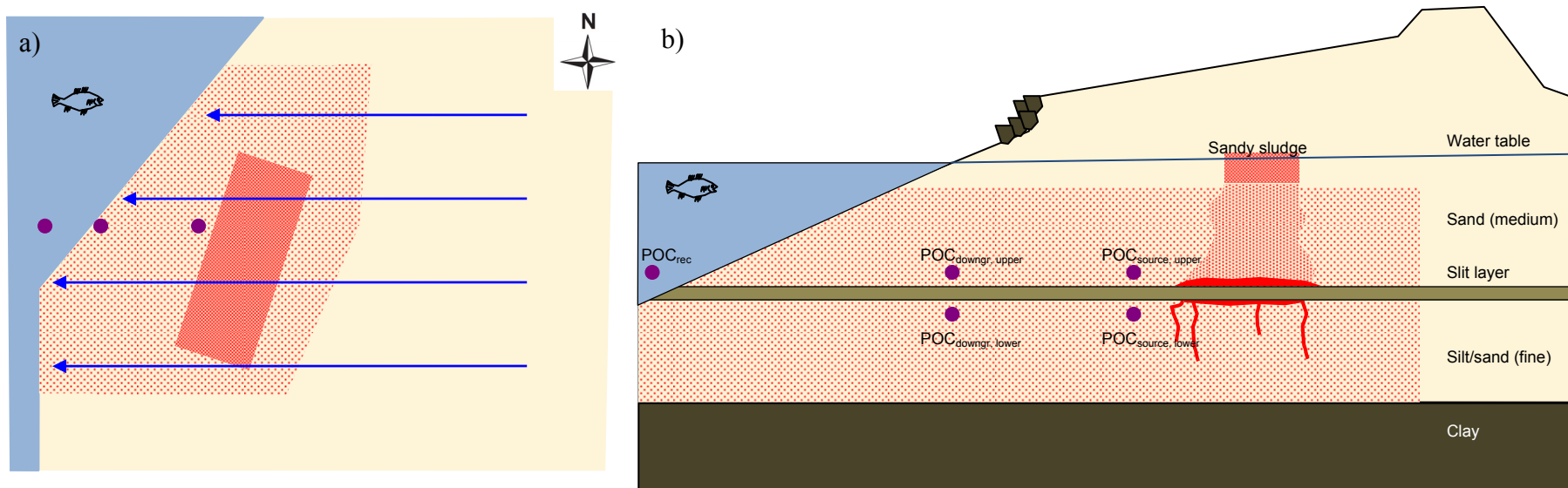
4.2.1 Baseline situation: Scenario A

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.
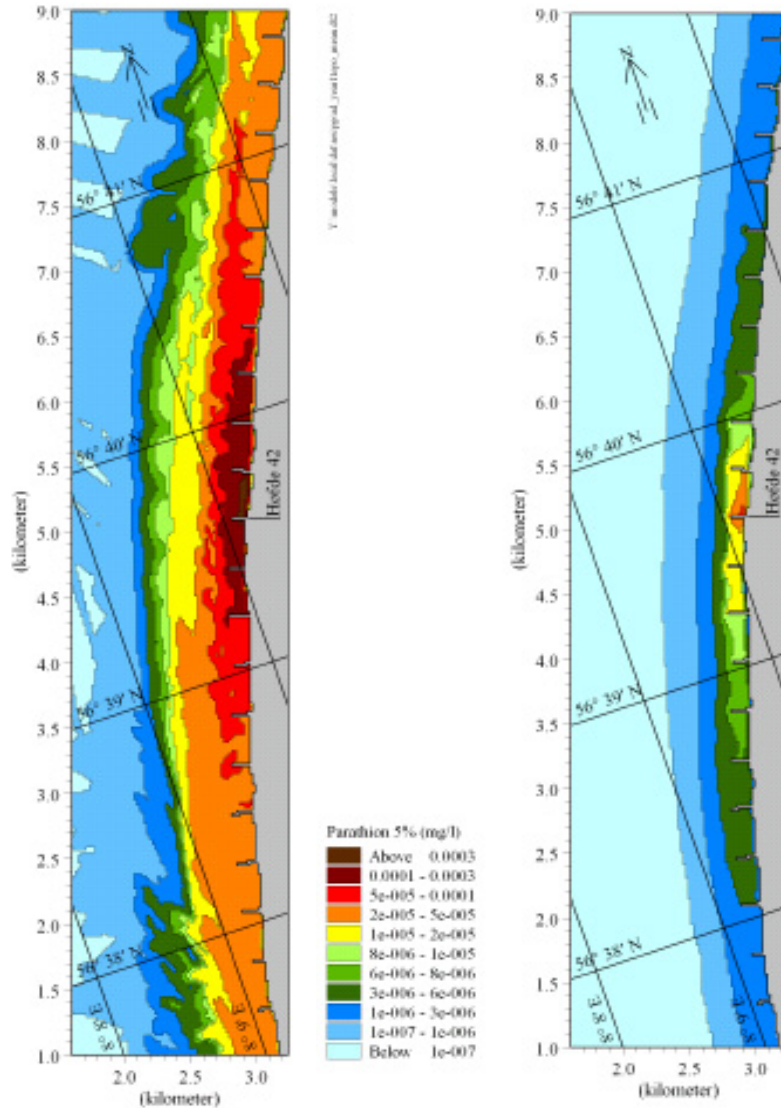
Figure 12. Concentration distribution of parathion (after 95 % reduction compared to the 2004 level) with input concentrations of around 0.3 mg/L. The distribution is given for: left) yearly peak situation; and right) yearly average situation /19/.

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 Bureaus 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_{source} and POC_{rec} can be determined based on the solute concentration of the contaminants in the source (C_i), the environmental quality standards that applies down-gradient in the North Sea (EQS_i) and the baseline concentrations already present in the North Sea ($C_{base, i}$):

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

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:

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

and the theoretical chemical based toxic unit (TU$_C$) as:

$$TU_C = \sum TU_i = \sum \frac{C_i}{EQS_i}$$

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 POC_{source} in the source area, where the remediation stop criteria should be complied with; the POC_{rec} in the North Sea, where the long-term criteria should be complied with; and the POC_{downgr} at the discharge point from the aquifer to the North Sea, which is primarily a calculation point.

The calculation point, POC_{downgr}, 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 POC_{source} to POC_{downgr}, will use the described leaching and solute transport modelling, while the dilution in the North Sea, from

POC$_{downgr}$ to POC$_{rec}$, 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$_{rec}$). The points should be placed closed 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$_{source}$.

The long-term criteria, to ensure good ecosystem health, should be fulfilled at POC$_{res}$ 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_{source}).

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 ($15,000 \text{ m}^2$); and a hotspot area where residual and mobile DNAPL is present ($6,000 \text{ m}^2$). 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 *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.

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 set 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.

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

[*]Depending of the desire for using this supplementary approach.

6   References

/1/   Ringkjøbing Amt, Teknik- og Miljøområdet (2001). Høfde 42: Undersøgelse af forureningssituationen ved høfde 42 og "Cheminovahullet" på Harboøre Tange.

/2/   Kirkegaard, C., Ramsay, L., Jørgensen, C. (2008). Skitseprojekt, Høfde 42. UDKAST Demonstration af basisk hydrolyse & biologisk nedbrydning: Skitseprojekt. DGE/Alectia/DHI.

/3/   NIRAS (2004). Høfde 42, Harboøre Tange: Supplerende forureningsundersøgelser. Ringkjøbing Amt.

/4/   NIRAS (2005). Notat: Høfde 42, Harboøre Tange. Beregning af forureningsmasse. Ringkjøbing Amt.

/5/   Petersen, F.S. (2005). Notat: Høfde 42, Harboøre Tange: Supplerende undersøgelser omkring planlagt spunsvæg. NIRAS.

/6/   WaterVision (2010). Høfde 42, Vurdering af de geologiske forhold og forureningens udbredelse omkring det nye forsøgsfelt. Region Midtjylland.

/7/   WaterVision (2009). Vurdering af geologiske og hydrauliske forhold på det gamle og det nye forsøgsfelt. Region Midtjylland.

/8/   Cowi (2011). Initial Characterization and Initial Draining/Reinfiltration (draft version). Region Midtjylland.

/9/   Ramsay, L. (2008). Notat om Høfde 42. Demonstration af basisk hydrolyse & biologisk nedbrydning: Geokemi. Alectia.

/10/   Elkjær, L. (2008). Notat om Høfde 42. Demonstration af basisk hydrolyse & biologisk nedbrydning: Borearbejde. DGE Group.

/11/   Poulsen, S.E., Christensen, S. (2010). Høfde 42: Hydrauliske beregninger vedrørende oprensning af et forsøgsvolumen. Geologisk Institut, Aarhus Universitet.

/12/   Rambøll (2002). Notat: Vurdering af pejledata fra Høfde 42. Ringkjøbing Amt.

/13/   Cowi (2005). Høfde 42, Harboøre Tange. Vurdering af grundvandssænkning ved etablering af dræn langs spunsvæg (foreløbige notat). Ringkjøbing Amt.

/14/   Jensen. B.S., Nielsen, C.Q. (2004). Etablering af spunsvæg ved høfdedepot på Harboøre Tange. Geoteknisk undersøgelse, Vurderinger. COWI.

/15/   Ladekarl, U., Ramsay, L. (2008). Notat om Høfde 42. Demonstration af basisk hydrolyse & biologisk nedbrydning: Vandretention. Alectia.

/16/ Niras (2005). Notat: HØFDE 42, HARBOØRE TANGE. Estimering af udsivning til Vesterhavet. Ringkjøbing Amt.

/17/ Poulsen, S.E. (2011). Høfde 42: Vurdering af specifik ydelse og hydraulisk ledningsevne i testcellerne TC1, TC2 og TC3. Geologisk Institut, Aarhus Universitet.

/18/ NIRAS (2001). Høfde 42, Harboøre Tange: KEMIKALIEAFFALDSDEPOT, Afværgekatalog. Ringkjøbing Amt.

/19/ Uhrenholdt, T., Zyserman, J.A. (2004). CHEMINOVA UDLEDNINGER, Spredningsberegninger for Vesterhavet. DHI, Institut for Vand og Miljø.

/20/ Frich, P., Rosenørn, S., Madsen, H. & J.J. Jensen (1997). Observed Precipitation in Denmark, 1961-90. Danish Meteorological Institute, Ministry of Transport.

/21/ Ringkjøbing Amt, Teknik og Miljø (2004). NOTAT: Bruttoliste over relevante parametre for høfdedepotet.

/22/ Køhrsen, M. (2004). NOTAT: Revurderet bruttoliste for høfdedepotet og udvalgte fokusstoffer til undersøgelse af forureningen øst for depotet. Ringkjøbing Amt, Teknik og Miljø.

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

/24/ Lanzky, V.F. (2005). NOTAT: Forurening efterladt udenfor den planlagte spunsvæg ved høfdedepotet. Ringkjøbing Amt, Teknik og Miljø.

/25/ Møller, T. (2002). Oprensning af tidligere kemikaliedepot ved Høfde 42. Ingeniørhøjskolen i Århus.

/26/ Sørensen, N., Laursen, M. (2005). NOTAT: Analyser af vandprøver fra havstokken omkring høfde 42. Ringkjøbing Amt, Teknik og Miljø.

/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.

/29/ Baun, A., Kusk, K.O. (2001). Økotoksikologiske effekter af grundvand og overfladevand fra området omkring Høfde 42 på Harboøre Tange - afrapportering af 1. fase af samarbejdsprojekt mellem Ringkjøbing Amt og M&R DTU. Miljø & Ressourcer, Danmarks Tekniske Universitet.

/30/ Baun, A., Kusk, K.O. (2002). Økotoksikologiske effekter af grundvand og overfladevand fra området omkring Høfde 42 på Harboøre Tange - afrapportering af 2. fase af samarbejdsprojekt mellem Ringkjøbing Amt og M&R DTU. Miljø & Ressourcer, Danmarks Tekniske Universitet.

/31/ Vastrup, T. (2005). Afprøvning af rensningsmetoder på pesticidforurenet grundvand. M.Sc. thesis, Institut for Miljø & Ressourcer, Danmarks Tekniske Universitet.

/32/ Fjordbøge, A. (2005). Evaluering af nul-valent jern til oprensning af høfde 42 depotet. M.Sc. thesis, Institut for Miljø & Ressourcer, Danmarks Tekniske Universitet.

/33/ Fjordbøge, A.S., Kjeldsen, P., Petersen, P.A., Dall-Jepsen, J., Durant, N. (2006). Oprensning af forureningen på depotet ved Høfde 42 ved hjælp af nul-valent jern. M&R DTU/COWI/GeoSyntec.

/34/ Ringkjøbing Amt, Teknik og Miljø (2004). NOTAT: Stoffer relevante for en spredningsmodel.

/35/ Ringkjøbing Amt, Teknik og Miljø (2004). NOTAT: Principper for risikovurdering af udledning/udsivning fra kilder ved Harboøre Tange.

/36/ Kimø, L. (2006). Midlertidig tilladelse til udledning af renset grundvand fra Høfde 42, Harboøre Tange samt drænvand fra det afskærende dræn langs havdiget øst for høfde 42 til Vesterhavet. Ringkjøbing Amt, Teknik og Miljø.

/37/ TGD (2003). Technical Guidance Document on Risk Assessment, Part II. Institute for Health and Consumer Protection, European Chemicals Bureau. European Commission, Joint Research Centre.

/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).

/39/ Note on the expected reactions between the Groyne 42 compounds and dissolved NaOH (2011). Cheminova/Region Midtjylland.

/40/ Bender, M.E., Westman, J.R. (1976). The Toxicity of Malathion and Its Hydrolysis Products to the Eastern Mudminnow, *Umbra pygmaea* (DeKay). Chesapeake Science, 17 (2), 125-128.

/41/ Køhrsen, M. (2001). Undersøgelser af kviksølv i muslinger. Notatark, Ringkjøbing Amt, Teknik og Miljø.

/42/ Förster, U., Wittman, G.T.W. (1979). Metal Pollution in the Aquatic Environment. Springer-Verlag, Berlin Heidelberg, New York.

/43/ ITRC (2008). In-situ Bioremediation of Chlorinated Ethane: DNAPL Source Zones. The Interstate Technology & Regulatory Council.

/44/ Overheu, N.D., Tuxen, N., Thomsen, N.I., Binning, P.J., Bjerg, P.L., Skou, H. (2011). Fastlæggelse af oprensningskriterier for grundvandstruende forureninger. Orbicon/DTU Miljø/Region Syddanmark. Miljøprojekt nr. 137.

/45/ S. E. Poulsen, S. Christensen, K. R. Rasmussen & A. D. Werner, 2011. Simulation of groundwater flow and salt transport in a shallow microtidal barrier aquifer during a storm surge. Conceptual and Modelling Studies of Integrated Groundwater, Surface Water, and Ecological Systems. Proceedings of Symposium H01, IUGG2011, Melbourne, Australia.

/46/ Andersen, T.T. (2005). Aerob omdannelse af parathion i havvand med suspenderet sediment. DHI, Institut for Vand og Miljø.

/47/ Andersen, T.T. (2005). Anaerob omdannelse af parathion I sediment fra Høfde 42. DHI, Institut for Vand og Miljø.

/48/ Parker, B.L., Chapman, S.W., Guilbeault, M.A. (2008). Plume persistence caused by back diffusion from thin clay layers in a sand aquifer following TCE source-zone hydraulic isolation. J. Contam. Hydrol. 102, 86-104.

/49/ Jacobsen, F., Petersen, O. (2006). Fortynding langs danske kyster. DHI, Institut for Vand og Miljø. (http://www2.mst.dk/fortynding).

/50/ CIS-WFS (2010). Technical Background Document on Identification of Mixing Zones. Common Implementation Strategy for the Water Framework Directive, European Commision.

/51/ Keddy, C.J., Greene, J.C., Bonnell, M.A. (1995). Review of Whole-Organism Bioassays: Soil, Freshwater Sediment, and Freshwater Assessment in Canada. Ecotoxicol. Environ. Saf. 30, 221-251.

/52/ Samsøe-Petersen, L., Gustavson, K. (2006). Miljøvurdering ved udsivning ved Kærgård Plantage forår 2006. DHI, Institut for Vand og Miljø.

/53/ Kresten, K.O., Bennedsen, L., Christophersen, M., Durant, N.D., Jørgensen, T.H., Rein, A., Rügge, K., Bjerg, P.L. (2011). Use of toxicity assays for evaluating the effectiveness of groundwater remediation with Fenton's reagent. Abstract Book, p. 128., 21st Annual Meeting - SETAC Europe, Milan, Italy.

/54/ Pedersen, F., Damborg, A., Kristensen, P. (1994). Industrispildevands miljøfarlighed. Miljøprojekt nr. 260, Danish Environmental Protection Agency, Ministry of the Environment, Denmark.

/55/ Pedersen, F., Kristensen, P., Damborg, A., Christensen, H.W. (1994). Ecotoxicological Evaluation of Industrial Wastewater. Miljøprojekt nr. 254, Danish Environmental Protection Agency, Ministry of the Environment, Denmark.

Appendix B

Numerical model

The following subsections describe the model domain and the formulation of the governing equations and the solvers employed in the numerical modelling. A description of the initial- and boundary conditions and the model parameters pertaining to flow and solute transport is provided and numerical stability is briefly discussed. Finally, two appendices (cf. Appendix C-Appendix D) are presented which serve as documentation for the conceptual model.

Model domain

The model domain extends from a water canal in the lagoon, from which measurements of the water stage are available (Mortensen, 2008), to the North Sea (Figure B1 & Figure B2).

Figure B1: The field site at groyne 42. The model domain is indicated by a red rectangle.
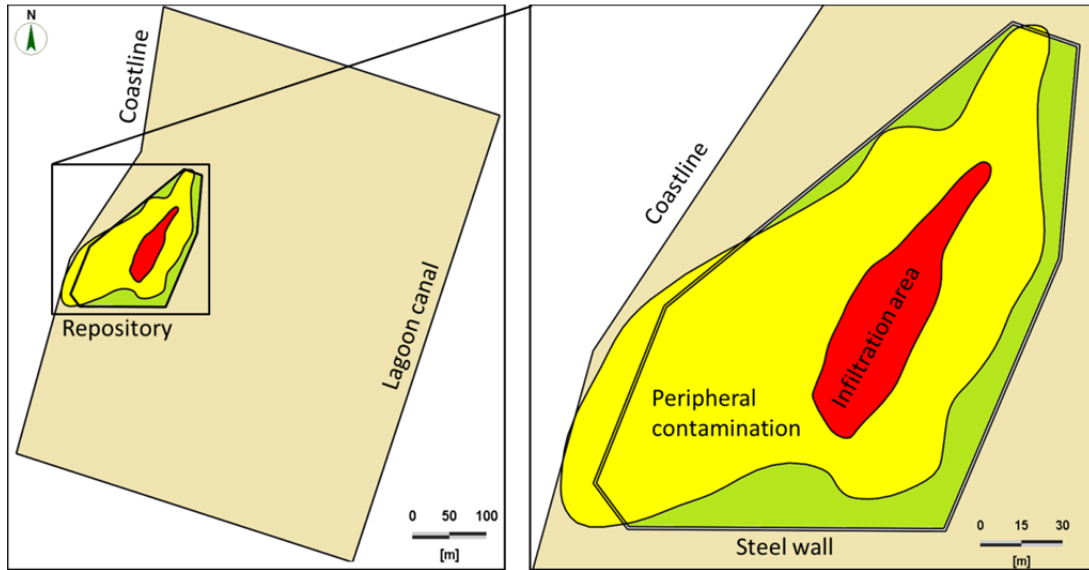
Figure B2: The model domain including the coastline, beach, repository, and the lagoon canal (left). The repository is surrounded by a sheet pile barrier and includes the infiltration area and the peripheral contamination (right). The sheet pile barrier is represented by a 1 m thick model segment.

The domain extends roughly 630 m and 450 m along and perpendicular to the coastline, respectively. The model grid is refined at the coastline and at the sheet pile barrier surrounding the repository (Figure B2). The sheet pile barrier is represented by a one meter thick model section for which the hydraulic- and solute transport parameters can be specified separately (Figure B2). The hydraulic conditions inside the repository are assumed to be similar to those in the aquifer. Preliminary model testing has shown that leakage of groundwater from the upper aquifer to the lower aquifer is negligible (see Appendix D). As such, the upper and lower aquifer can be simulated separately and the model domain terminates vertically at the surface of the silt layer at -2.7 m above mean sea level. In the forthcoming, all elevations are relative to mean sea level.

Formulation, solvers and convergence criterion

The governing equations for 3D, steady-state confined groundwater flow and conservative solute transport are solved by the numerical finite element model FEFLOW (Diersch, 2009):

$$\nabla \cdot \mathbf{q} = Q_f \tag{1}$$

$$\mathbf{q} = -\mathbf{K}\nabla h \tag{2}$$

$$\mathbf{q} \cdot \nabla C - \nabla \cdot \left[(\varepsilon D_d \mathbf{I} + \mathbf{D}) \cdot \nabla C \right] + Q_f C = Q_c \tag{3}$$

The physical quantities are listed in the Notations section. Free surface conditions are employed by FEFLOW's BASD (**B**est **A**daption to **S**tratigraphic **D**ata) technique. For further details see Diersch (2009) pp. 45-49. The governing equations are solved by the standard Petrov-Galerkin formulation in conjunction with FEFLOW's Algebraic Multigrid solver. The convergence criterion for the steady-state simulation is defined as the averaged head residual normalized by the maximum hydraulic head in the initial and boundary conditions (to be less than 0.001). The averaging of residuals was done by the Euclidian L2 integral root mean square norm.

Hydraulic and solute transport parameters

The hydraulic conductivity and porosity of the upper aquifer is set equal to $4 \cdot 10^{-4}$ m/s and 30%, respectively. Longitudinal and transversal dispersivity (α_L and α_T) are set equal to 1 m and 0.1 m, respectively (Gelhar *et al.*, 1992). The molecular diffusion in the porous media is set equal to 10^{-9} m^2/s.

Scenario B1 & B2

The hydraulic conductivity of the sheet pile barrier surrounding the repository is set equal to $4 \cdot 10^{-6}$ m/s (1/100 of that of the upper sand) to represent the deterioration of the sheet pile barrier that surrounds the repository. Recharge is set equal to 584 mm/y and zero in the repository when the membrane is fully intact (B1) and deteriorated (B2), respectively.

Numerical stability and discretization

The spatial discretization is restricted by the mesh Péclet number. For solute transport with dispersion primarily due to longitudinal mixing, Pe is approximately $\Delta L / \alpha_L$, where ΔL is the local distance between nodes (Voss & Provost, 2003). When transverse dispersion dominates $\Delta L < 10 \, \alpha_T$ is suggested. Spatial stability is guaranteed when Pe ≤ 2. In the present model both types of mixing occur. The longitudinal dispersion occurs between the repository and the North Sea while transverse mixing occurs 1) along the northern and southern boundaries of the repository (as they are somewhat parallel with the direction of flow) and 2) above the peripheral contamination at -2.2 m (yellow area in Figure B2). Thus, an upper bound of 1 m is imposed on the distance between model nodes near concentration fronts (i.e. at the coastline and the repository as shown in Figure B2).

Boundary and initial conditions

The numerical model has four boundaries representing the lagoon canal, the aquifer water table, the North Sea and the bottom of the aquifer (Figure B3).
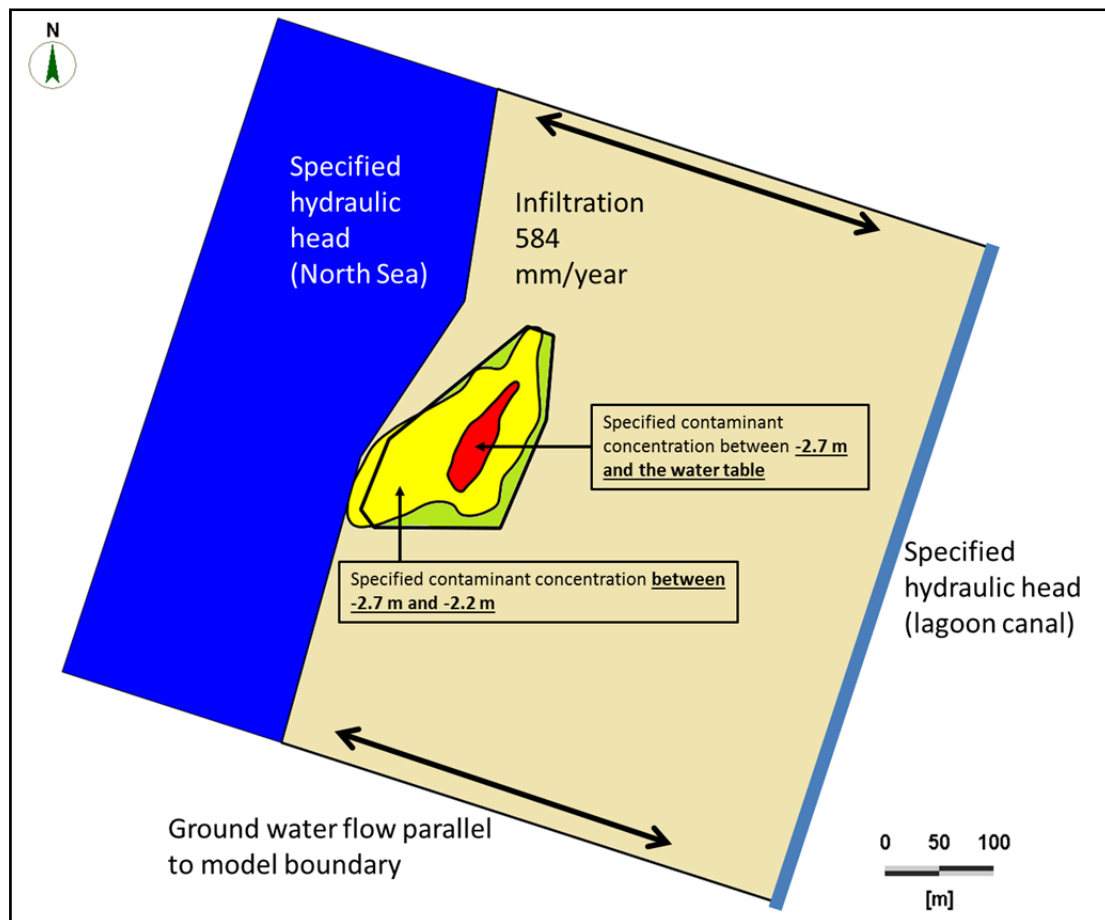
Figure B3: The model domain and boundary conditions. Please notice that the contaminant concentration in the infiltration area (*red area*) is specified between -2.7 m (the silt layer) and the water table and between -2.7 m and -2.2 m in the peripheral, contaminated area (*yellow area*). In the model, the peripheral contamination does not extend outside the confines of the sheet pile barrier (as otherwise indicated).

Preliminary model testing has shown that groundwater flow is parallel with the northern and southern model boundary in all model scenarios (see Appendix C). Recharge was estimated to be 584 mm/year by a simple root zone model utilizing precipitation data from 2008 (Poulsen *et al.*, 2010). The ocean is represented by a specified head condition corresponding to the average sea level (~ 0 m). The dilution of groundwater from inundation of the beach during storm surges was estimated as follows. During storm surges, ocean water levels exceed the mean sea level by 2 m and the coastline at groyne 42 is shifted inland by approximately 50 m. The hydraulic conditions during storm surges cause rapid inflow of seawater into the beach. The inflow is limited only by the hydraulic properties of the beach sand and the rate of infiltration of seawater is comparable to that of the hydraulic conductivity of the sediment (34.6 m/d). The total, average, daily recharge of the inundated section of the beach is calculated as the time-weighted inflow of water from percolation of precipitation and storm-induced infiltration. In 2008, the ocean water level exceeded 2 m for 0.23 days. By employing these numbers the time-weighted, average, daily recharge of the inundated section of the beach is $2.33 \cdot 10^{-2}$ m/d.

The water table in the lagoon channel is set equal to 0.40 m which is estimated from piezometer measurements at groyne 44 and in the lagoon (Mortensen, 2008; Poulsen *et al.* 2010). The northern and southern boundaries are represented by hydraulic and dispersive no-flow conditions. The aquifer is simulated as being unconfined and the moveable surface of the model coincides with the aquifer water table. The steady-state flow conditions imply a specific discharge (Darcy velocity) of approximately $1.8 \cdot 10^{-6}$ m/s and a pore water velocity of $6.1 \cdot 10^{-6}$ m/s at the coastline (positive towards the sea).

The contamination source is represented by a specified normalized concentration of 1 (dimensionless). Water flowing through specified concentration nodes (the contamination source) instantly obtains a (maximum) concentration of 1. The actual concentration can be calculated by multiplying the normalized concentration by the actual concentration in the contaminated areas (infiltration area and peripheral area at the respective depths). The assumption is rather crude but at this time it is not possible to parameterize a more detailed model of the interaction between the contamination and the groundwater. The spatial extent of the contamination source is illustrated in Figure B3. In the infiltration area, the source extends from the silt layer (-2.7 m) to the aquifer water table (red area in Figure B3). A peripheral contamination is located outside the infiltration area between -2.7 m (the silt layer) and -2.2 m (yellow area in Figure B3).

Scenarios

The scenarios presented in this report fall into three main categories:

Scenario B1-B2: The sheet pile barrier is partly deteriorated. In scenario B1 the plastic membrane is intact and prevents recharging water from percolating to the water table in the repository. Conversely, in scenario B2 the membrane is deteriorated and recharge in the repository is 584 mm/yr. The hydraulic conductivity of the sheet pile barrier is two orders of magnitude less than that of the surrounding sand (as it is only partly deteriorated). As such, groundwater is no longer prevented from flowing through the repository. Because of the low hydraulic conductivity of the sheet pile barrier, less water flows through the repository than under natural conditions. Inundation of the repository by seawater during storm surges is prohibited in both cases.

Scenario C1-C2: The sheet pile barrier and the plastic membrane have been removed and the hydraulic properties of the repository are identical to those of the surrounding sand. In scenario C1, the infiltration area (red area in Figure B3) has been remediated and the remaining source of contaminants is limited to the peripheral contamination (yellow area in Figure B3). Conversely, in scenario C2 the entire peripheral contamination has been remediated and the primary source of contamination is limited

to the infiltration area. Inundation of the repository by seawater during storm surges is no longer prohibited.

Scenario D: Both the infiltration area and the peripheral contamination constitute sources of contamination. Inundation of the repository by seawater during storm surges is no longer prohibited. Scenario D is a reference scenario in which no remediation has been carried out.

Results

The results from the simulation of the contaminant transport in the previously described scenarios are illustrated by contour maps of the contaminant concentration. Two maps show the horizontal extent of the dissolved contamination on top of the silt layer (-2.7 m) and at 0 m, respectively. The maps serve to illustrate the effect of dilution from recharge and overtopping of seawater in the shallow part of the aquifer (at 0 m) and the increased contamination of groundwater just above the silt layer (at -2.7 m), respectively. Finally, vertical profiles of the concentration of dissolved contaminants along the coastline in the vicinity of the repository are provided for all scenarios.

In the following, reference is given to C_{exit} and C_{source}. The former is the concentration of contaminants of the groundwater that exits to the North Sea at the coastline (referred to as "exit concentration" in the forthcoming). C_{source} refers to the contaminant concentration at the source. This value typically is set equal to the solubility of the solute of interest but can be assigned any value. The vertical profile of exit concentrations is indicated by **A**, **B** and **C** on the contour maps of the horizontal extent of the dissolved contamination. The statistics calculated for the exit concentrations are based on a dense, uniform grid spanning the cross-section (spacing 0.1 m in the vertical and horizontal direction). The discharge area that forms the basis for the calculations is identical in all scenarios. The dilution factor is defined as $1/C_{mean}$. The estimated contaminant discharge is normalised with the source concentration C_{source} and the corresponding unit is L/d. Thus, it can be interpreted as the daily discharge of groundwater (to the North Sea) with a contaminant concentration of C_{source}. Actual discharge values (e.g. mg/d and g/d) are obtained by multiplying normalised discharge values by the source concentration (which must be given in any mass unit per litre like e.g. mg/L and g/L).

Scenario B1

In scenario B1 the sheet pile barrier is partly deteriorated. However, the plastic membrane is intact and prevents recharging water from percolating to the water table in the repository. In Figure B4, the two top figures show the normalized contaminant concentration C/C_{source} at -2.7 m (on top of the silt layer) and 0 m, respectively.
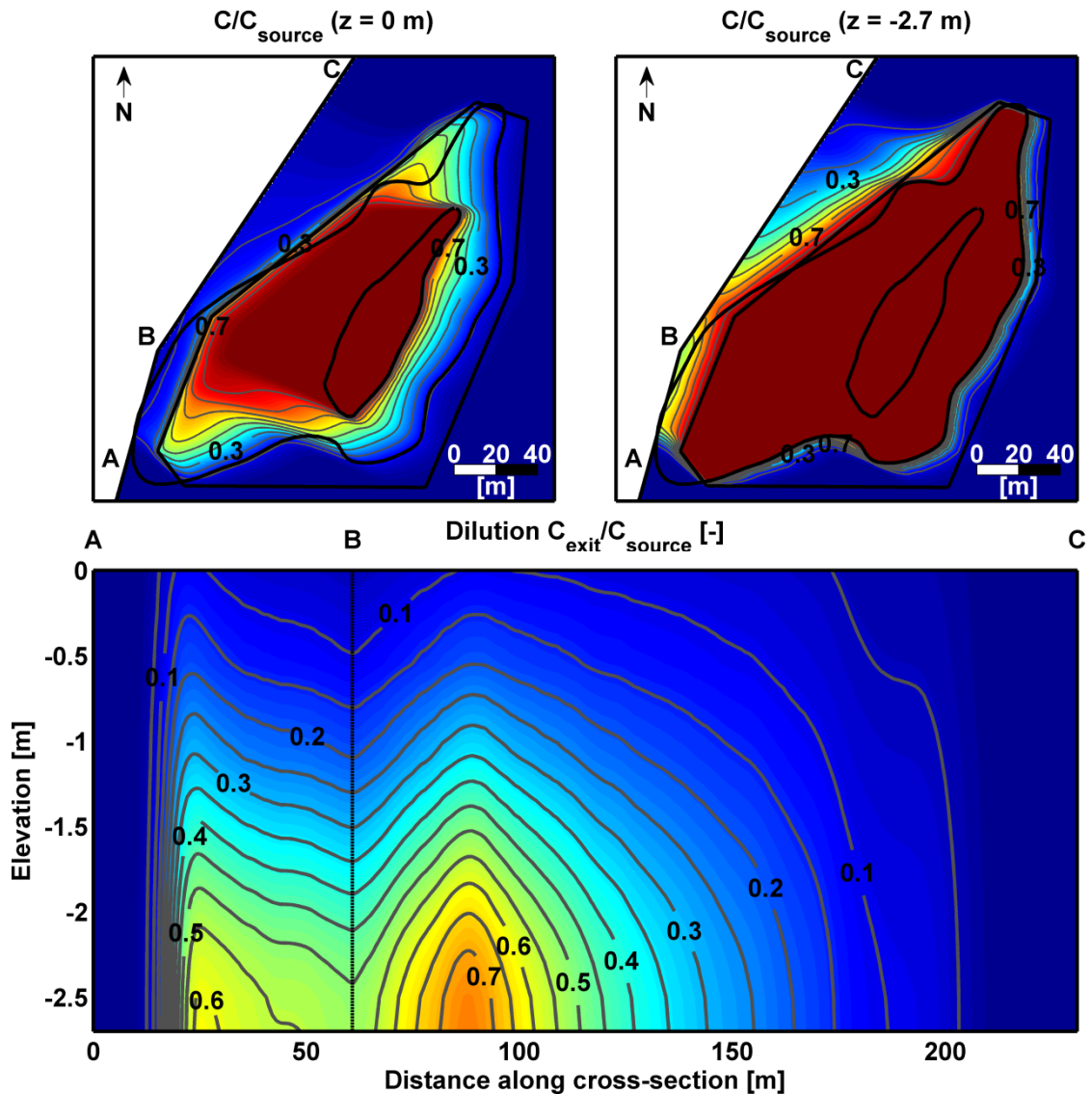
Figure B4: Contaminant concentration C/C_{source} in scenario B1 at: 0 m (top left) and the top of silt layer -2.7 m (top right). Contaminant exit concentration C_{exit}/C_{source} along the vertical coastline cross-section indicated by ABC in the top left and right figures (bottom figure). Equidistance = 0.1 (top figures) and 0.05 (bottom figure). Aspect ratio is 40:1 in the bottom figure.

The dissolved contaminants in the zone between the repository and the North Sea are diluted by recharge and the overtopping of seawater. The relatively low concentrations in the shallow part of the aquifer are in the interval 0.05-0.20. In the deeper parts of the upper sand, concentrations increase due to the relatively large extent of the peripheral contamination. The largest concentrations are found at –2.7 m just above the silt layer. The maximum exit concentration is 0.75. Two local concentration maxima, whose positions are controlled by the geometry of the repository, are present at the coastline. The mean and median exit concentrations C_{mean} and C_{median} are 0.21 and 0.15, respectively. The standard deviation (referred to as "std" in the following) is 0.18 and the mean dilution factor is 4.8. The daily contaminant discharge to the North Sea is 30297 L/d.

Scenario B2

In scenario B2 the sheet pile barrier and the plastic membrane are partly deteriorated and recharging water percolates to the water table in the repository. In Figure B5, the two top figures show the normalized contaminant concentration C/C_{source} at -2.7 m (on top of the silt layer) and 0 m, respectively.
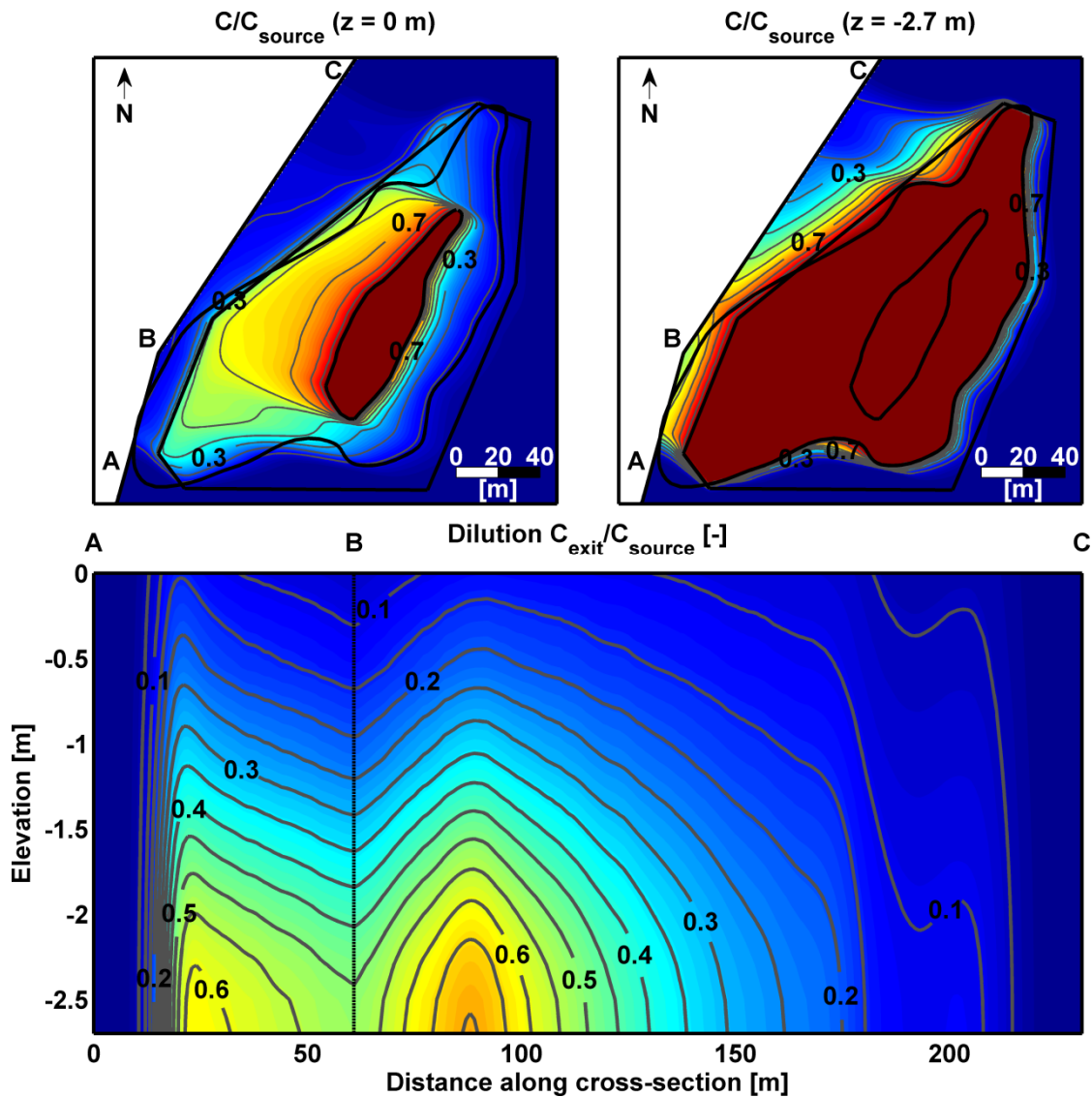

Figure B5: Contaminant concentration C/C_{source} in scenario B2 at: 0 m (top left) and the top of silt layer -2.7 m (top right). Contaminant <u>exit</u> concentration C_{exit}/C_{source} along the vertical coastline cross-section indicated by ABC in the top left and right figures (bottom figure). Equidistance = 0.1 (top figures) and 0.05 (bottom figure). Aspect ratio is 40:1 in the bottom figure.

Dissolved contaminants in the zone between the repository and the North Sea are diluted by recharge and the overtopping of seawater. The relatively low concentrations in the shallow part of the aquifer are in the interval 0.05-0.20. In the deeper parts of the upper sand concentrations increase due to the relatively large extent of the peripheral contamination. The largest concentrations are found at −2.7 m just above the silt layer. The maximum exit concentration is 0.70. Two local

concentration maxima, whose positions are controlled by the geometry of the repository, are present at the coastline. The mean and median exit concentrations C_{mean} and C_{median} are 0.23 and 0.18, respectively. The standard deviation is 0.18 and the dilution factor is 4.3. The total contaminant discharge to the North Sea is 37934 L/d.

Scenario C1

In scenario C1 the sheet pile barrier and the plastic membrane have been removed and the hydraulic properties of the repository are identical to those of the surrounding sand. In scenario C1, the infiltration area (red area in Figure B3) has been remediated and the remaining source of contaminants is limited to the peripheral contamination (yellow area in Figure B3). Inundation of the repository by seawater during storm surges is no longer prohibited. In Figure B6, the two top figures show the normalized contaminant concentration C/C_{source} at -2.7 m (on top of the silt layer) and 0 m, respectively.
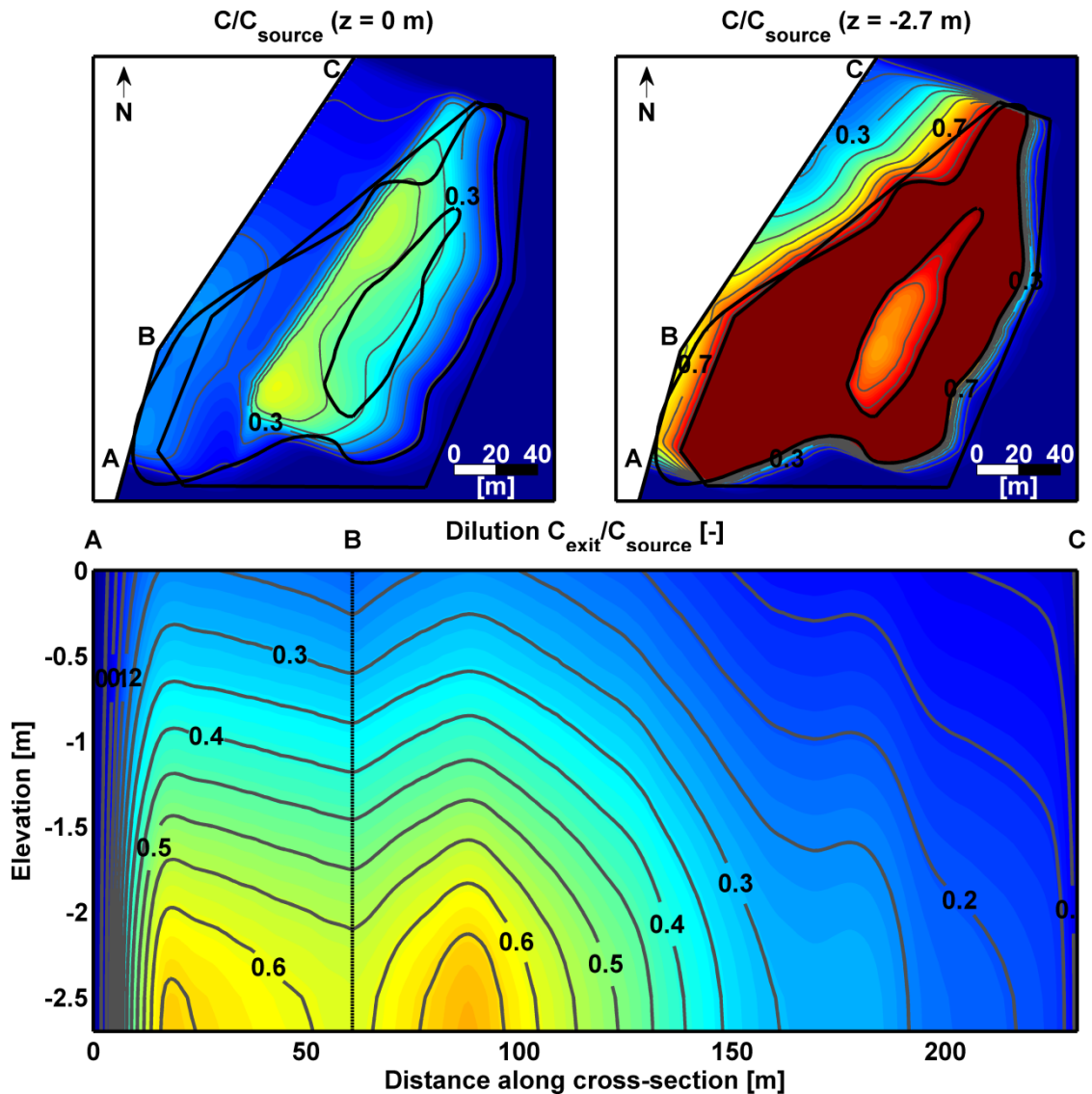
Figure B6: Contaminant concentration C/C_{source} in scenario C1 at: 0 m (top left) and the top of silt layer -2.7 m (top right). Contaminant <u>exit</u> concentration C_{exit}/C_{source} along the vertical coastline cross-section indicated by ABC in the top left and right figures (bottom figure). Equidistance = 0.1 (top figures) and 0.05 (bottom figure). Aspect ratio is 40:1 in the bottom figure.

Dissolved contaminants in the zone between the repository and the North Sea are diluted by recharge and the overtopping of seawater. The moderate concentrations in the shallow part of the aquifer are in the interval 0.1-0.30. In the deeper parts of the upper sand concentrations increase due to the relatively large extent of the peripheral contamination. The largest concentrations are found at –2.7 m just above the silt layer. The maximum exit concentration is 0.69. Two local concentration maxima, whose positions are controlled by the geometry of the repository, are present at the coastline. The mean and median exit concentrations C_{mean} and C_{median} are 0.33 and 0.29, respectively. The standard deviation is 0.16 and the dilution factor is 3.1. The total contaminant discharge to the North Sea is 105640 L/d.

Scenario C2

The sheet pile barrier and the plastic membrane have been removed and the hydraulic properties of the repository are identical to those of the surrounding sand. In scenario C2, the peripheral contamination has been remediated and the primary source of contamination is limited to the infiltration area. In Figure B7, the two top figures show the normalized contaminant concentration C/C_{source} at -2.7 m (on top of the silt layer) and 0 m, respectively.
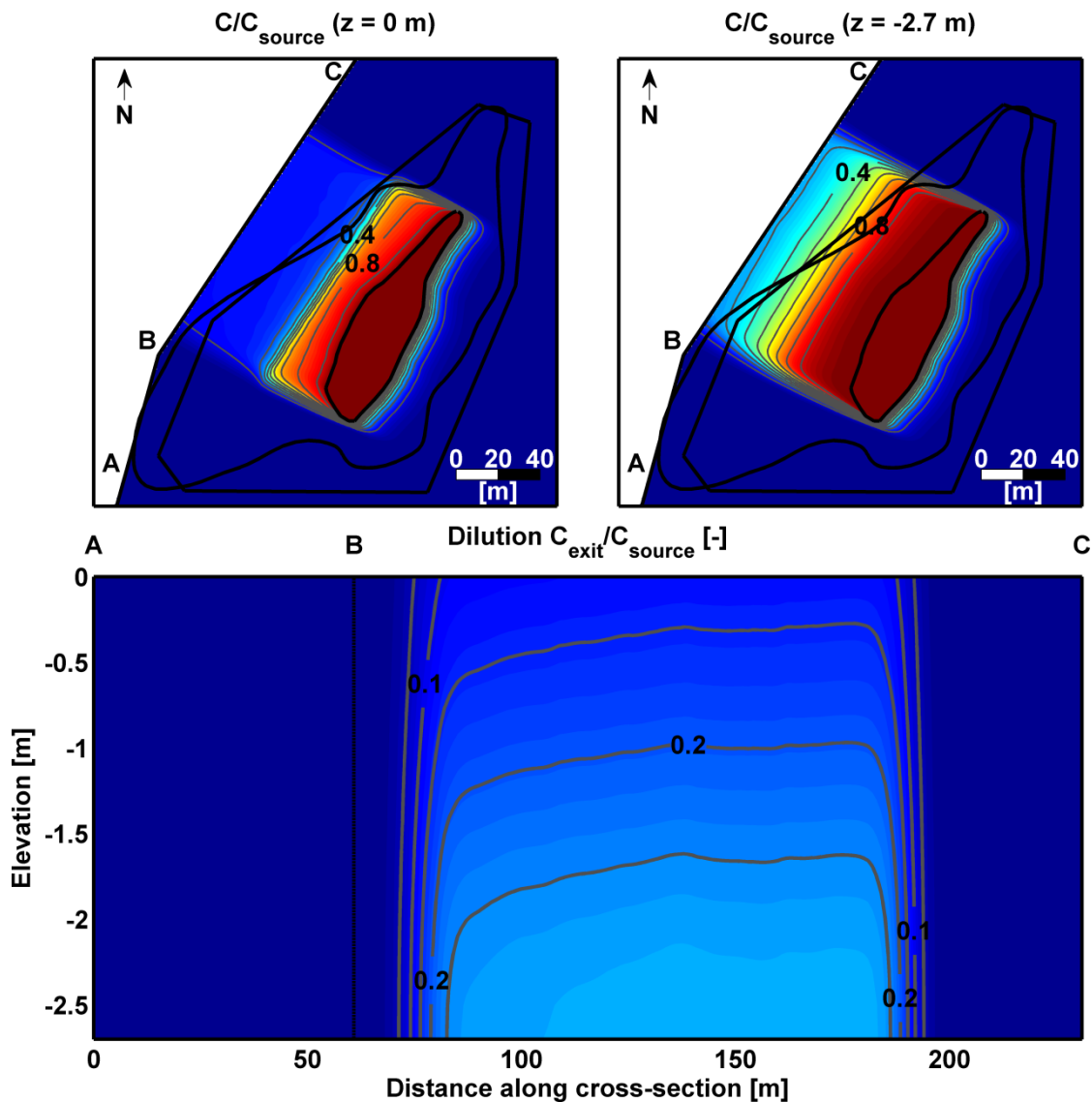

Figure B7: Contaminant concentration C/C_{source} in scenario C2 at: 0 m (top left) and the top of silt layer -2.7 m (top right). Contaminant exit concentration C_{exit}/C_{source} along the vertical coastline cross-section indicated by ABC in the top left and right figures (bottom figure). Equidistance = 0.1 (top figures) and 0.05 (bottom figure). Aspect ratio is 40:1 in the bottom figure.

Dissolved contaminants in the zone between the repository and the North Sea are diluted by recharge and the overtopping of seawater. The low concentrations in the shallow part of the aquifer are in the interval 0.05-0.15. Relative to scenarios B1, B2 and C1, concentrations are significantly lower in the shallow part of the aquifer and

the discharge plume is much smaller. The largest concentrations are found at –2.7 m just above the silt layer. The maximum exit concentration is 0.29. The mean and median exit concentrations C_{mean} and C_{median} are 0.11 and 0.085, respectively. The standard deviation is 0.11 and the dilution factor is 9.3. The total contaminant discharge to the North Sea is 35408 L/d.

Scenario D

Both the infiltration area and the peripheral contamination constitute sources of contamination. Scenario D is a reference scenario in which no remediation has been carried out.

In Figure B8, the two top figures show the normalized contaminant concentration C/C_{source} at -2.7 m (on top of the silt layer) and 0 m, respectively.

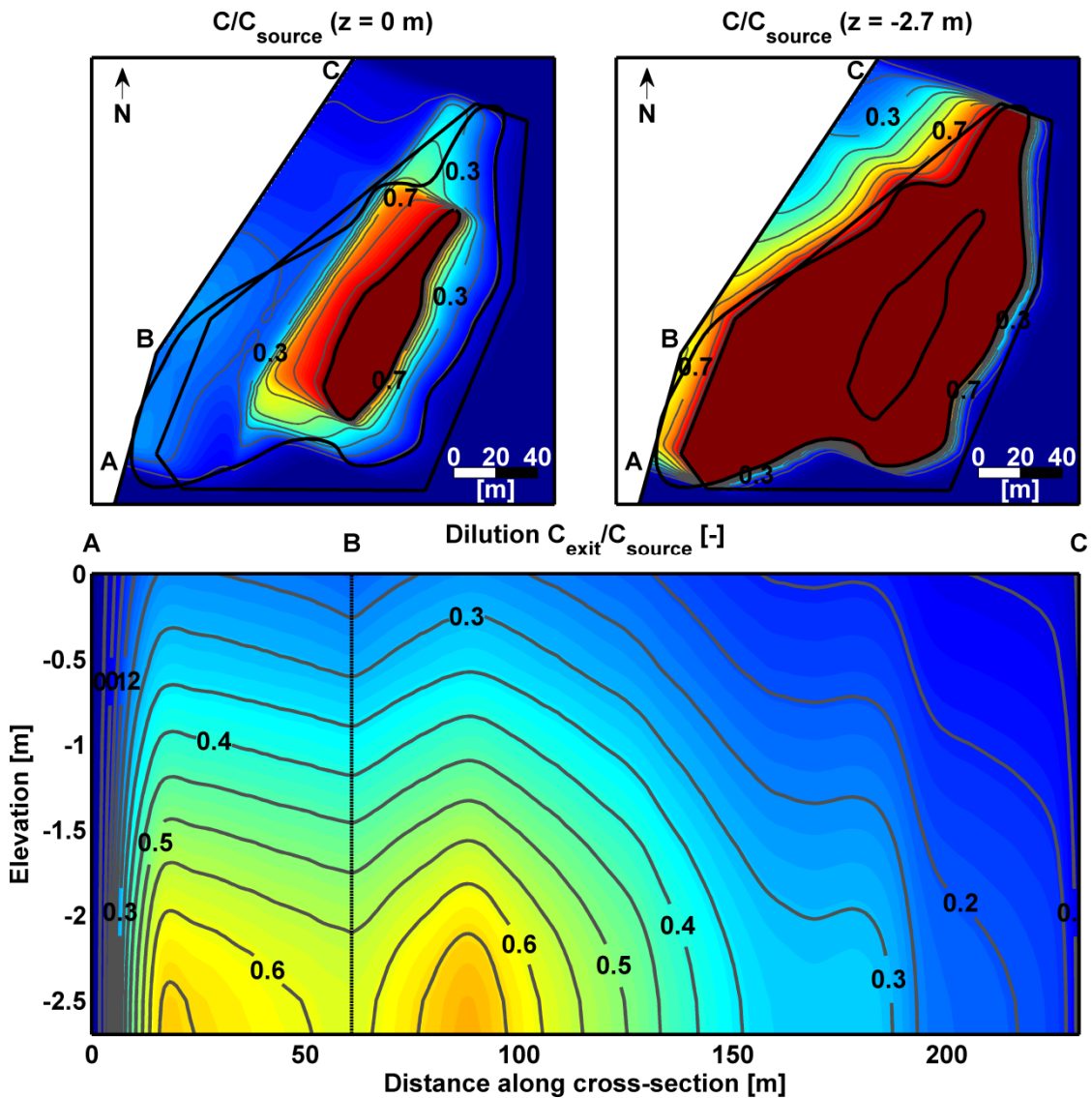
Figure B8: Contaminant concentration C/C_{source} in scenario D at: 0 m (top left) and the top of silt layer -2.7 m (top right). Contaminant exit concentration C_{exit}/C_{source} along the vertical coastline cross-section indicated by ABC in the top left and right figures (bottom figure). Equidistance = 0.1 (top figures) and 0.05 (bottom figure). Aspect ratio is 40:1 in the bottom figure.

Dissolved contaminants in the zone between the repository and the North Sea are diluted by recharge and the overtopping of seawater. Moreover, the inundation of the beach during storm surges now extends into the former repository as the sheet pile barrier and plastic membranes have been removed. The relatively low concentrations in the shallow part of the aquifer are in the interval 0.1-0.35. In the deeper parts of the upper sand concentrations increase due to the relatively large extent of the peripheral contamination. The largest concentrations are found at –2.7 m just above the silt layer. The maximum exit concentration is 0.70. Two local concentration maxima, whose positions are controlled by the geometry of the repository, are present at the coastline. The mean and median exit concentrations C_{mean} and C_{median} are 0.33 and 0.31, respectively. The standard deviation is 0.16 and the dilution factor is 3.0. The total contaminant discharge to the North Sea is 107670 L/d.

Dilution factors & contaminant discharge to the North Sea

The statistics for the different scenarios provided in the previous sections are summarized in Table B1.

Table B1: Normalised maximum, mean and median concentration C_{max}, C_{mean}, C_{median}, the standard deviation on C_{mean} (std) and the dilution factor for scenarios B1, B2, C1, C2 and D. Solute discharge to the North Sea is normalised. Actual discharge (mg/d) is obtained by multiplying the normalized discharge (L/d) by C_{source} (in mg/L).

Scenario	C_{max}	C_{mean}	C_{median}	std	Dilution factor	Contaminant discharge [L/d]
B1	0.75	0.21	0.15	0.18	4.8	30297
B2	0.70	0.23	0.18	0.18	4.4	37934
C1	0.69	0.33	0.29	0.16	3.1	105640
C2	0.29	0.11	0.085	0.11	9.3	35408
D	0.70	0.33	0.31	0.16	3.0	107670

Conclusions

This report presents key results from a model-based assessment of the long term development in contaminant discharge to the North Sea from the chemical waste repository at groyne 42, Harboøre Tange, Denmark. The assessment is based on five scenarios which represent different stages of the remediation and some likely end scenarios. In scenarios B1 and B2, the sheet pile barrier is deteriorated and the plastic membrane is intact and deteriorated, respectively. In scenarios C1 and C2, the sheet pile barrier and the plastic membrane have been removed and residual contamination is present in the infiltration area and in the periphery of the infiltration area, respectively. In scenario D, the infiltration area and the peripheral contamination both constitute sources of contamination. Scenario D is a reference scenario in which no remediation has been carried out. Estimates of dilution factors and contaminant discharge form the basis for evaluating the impact of different remediation strategies.

The results can be summarized as follows. In scenario B1 and B2, the dilution of contaminants is increased by 47% and 60% relative to the reference scenario D. The presence of the semi-permeable sheet pile barrier hampers the ambient flow of groundwater in the repository (that which enters from the sides and not as recharge from above). In scenario B1, recharge in the repository is prohibited as the plastic membrane is intact. Consequently, less contamination is mobilized since there is no infiltration of water directly into the repository, which yields a higher dilution factor in scenario B1, relative to scenario B2. In scenario B2, the water infiltrating vertically into the infiltration area instantly obtains the maximum concentration as it comes into direct contact with the specified contaminant concentration. Thus, in scenario B2, additional contamination is mobilized as water infiltrates directly into the contaminated areas. Since the infiltration of precipitation and seawater between the repository and the sea (the zone where the contamination is diluted) is identical in the two scenarios, the dilution is less in scenario B2. This, naturally, reflects closely the assumptions made in the model i.e. the conceptual model for the interaction between the contamination and the groundwater. It can be conjectured that the results and conclusions would have been different if a more elaborate model of the interaction between the contamination and the groundwater was utilized. However, this remains speculative as no field data or current knowledge can justify a more sophisticated approach to modelling the soil-groundwater exchange of contaminants. Consequently, the discharge of contaminated water from the repository is reduced which yields a higher dilution factor in scenario B1, relative to scenario B2. In scenarios C1 and C2, the sheet pile barrier and the plastic membrane have been removed and the hydraulic properties of the repository are identical to those of the surrounding sand. As such, the ambient groundwater flow in the repository is increased relative to scenarios B1 and B2. In scenario C1, the discharge of contaminants to the North Sea is increased by 249% and 178%, relative to scenario B1 and B2, respectively. It is worth noting that the contaminant discharge and exit concentrations in scenario C1 are almost identical to those of the reference scenario D. In scenario C2, remediation efforts have been focused on the peripheral contamination. Consequently, the distance between the source (infiltration area) and the recipient has been increased and the horizontal extent of the contaminated area has been reduced significantly. Due to the longer path of transport from source to recipient, the dilution is significantly increased in scenario C2. The mean dilution factor is 9.3 and thus 2-3 times greater than in the remaining scenarios.

The dilution of solute contaminants is controlled by the ratio between the discharge from the repository and the combined inflow of recharge and seawater in the swash zone. The results in this report demonstrate that the presence of a hydraulically semi-permeable body (the deteriorated sheet pile barrier) enclosing the contamination in scenarios B1 and B2, hampers the contamination of the swash zone and in turn the North Sea. When the semi-permeable body is removed, water flows freely through the

repository (scenarios C1 and C2) and the discharge of contaminants to the North Sea increase (given an almost identical contamination source as in scenario C1). Remediation of the infiltration area while ignoring the peripheral contamination (scenario C1) implies an insignificant reduction in exit concentrations. Conversely, the results suggest that the peripheral contamination contributes significantly to the contamination of the North Sea.

Notation

h = hydraulic head [m]

C = concentration of the dissolved contaminant [kg/m^3]

S = specific storage [1/m]

ε = porosity [-]

D_d = molecular diffusion of the dissolved contaminant in the porous media [m^2/s]

t = time [s]

Q_f = fluid source [1/s]

Q_c = contaminant source [kg/m^3/s]

$\mathbf{q}$ = Darcy flux vector [m/s]

$\mathbf{K}$ = tensor of hydraulic conductivity [m/s]

$\mathbf{I}$ = unit tensor [-]

$\mathbf{D}$ = tensor of mechanical dispersion [m^2/s]

References

Diersch, H.-J. G., 2009. FEFLOW. Finite element subsurface flow and transport simulation system, Reference manual, DHI-WASY, GmBH.

Gelhar, W. L., Welty, C., Rehfeldt, K. R., 1992. A critical review of data on field-scale dispersion in aquifers, Water Resources Research, 28, 7, pp. 1955–1974.

Mortensen, J. S., 2008. Opstilling af grundvandsmodel for området nord for høfde 42 på grundlag af indsamlede geofysiske, hydrologiske og kemiske data, Master thesis, Aarhus University.

NIRAS, 2004. Høfde 42, Harboøre Tange. Supplerende forureningsundersøgelser, report.

Poulsen, S. E., Rasmussen, K. R., Christensen, N. B., Christensen, S., 2010. Evaluating the salinity distribution of a shallow coastal aquifer by vertical multielectrode profiling (Denmark), Hydrogeology Journal, 18, 1, pp. 161-171.

Voss, C. I., Provost, A. M., 2003. A model for saturated-unsaturated flow variably density ground water flow with solute or energy transport, Water resources investigations report 02-4231.

Appendix C

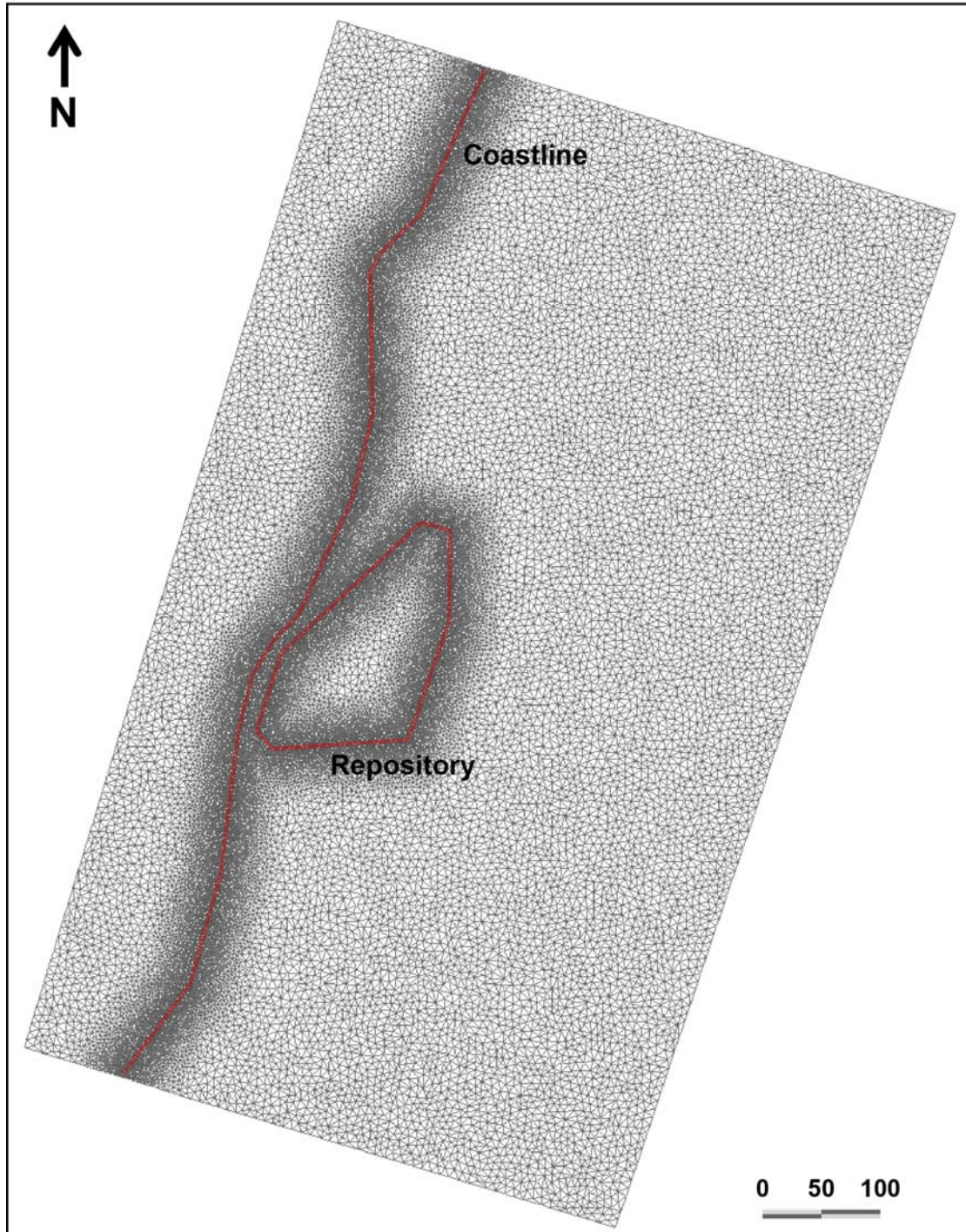## Extended model domain

Figure C1: Extended model domain and the finite element mesh. Red lines indicate the coastline and the repository.
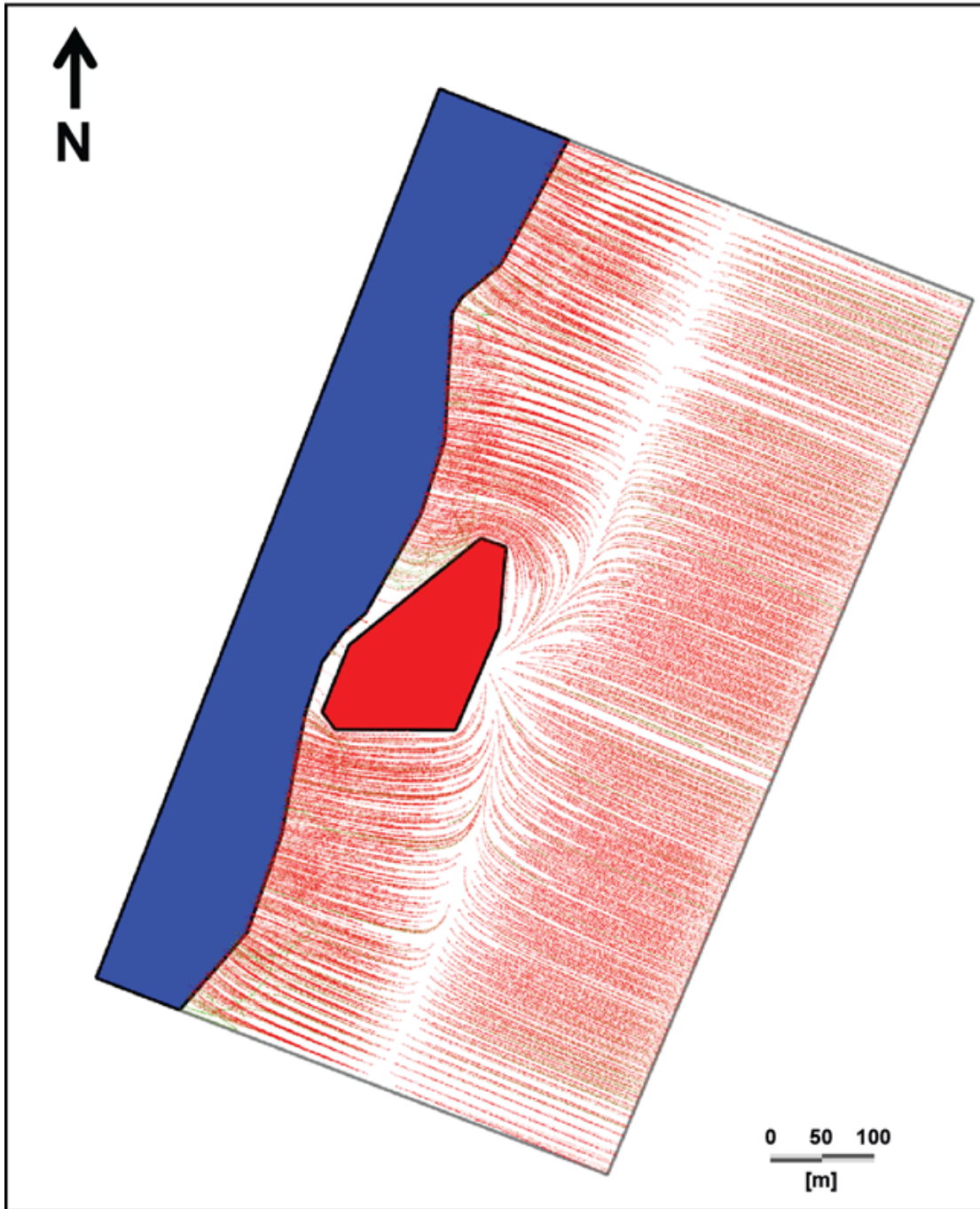
Figure C2: Stream lines in case the sheet pile barrier is impermeable. It is noticed that at a short distance (roughly 200 m) from the northern and southern boundary of the repository, groundwater flow is parallel with the northern and southern model boundary.

Appendix D

Leakage from the upper to the lower aquifer

Mortensen (2008) and Poulsen *et al.* (2010) showed that groundwater with salinity comparable to that of seawater is found at around -6 m to -5 m at groyne 41, 42 and 44. They also showed that a coast-parallel water divide is present in the lagoon just east of the dunes. Earlier field investigations (e.g. NIRAS, 2004) further demonstrate that groundwater flows towards the sea in the lower aquifer (-9 m to -3 m).

To test the implications of leakage from the upper to the lower aquifer, a numerical model was set up for the two scenarios, with and without leakage, respectively. The model simulates density-dependent flow in the vertical and horizontal direction perpendicular to the coastline at groyne 42 (further model details are available upon request). The calculated salinity distributions were then compared to the observed salinity distribution in the coastal barrier at the field site (Figure D1 & Figure D2).
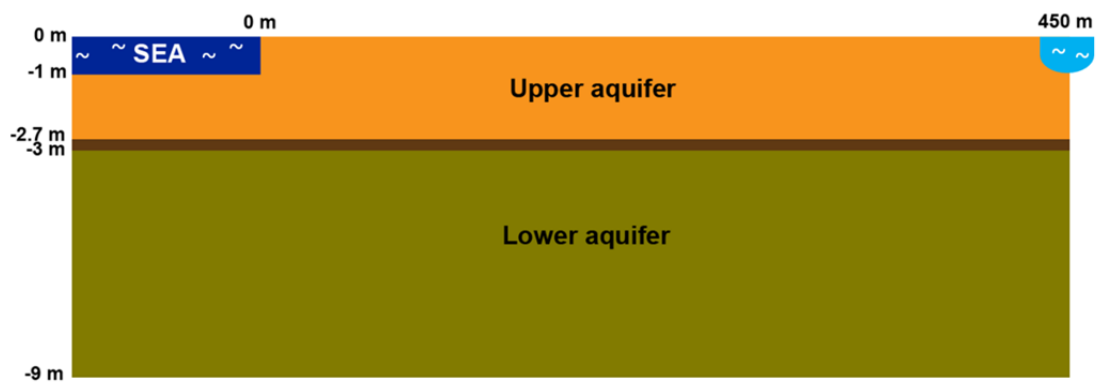

Figure D1: The conceptual model that forms the basis for the numerical model. Hydraulic head is specified (0.4 m) at the boundary condition to the east (right) which represents the lagoon canal (marked in light blue at the 450 m marker). The clayey silt layer (brown) separates the upper and lower aquifer.
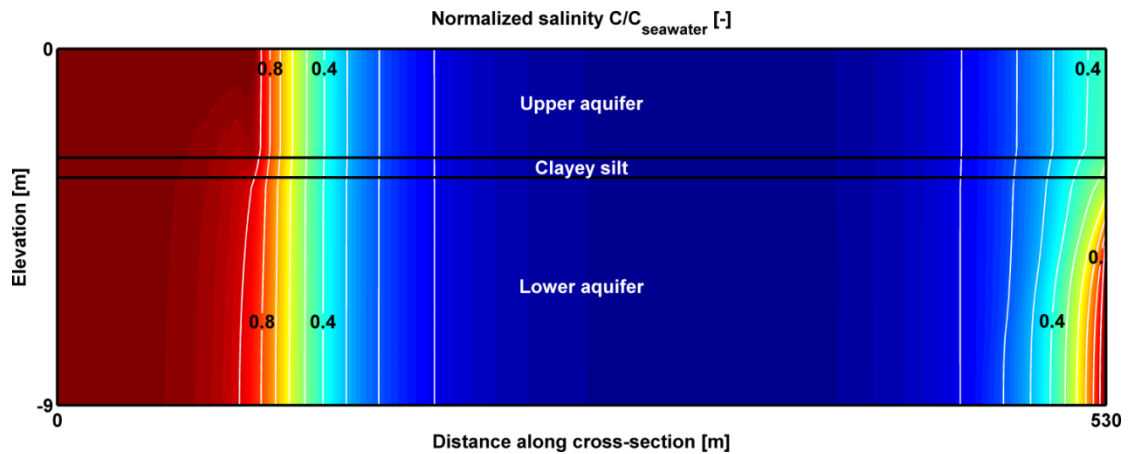
Figure D2: Simulated steady-state salinity distribution when the leakage from the upper to the lower aquifer (separated by the clayey silt) is 30% of the infiltration. Equidistance is 0.1 and aspect ratio is 20:1.
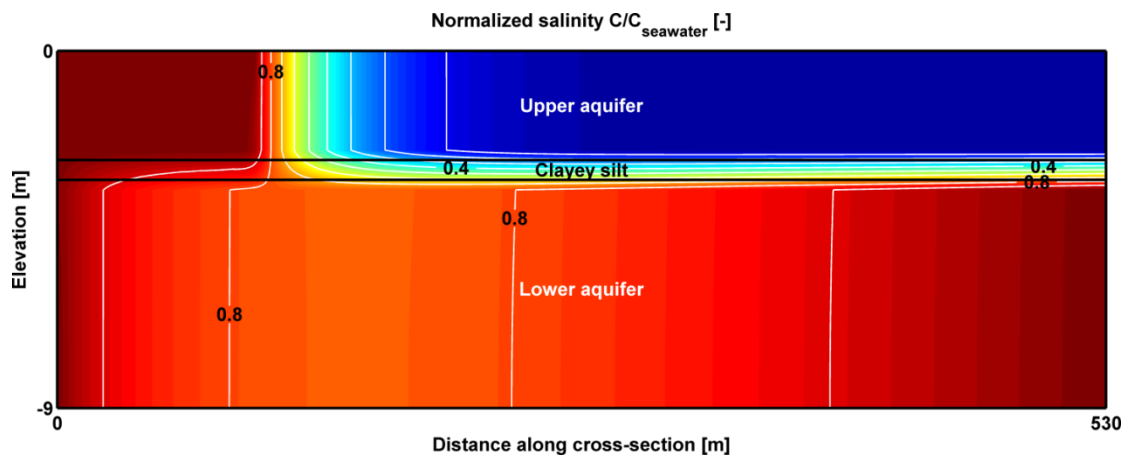
Figure D3: Simulated steady-state salinity distribution when leakage from the upper to the lower aquifer (separated by the clayey silt) is 0.003% of the infiltration. Equidistance is 0.1 and aspect ratio is 20:1.

The simulated salinity distribution, when assuming negligible leakage to the lower aquifer (Figure D3), fits better the observed salinity distribution in the coastal barrier, relative to the case where leakage is significant (Figure D2). Thus, the simulations suggest that it is reasonable to simulate the upper and lower aquifer separately.

Appendix E

Note on the contaminant mass discharge from the lower secondary aquifer at Groyne 42 (in Danish)

Central Denmark Region
May 2014

Notat om stofflux i det nedre magasin på Høfde 42

Indledning

I udkast til "NorthPestClean: Remediation Stop Criteria" af januar 2014 er antaget, at flux af pesticider ud i havet fra det nedre magasin (under det indskudte siltlag omkring kote -3,0) er ubetydelig i forhold til flux af pesticider ud i havet fra det øvre magasin (over det indskudte siltlag).

Dette notat belyser, hvor store mængder af pesticider der teoretisk via konvektiv og diffusiv transport kunne trænge igennem det indskudte siltlag. Desuden beskrives grundvandstrømningshastighed i det nedre magasin, og der foretages vurdering af fluxen af pesticider til havet fra dette magasin i forhold til fluxen i det øvre magasin. Vurderingerne er foretaget ud fra situationen uden spuns, altså under naturlige strømningsforhold.

Da fluxen er bestemt af koncentration og transporthastighed, er spørgsmålet således 2-delt:

- Kan der være en betydelig diffussiv eller konvektiv transport af pesticider gennem det indskudte siltlag
- Er der er en høj grundvandsstrømningshastighed i det nedre magasin, der kan give en stor flux ud i havet.

Status

Søren Erbs (*Fjordbøge et al., NorthPestClean: Remediation Stop Criteria* - Appendix D) argumenterer for, at der ikke findes væsentlig konvektiv transport igennem siltlaget. Dette pga. betragtninger om saltindhold over og under siltlaget:

- *1-2 m DNN: lav salinitet (ledningsevne ~ 3 mS/cm)*

- *3 m DNN: siltlag*

- *3,5-4,5 m DNN: høj salinitet (ledningsevne ~ 40,5 mS/cm)*

For at kunne simulere denne tilstand skulle Søren sætte den konvektive transport igennem siltlaget på 0,003% eller en tilbageholdelsesfaktor på 0,00003.

Grundlæggende ville denne argumentation gælde for enhver transport om det nu er konvektivt eller diffusivt transport.

Evt. svagheder med betragtningen:
Salinitetsforskellen er målt ca. 0,5-1,5 m under siltlaget, teoretisk kunne der ligge et relativ tyndt lag med lavere salinitet lige under siltlaget. Dette kunne man forstille sig ved en relativ langsom vertikal transport igennem siltlaget og en kraftigere horisontal transport lige under siltlaget.

Diffusion

Kan diffusion udgøre, at evt. transport igennem siltlaget er væsentligt?

Stoftransport igennem diffusions beskrives med Ficks law:

$$J_d = -D_0 \frac{d_c}{d_x}$$

Hvor
- J_d: stoftransport (flux)
- D_0: Diffusionskoefficent i frit væske

Ved transport igennem jord erstattes D_0 med D_s (hvor s står for *soil*), D_s fremkommer ved at gange D_0 med en faktor (α). α er en faktor på D_0 for at godtgøre for jordens tortuosity altså at porer snoer sig (τ), at der kun en del af jordvolumen som er væskefyldt (θ), at væskens viskositet kan ændre sig alt efter jordtype og porestørrelse etc.

$$J_s = -D_s \frac{d_c}{d_x}$$

eller

$$J_s = -D_0 \theta \tau \frac{d_c}{d_x}$$

Vi kender ikke D_0 for parathion: Der regnes derfor med 6×10^{-10} m^2/s, som regnes at være et konservativt valg. (Se vedhængte tabel med forskellige D_0 for forskellige pesticider. Ved beregninger viser det sig at, når D_0 er i samme størrelsesorden, er den ikke særligt følsom)

Den effektive væskefyldte porøsitet kan antages at ligge på ca. 0,3.

Fra JAGG modellen findes en τ på 0.11 for sand og en på 0.008 for ler. τ for siltlaget forventes at ligge tæt på ler.

Beregningseksempler

Uden lud er der meget lave indhold af stoffer i vandfasen (ca. en faktor 15 lavere end med lud), dvs. med lud op til 4 kg/m^3 uden lud ca. 0.27 kg/m^3 (fra masseberegninger i testcellerne).

Der regnes for hele det indspunsede areal på 20.000 m^2.

For konvektion regnes med en infiltration af 0,525 m/år og der regnes med Sørens tilbageholdelsesfaktor af 0,00003.

Konvektion

infiltration   0,525   m/år

tilbageholdelsesfaktor (Søren)	0,00003	
d_C	0,27	kg/m³
J_S	4,25E-06	kg/m² år
Høfden	**0,09**	**kg/år**
Høfden 50 år	**4**	**kg**

Fra denne beregninger kan ses, at der ved antagelse af Søren Erb's betragtninger er sivet ca. 4 kg stof igennem siltlaget i de 50 år som depotet har bestået.

For diffusion regnes både for en tortuosity for ler og en for sand.

Diffusion

sand			*ler*		
D_0	6,00E-10	m²/s	D_0	6,00E-10	m²/s
θ (porevolumen)	0,3		θ (porevolumen)	0,3	
τ (tortuosity)	0,11		τ (tortuosity)	0,008	
d_C	0,27	kg/m³	d_C	0,27	kg/m³
d_X	0,3	m	d_X	0,3	m
J_S	1,78E-11	kg/m² s	J_S	1,30E-12	kg/m² s
J_S	5,62E-04	kg/m² år	J_S	4,09E-05	kg/m² år
Høfden	**11,24**	**kg/år**	**Høfden**	**0,82**	**kg/år**
Høfden 50 år	**562**	**kg**	**Høfden 50 år**	**41**	**kg**

Fra denne beregning kan ses, at der i værste fald er diffunderet mellem 50-500 kg forurening igennem siltlaget, som svarer til mellem 0,25 og 0,025 % af forureningsmassen på Høfden.

Som nævnt indledningsvis, ville en diffusion i denne størrelsesorden formentligt også påvirke saltindholdet i magasinet under siltlaget, som ikke er observeret.

Grundvandsstrømning i det nedre magasin
Geologi
I de seneste undersøgelser (siden 2010) er det såkaldte "indskudte siltlag" karakteriseret som gytje. Det vurderes, at boremetoden, der er anvendt siden 2010, giver bedre beskrivelse og kotefastsættelse af de geologiske lag, end de tidligere anvendte metoder. I de fleste nyere boringer, der gennembryder gytjelaget, er der under gytjen truffet 0,2-0,4 m silt. Dvs. i alle nyere boringer (siden 2010), der gennembryder gytje/siltlaget, er tykkelsen af dette gytje/siltlag mindst 0,5 m. Idet tykkelsen af laget i ovenstående diffusionsberegning er sat til 0,3 m (d_X), må diffusionsberegningerne vurderes at være konservative på denne faktor.

Under gytje/siltlaget er der truffet finsand med indslag af silt, ifølge rapport "Høfde 42, Supplerende forureningsundersøgelser" af 14. juni

2014, af Niras, er det kun magasinet ned til ca. 2 m under siltlaget, der kan tilskrives en egentlig vandføringsevne.

Hydrauliske parametre
I rapporten "Høfde 42, hydrauliske beregninger vedrørende oprensning af et forsøgsvolumen" af Søren Erbs Poulsen og Steen Christensen, november 2010, er de hydrauliske parametre fastsat til:

Hydraulisk ledningsevne: Over siltlaget $2,1 \times 10^{-3}$ m/s
                                              Siltlaget $4,2 \times 10^{-6}$ m/s
                                              Under siltlaget $1,72 \times 10^{-4}$ m/s

Gradient: Ifølge ovennævnte rapport fra 2004 er gradienten over siltlaget ca. 0,008 og under siltlaget ca. 0,006

Grundvands hastighed
Ifølge Darcys lov kan grundvandets hastighed bestemmes ved:
$V = K \times i$

Hvor V er hastighed i m/s.
K er hydraulisk ledningsevne m/s
og i er gradienten.

Strømningsretning antages at være fra grundvandsskellet under havdiget ud mod havet.

Herved fås følgende grundvandstrømningshastigheder:

Over siltlaget: $V = 2,1 \times 10^{-3} \times 0,008 = 1,68 \times 10^{-5}$ m/s
= 530 m/år
Under siltlaget: $V = 1,72 \times 10^{-4} \times 0,006 = 1,03 \times 10^{-6}$ m/s
= 32 m/år.

Det er vurderet at der er ca. 100 tons pesticider i høfde depotet. Jf. ovenstående beregning er den konvektiv og diffussiv transport gennem siltlaget beregnet til mellem 0,8 kg/år (ved ler) og 11 kg/år (ved sand).

Sammenholdt med at grundvandets strømningshastighed over siltlaget er mere end 10 gange højere end under siltlaget, vurderes det, at fluxen af forurening ud til havet under siltlaget er ubetydelig, set i forhold til fluxen over siltlaget.

Denne vurdering understøttes af, at forureningskoncentrationen var relativ lav i magasinet under det indskudte siltlag, tæt ved havstokken (moniteringsboringerne MB6, MB7 og MB8) ved målingen i 2007, kort tid efter etablering af spunsen.

Konklusion
Det vurderes, at forureningsfluxen ud til havet fra magasinet under det indskudte siltlag er ubetydelig i forhold til forureningsfluxen fra magasinet over det indskudte siltlag.

Bilag: Tabel med diffusionskoefficienter for forskellige stoffer (fra *Pesticides Research Nr. 66 2003 - Bekæmpelsesmiddelforskning fra Miljøstyrelsen - Dry Deposition and Spray Drift of Pesticides to Nearby Water Bodies*)

Tabel 4. Diffusionskoefficient i vand ved 298.15 °K beregnet med FSG-metoden og den simple metode.

	molecular weight (g mol^{-1})	Diffusivity Hayduk and Laudie method (m^2 s^{-1})	Diffusivity simple method (m^2 s^{-1})	% difference
Ethylene dichloride	99.0	1.04×10^{-9}	9.60×10^{-10}	7.9
Fenuron	164.2	6.80×10^{-10}	7.10×10^{-10}	-5.0
DNOC	198.1	7.00×10^{-10}	6.40×10^{-10}	9.3
Ethylchlorate	238.7	5.90×10^{-10}	5.70×10^{-10}	2.4
Bentazone	240.3	6.05×10^{-10}	5.70×10^{-10}	5.8
Formethanate hydrochlorid	222.3	5.60×10^{-10}	6.00×10^{-10}	-6.5
Desmedipham	300.3	5.00×10^{-10}	5.00×10^{-10}	-1.0
DDT	354.5	4.90×10^{-10}	4.50×10^{-10}	8.1
Dimethomorph	387.9	4.30×10^{-10}	4.30×10^{-10}	0.2
Lactofen	461.8	4.20×10^{-10}	3.90×10^{-10}	7.2
Deltamethrin	505.2	4.10×10^{-10}	3.70×10^{-10}	9.6

midt
regionmidtjylland

Appendix F

Concentration distribution (statistics)

The statistical processing of the data shows a positively skewed concentration distribution for both the full area (Figure F1), the peripheral area (Figure F2) and the infiltration area (Figure F3).
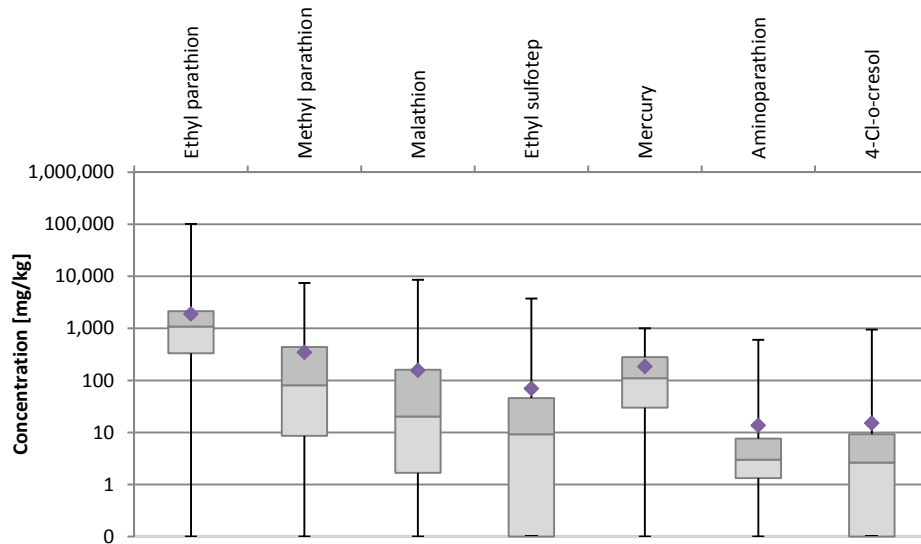

Figure F1. The average concentration (diamond) of seven focus compounds in the infiltration area shown on a logarithmic scale. Additionally, the box plot shows the median, the interquartile range (box) and the extremes (whiskers).

Figure F2. The average concentration (diamond) of seven focus compounds in the peripheral area shown on a logarithmic scale. Additionally, the box plot shows the median, the interquartile range (box) and the extremes (whiskers).

Figure F3. The average concentration (diamond) of seven focus compounds in the full area shown on a logarithmic scale. Additionally, the box plot shows the median, the interquartile range (box) and the extremes (whiskers).

Appendix G
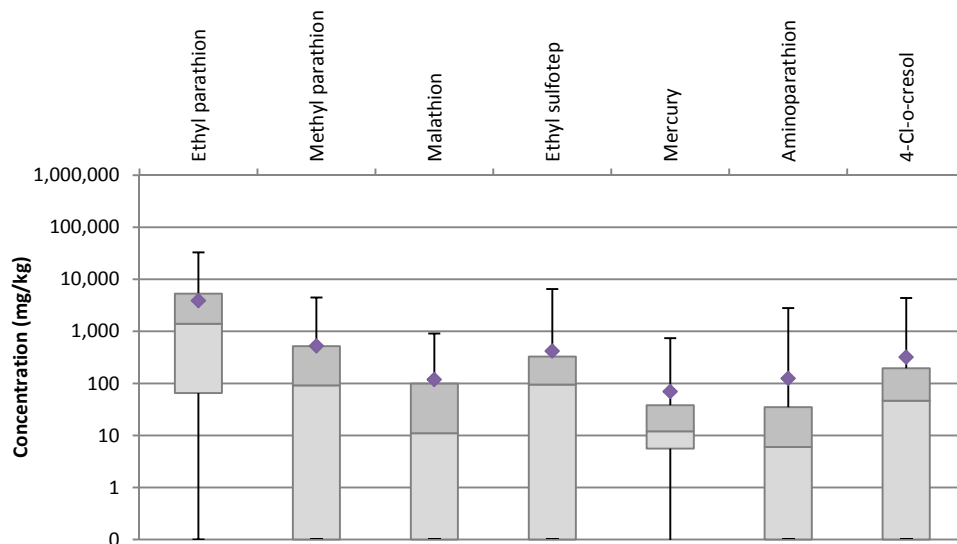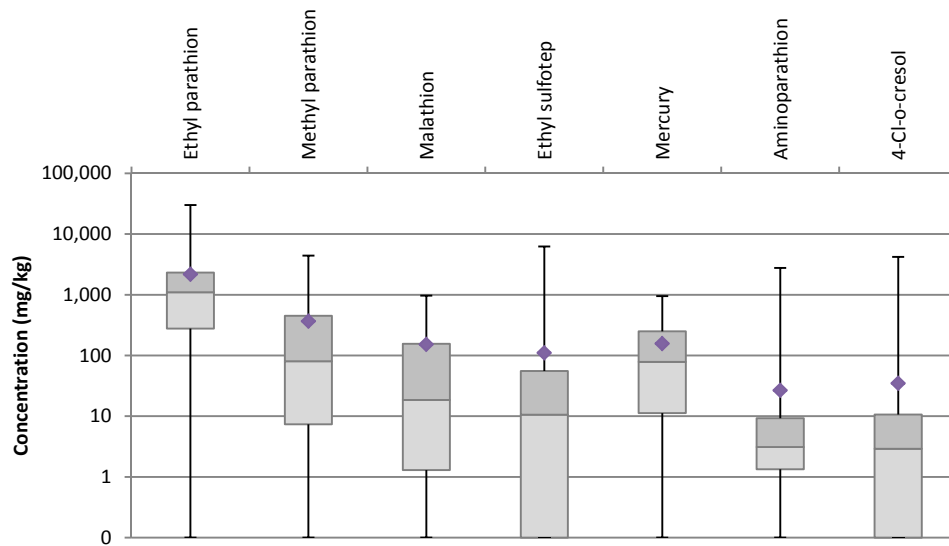
Note on the considerations in connection with the contaminant distribution, February 25th 2013 (in Danish)

Overvejelser i forbindelse med forureningsudbredelsen

I modelarbejdet for at fastlægge stopkriterier har vi besluttet at anvende Rambølls forureningsudbredelse som grundlag for vores model simuleringer. Vi mener ikke, at der er tid til at lave en yderligere forfining i lyset af den allerede forsinkede tidsplan. Samtidig mener vi, at Rambøls optegninger understøttes af de tidligere optegninger og supplerende beregninger af fri fase. Der er dog noget som tyder på, at det er en forholdsvis konservativ optegning af forureningsudbredelsen.

I forbindelse med disse betragtninger har vi lavet beregninger, som vi mener kunne være af interesse for regionen. Disse beregninger omfatter bl.a. vurdering af fri fase fra jordkoncentrationer og brug af disse overvejelser til en forfinet afgrænsning (Excel sheet og optegninger vedlagt som bilag).

### *Vurdering af fri fase ud fra jordkoncentrationer*

Udover masseberegning kan jordkoncentrationerne med fordel anvendes til at bestemme, hvorvidt der er indikation af DNAPL i de forskellige zoner. Forekomsten af DNAPL er et vigtigt input til en risikovurdering, især i et sceanrie hvor randzonen ikke oprenses.

Ved kendskab til en række egenskaber for stofferne og lokaliteten er dette en relativ simpel estimering at foretage. Baseret på opslagsværdier for parathion og værdier fra Høfde 44 er DNAPL mætningen for parathion (Raoults lov kan anvendes og estimering udvides til blandingen af alle fokusstofferne) estimeret for Rambølls samlede datasæt med de 9 zoner. Estimeringen kan forbedres ved indsamling af værdier for Høfde 42 (f.eks. f_{oc} til bedre estimering af K_d).

Værdierne viser, at nedsivningszonen er godt karakteriseret. Der er indikation på DNAPL i de fleste jordprøver, og at DNAPL mætningen er generelt højere end i de omgivende zoner.

For randzonen ses det også fint, at DNAPL indikation hovedsageligt findes i den nederst meter over det indskudte silt/lerlag.

For den ydre randzone er der generelt ikke fundet DNAPL indikation (hører LK 10a og V06 ikke til i andre zoner?) med undtagelsen er det sydvestlige hjørne (E+X7), der er udenfor spunsen (jf. fig. F1). Modelleringen vil kun inkludere forurening indenfor spunsen, da udbredelsen af forureningen udenfor spunsen er for uklar.
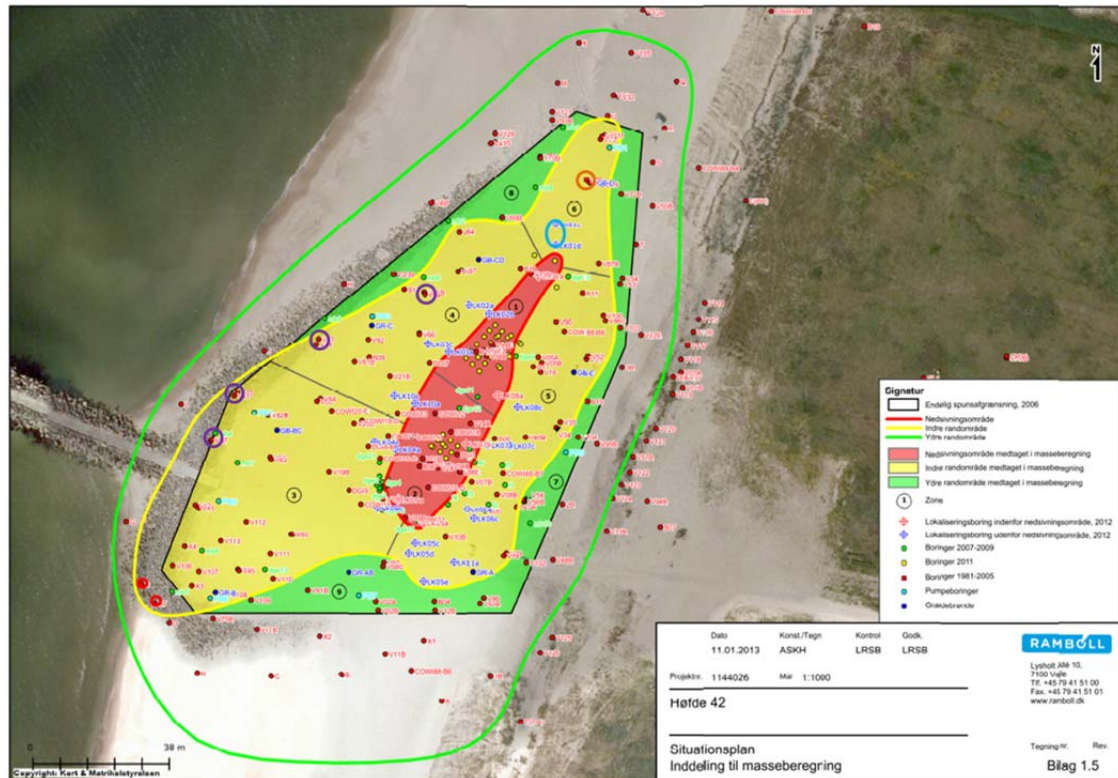
Figur F1: Oversigt over Rambølls afgrænsningszoner (1-9). Små røde cirkler angiver DNAPL indikation udenfor spunsen. Lilla cirker angiver boringer uden indikation på DNAPL (eller meget lav indikation) i zone 3-4 tæt på den ydre zonegrænse. Den lyseblå oval angiver boringer, hvor DNAPL indikation kun er fundet i omkring kote 0-1 m (slamlaget). Den brune cirkel angiver DNAPL indikation i en ukendt dybde.

Mulig indskrænkning af randzonen

Mens nedsivningszonen (zone 1-2) er godt afgrænset, da er afgrænsningen af randzonens (zone 3-6) udbredelse mere usikker. Usikkerheden ligger hovedsageligt i hvor langt ud mod havet zone 3/4 er udbredt, samt hvor langt mod nord zone 6 er udbredt (i denne forbindelse ville et kort udelukkende med de boringer, hvor der er medtaget data fra, være behjælpeligt).

For zone 3/4 er der flere af boringerne tæt på havet hvor der ingen (f.eks. V36, V40 og V76) eller meget lav (f.eks. V85) DNAPL indikation er (jf. fig. F1).

For zone 6 er der meget få data (4 boringer) med ret forskellige indikationer (DNAPL indikation kun i det øvre slam lag, i ukendt dybde, eller lidt i bunden af det øvre siltlag; jf. fig. F1).

Sammenholdes betragtningerne for zone 3, 4 og 6 med DNAPL observationer (Niras, 2005) og vandkoncentrationer (Niras, 2004), da synes der at være yderligere grundlag for at trække randzonen tilbage fra havet, samt evt. en anelse mod syd (zone 6 er dog stadig ikke særlig godt belyst). Dette kræver dog yderligere bearbejdning af data – og især for zone 6 kunne et bedre datagrundlag være ønskeligt.

Appendix H

Minimum dilution

The minimum dilution (0.05 quantile) represents a "worst-case" situation, where the (average) contaminant discharge from the upper secondary aquifer is diluted less than normal. The overall dilution (cf. Table H1) is approximately one order in magnitude less than the average situation.

Table H1. Minimum dilution (0.05 quantile) from transport from the source area to the North Sea and mixing within the North Sea along with the overall dilution for the different scenarios.

Dilution	Scenario B1	Scenario B2	Scenario C1	Scenario C2	Scenario D
Source to sea	4.8	4.4	3.1	9.3	3.0
Sea	2690	2150	772	2300	758
Overall	12900	9460	2390	21400	2270

Remediation stop criteria

The remediation stop criteria based on the minimum dilution (0.05 quantile) and the MAC-EQS for been calculated for the same scenarios as the average based stop criteria (cf. chapter 5).

Table H2. Remediation stop criteria for the full area (scenario D) are given for both the water phase (mg/L) and the total matrix (mg/kg). The total matrix stop criteria are also given at limited flow though the source area (scenario B2).

Compound	Water concentration	Total concentration	Total concentration (limited flow)
	(mg/L)	(mg/kg)	(mg/kg)
Ethyl parathion	0.07	0.49	2.0
Methyl parathion	0.07	0.06	0.24
Malathion	0.05	0.02	0.07
Ethyl sulfotep	0.05	0.47	2.0
Mercury (total species)	1.6	83	345
Aminoparathion	295	156	648
p-nitrophenol	91	21	88
EP2-acid	955	-	-
MP2-acid	659	-	-
4-chloro-*o*-cresol	14	9.9	41

The remediation stop criteria based on the minimum dilution (0.05 quantile) and the MAC-EQS are generally higher under the average condition (cf. Table 5.3). However, it is seen (Table H2) that the remediation stop criterion for methyl parathion is 2.6 times lower with 0.07 mg/L (0.06 mg/kg) compared to 0.18 mg/L (0.15 mg/kg). For 4-chloro-*o*-cresol the remediation stop criterion is 7.3 times lower with 14 mg/L (9.9 mg/kg) compared to 99 mg/L (72 mg/kg).

Table H3. Remediation stop criteria for the peripheral area (scenario C1) are given for both the water phase (mg/L) and the total matrix (mg/kg).

Compound	Water concentration (mg/L)	Total concentration (mg/kg)
Ethyl parathion	0.07	0.51
Methyl parathion	0.07	0.06
Malathion	0.05	0.02
Ethyl sulfotep	0.05	0.50
Mercury (total species)	1.7	87
Aminoparathion	311	164
p-nitrophenol	96	22
EP2-acid	1005	-
MP2-acid	694	-
4-chloro-*o*-cresol	14	10

The remediation stop criteria for the peripheral area (clean infiltration area) are logically still very similar to the full area remediation situation (Table H3).

Table H4. Remediation stop criteria for the infiltration area (scenario C2) are given for both the water phase (mg/L) and the total matrix (mg/kg).

Compound	Water concentration (mg/L)	Total concentration (mg/kg)
Ethyl parathion	0.64	4.6
Methyl parathion	0.64	0.54
Malathion	0.43	0.16
Ethyl sulfotep	0.43	4.4
Mercury (total species)	15	782
Aminoparathion	2785	1467
p-nitrophenol	857	198
EP2-acid	8998	-

MP2-acid	6213	-
4-chloro-*o*-cresol	129	93

The remediation stop criteria based on the minimum dilution (0.05 quantile) and the MAC-EQS are generally higher under the average condition (cf. Table 5.5). However, it is seen (Table H4) that the remediation stop criterion for methyl parathion only 0.64 mg/L (0.54 mg/kg) compared to 1.7 mg/L (1.4 mg/kg). For 4-chloro-*o*-cresol the remediation stop criterion is 129 mg/L (93 mg/kg) compared to 937 mg/L (679 mg/kg).

Comparison between modelled and measured concentrations in the North Sea

The agreements between the modelled and the measured concentrations in the North Sea are similar when median concentrations (Table H5) are used instead of average concentrations.

Table H5. Modelled and measured contaminant median concentrations (µg/L) in the North Sea before remediation based on the scenario specific dilution. The discrepancy between the modelled and measured concentrations in the North Sea before remediation (2004-2005) is given in percentages. **Bold values** indicate values within the same order of magnitude.

Compound	Full area (scenario D)			Infiltration area (scenario C2)		
	Modelled	Measured	Discrepancy	Modelled	Measured	Discrepancy
	(µg/L)	(µg/L)	(%)	(µg/L)	(µg/L)	(%)
Ethyl parathion	0.55[*]	0.006	9120	**0.06**[*]	**0.006**	**878**
Methyl parathion[1]	1.4	0.02	6220	**0.15**	**0.02**	**569**
Malathion	0.73	<0.005	>14600	0.08	<0.005	>1600
Ethyl sulfotep	**0.01**	**0.01**	**48**	**0.001**	**0.01**	**-86**
Mercury	0.02	0.002	1360	**0.003**	**0.002**	**117**
Aminoparathion	0.09	0.97	-91	0.009	0.97	-99
4-Cl-*o*-cresol[1]	**0.06**	**0.14**	**-57**	0.006	0.14	-96

[1]The values are based on the solubility of the compounds, since the average soil concentrations indicate DNAPL and direct conversion would result in concentrations above the solubility.

Observation based dilution and remediation stop criteria indications

The observed average and minimum dilution based on the observed North Sea concentrations in 2004/2005 before the sheet piling and the current average source concentrations are given in Table H6. Remediation stop criteria and needed removal

efficiencies are also given under the assumption that the average current source concentrations and the observed North Sea concentrations in 2004-2005 are representative for the overall situation.

Table H6. Average and minimum dilution based in observed North Sea concentrations (2004/5) and the current source concentrations. The corresponding remediation stop criteria (mg/L) are given under the assumption that the numbers are representative for the overall situation at the site. The corresponding needed removal efficiency is also given.

Compound	Average dilution	Minimum dilution	Remediation stop criteria (mg/L)	Removal efficiency (%)
Ethyl parathion	579000	57900	0.17	99.9
Methyl parathion	655000	120000	3.6	98.6
Malathion	20000000	6660000	20	95.2
Ethyl sulfotep	103000	22100	0.02	99.8
Mercury (total species)	581000	396000	23	0
Aminoparathion	3950	524	4.0	92.2
p-nitrophenol	-	-	-	-
EP2-acid	-	-	-	-
MP2-acid	-	-	-	-
4-chloro-*o*-cresol	44400	9270	56	0