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NorthPestClean

Kontraktbilag 2: Technical specifications

November 2010

Projekt nr.: Life09/ENV/DK368

NorthPestClean
Pesticide Remediation

Life

Table of contents

0 Introduction

0.1 Objectives of the NorthPestClean project

NorthPestClean is a Danish environmental project funded in part by the European Commission under the LIFE+ programme. Two of the primary objectives of the NorthPestClean project are:

1. To demonstrate in large-scale pilot experiments the efficiency of a novel remediation method based on *in situ* alkaline hydrolysis to decontaminate pesticide contaminated soil and groundwater.

2. To demonstrate the effect and usability of different “enhancement” technologies in side-by-side pilot experiments.

The large-scale pilot experiments mentioned in the first objective refer to use of a series of test cells and test pipes soon to be under construction at the Groyne 42 site. The experiments are to be conducted over a period of approximately three years. In the long-term, the experiments should provide a basis for determining the technical, environmental and economic effect of a full-scale remediation based on enhanced alkaline hydrolysis.

0.2 Site background

The site called “Groyne 42” in Denmark is an old pesticide dumpsite, heavily contaminated with 200-300 tons of chemicals, mainly the organophosphorous insecticide parathion.

The deposition period was from 1953 – 1962 where chemical waste was deposited between two sand dunes close to the North Sea. The chemical waste was dumped at the site mainly by the agrochemical company Cheminova situated nearby, but some deposition was also made by the state.

In 1971 and in 1981, the site was exposed by erosion and partial remediation was carried out. In 1971 after a storm had exposed the site, 1250 m^3 contaminated sand was removed, and the rest of the site was covered by an asphalt cap. In 1981, another storm damaged the asphalt cap. At that time, 1200 tons of chemicals situated above groundwater level were removed. The remaining of the contamination at the dumpsite was now located under the groundwater level. It was covered with sand, and it was at the time concluded that the remaining contamination no longer posed a problem.

In 2000, it was discovered, however, that a heavy odour came from the site. New investigations with drillings and chemical analysis of soil and groundwater samples showed that the dumpsite still posed a threat to the environment and that 200-300 tons of pesticides and other chemicals remained in the soil and groundwater, below the groundwater table.

A detailed investigation to identify the exact location of the contamination in the saturated zone and the amount of contaminants remaining was completed in 2005. Following several years of characterization, it was decided that the site should be enclosed as a temporary measure. An area of approximately 20,000 m^2 is enclosed by 14 meter deep steel sheet piling, which is keyed in to a clay layer. The entire area is capped with a plastic membrane, which is covered with about 60 cm sand and sparsely planted with sage. The purpose of the enclosure was to prevent further leaching of toxins to the seawater.

The lithology is composed of medium/fine-grained sand underlain by a silt layer with a thickness of approximately ½ meter. The silt layer is located at a depth of 8-10 meters below surface and has an uneven surface. Under the silt layer, layers of fine sand, silt and clay are found with lower conductivity at greater depths.

More than 100 contaminants have been found at the site, with parathion found in greatest amounts (estimated mass is 170 tons) /2/. The greatest risk to the North Sea is assumed to be due to parathion, methyl parathion, ethyl sulfotep, malathion, mercury, EP1 and EP2-acid. Residual Dense NonAqueous Phase Liquid (DNAPL) is widespread in hotspots, but very little is found as a mobile separate phase. The highest concentrations are found immediately above and in the silt layer. In some areas, the contamination has penetrated the silt layer. The groundwater is strongly reduced in hot spot areas resulting in the production of methane and hydrogen sulphide. The groundwater is brackish. Although the salt content in the groundwater at the site is not well mapped, this factor is important for determining the extent of density flow. More information about the site can be found in /1/ and /3/.

0.3 Principle of *in situ* alkaline hydrolysis

The site is heavily contaminated with the highly toxic organophosphorous insecticides parathion, methyl parathion and similar compounds. These compounds have low water solubility and absorbs strongly to the soil. Increasing pH in the subsurface to about pH 12, by infiltration of diluted caustic soda, induces alkaline hydrolysis of the organophosphorous compounds (Figure 1). The major hydrolysis products *p*-nitrophenol (PNP) and O,O-dimethyl-thiophosphoric acid (MP2-acid) or O,O-diethyl-thiophosphoric acid (EP2-acid) have relatively low toxicity, are water soluble and can be removed from the subsurface by pump-and-treat.

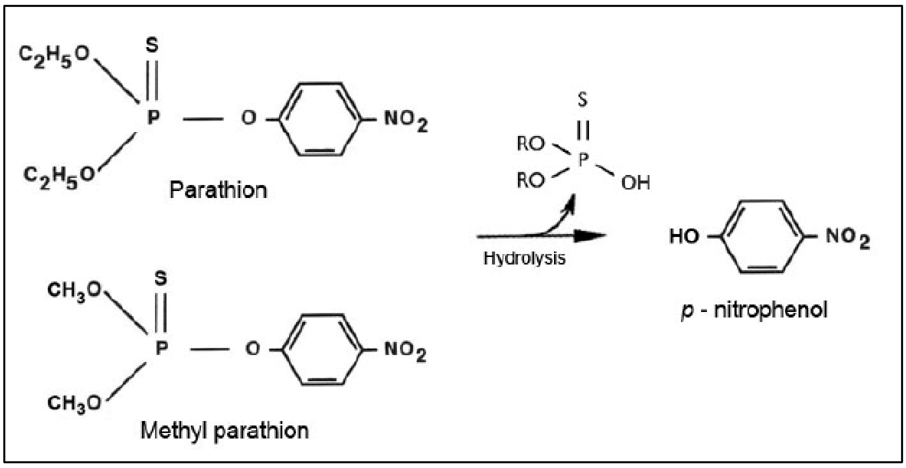

Figure 1. Chemical reaction showing the principle of the alkaline hydrolysis of organophosphorous pesticides.

0.4 Previous feasibility studies

A number of laboratory hydrolysis experiments were carried out in 2006 and again in 2008. The main goals of these experiments were to demonstrate the treatability of parathion-contaminated sediment samples from the site with caustic soda, to determine which pH value is necessary in order to reach an acceptable rate of hydrolysis, to quantify the natural buffer capacity of the sediments (how much caustic soda must be added to raise the pH to an adequate level), to identify significant geochemical changes from the high pH, etc.

Results clearly showed that hydrolysis of parathion with caustic soda does take place in-situ. A pH of 12 was shown to be adequate. Since caustic soda is often sold at 27%, a 1:20 dilution is adequate and economically acceptable for the full-scale project. Results also showed that pH values above 13 should be avoided, since large amounts of silica dissolve. Field testing in 2008 showed that caustic soda can be gravity infiltrated at the site with no problem and that high pH values can be maintained without further caustic soda additions for over a year.

Additional information about these experiments is found in /1/ and /3/.

0.5 Current work at the site

Construction of a test area including test cells, test pipes, fencing, a container etc to be used in this project is currently underway under separate auspices and is not part of this tender.

It is the intention to construct three test cells (approx. 10 x 10 m) in one of the most contaminated areas within the sheet-piled boundaries of the Groyne 42 site. The cells will be enclosed with steel sheet piling to a depth of 14 meters. The top of the test cells will be covered by a waterproof sealing (probably a bentonite mat). The idea is to create watertight test cells that allow full hydraulic control during the demonstration experiments. In addition, three steel casing pipes (approximately two meters in diameter, and 14 meters in length) will be vibrated into an adjoining area.

The test area will be constructed in April-May 2011.

A 20-foot container will be placed immediately next to the test site. The container will be maintained frost free and will include an emergency shower, a table for working with soil samples, shelves, point suction etc.

“Kulhuset” is a building, several hundred meters from the site, containing carbon filters, etc. Storage space, a toilet and bathing facilities are available in the building.

The entire test area including the test cells and the container will be fenced in, including space large enough for a drill rig to manoeuvre.

A dry well “teknikbrønden” within the fenced area has electricity and water:

- Electricity (32 Amp. CEE-plug, 16 Amp. CEE-plug, 380 V)

- Water: The pipeline from "kulhuset" to the dry well is 40 or 50 mm in diameter. The maximum flow from the water connection in the dry well is approximately 50 liters/min.

Eight wells named "grædebrønde" also have electricity; CEE-plug, 220 V. These wells are located in the vicinity of the test area.
A gravel road passes within a few meters of the gate to the fenced area.

A schematic overview of the site as it may look when established is given in Figure 2.

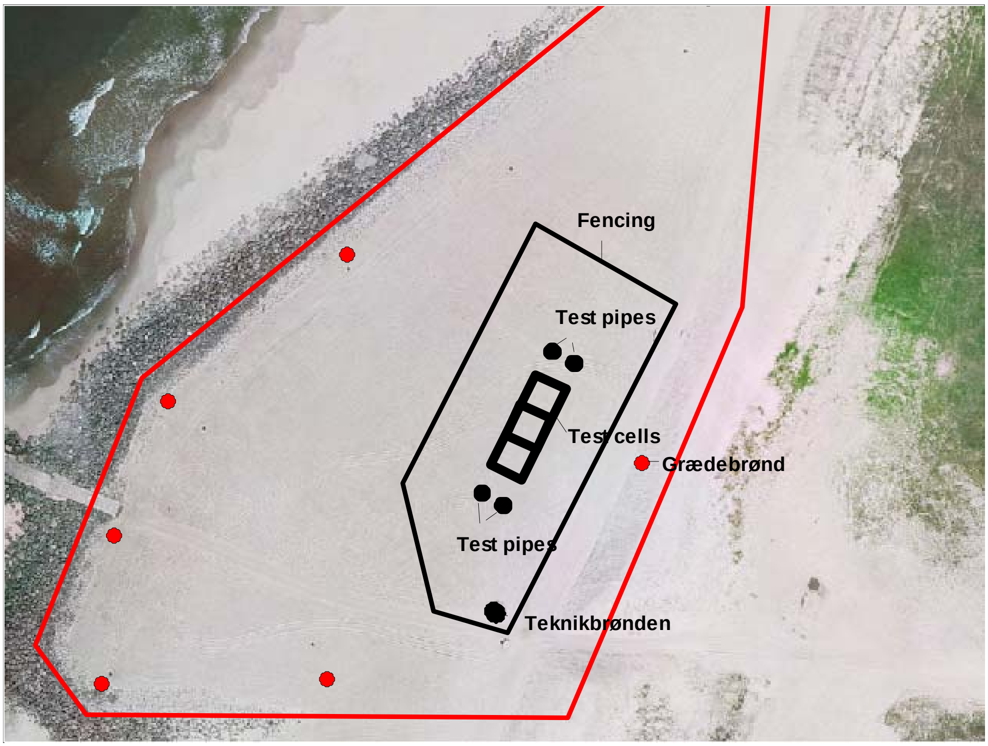

Figure 2: Location of teknikbrønden, grædebrønde (red dots) and a proposed location of test cells, test pipes and fence. The exact location of the test area may be subject to change.

0.6 Project idea

The aim of the project is to document the efficiency of *in situ* alkaline hydrolysis through a series of hydrolysis cycles in the test cells. Three hydrolysis cycles are to be carried out in the test cells and test pipes and at the same time, different contact enhancement technologies will be implemented side-by-side in the test cells.

A prerequisite for the implementation of the experiments are the full hydraulic control with in the test cells. The hydraulic control enables us to monitor the hydrolysis progress and to quantify the extent of the alkaline hydrolysis by analysing the hydrolysis products.

The test cells and test pipes will have the following functions in the demonstration project:

Test area	Function in the demonstration project
Test pipe 1:	Blank 1. This test pipe is left undisturbed during the experiments.
Test pipe 2:	Blank 2. In all three cycles, this test pipe is to be filled with water similar to that used for the dilution of the caustic soda in the test cells. No enhancements are to be used in test pipe 2.
Test pipe 3:	Control. This test pipe is to be used as a control with caustic soda treatment only. The test pipe is refilled with caustic soda during the three cycles, but no contact enhancements are implemented.
Test cell 1:	Treated with caustic soda in three cycles + enhancement no. 1
Test cell 2:	Treated with caustic soda in three cycles + enhancement no. 2
Test cell 3:	Treated with caustic soda in three cycles + enhancement no. 3

Initially, the three test cells and test pipe 2 and 3 will be drained.
Subsequently, each hydrolysis cycle will include 4 steps:

1) Filling the test cells/test pipes with diluted caustic soda, raising the pH in the groundwater to 12 (test pipe 2 is filled with water).

2) A 6-12 months period in which parathion and other organophosphorous pesticides are hydrolysed *in situ* while various contact enhancements technologies are tested. During this period groundwater is sampled in several rounds in order to monitor the hydrolysis progress.

3) Draining the caustic soda and the newly-formed hydrolysis products out of each test cell/test pipe.

4) Sediment sample control.

In the first cycle, caustic soda will be infiltrated by gravity in all test cells and test pipe 3. Gravitation is probably the simplest and least efficient method of delivery. No contact enhancements technologies are tested in the first cycle. Other methods of delivery will be used for cycle 2 and 3. This should allow the comparison of the effect of the delivery method.

After refilling the test cells with caustic soda in the 2nd and 3rd cycle, alkaline hydrolysis in each cell will be enhanced through different methods:

1) Test cell 1: the effect of recirculation of groundwater/diluted caustic soda will be tested.

2) Test cell 2: the effect of the addition of a surfactant/co-solvent will be tested.

3) Test cell 3: the effect of acoustic/vibration remediation will be tested.

1 Management

1.1 Staffing

The following staffing **must** be appointed (by name) in the bidder's proposal:

- Project manager (only one person can be appointed)
- Substitute for the project manager (only one person can be appointed)
- Quality assurance manager (only one person can be appointed)
- Personnel involved in supervision of drilling (several persons can be appointed)
- Personnel involved in collecting soil sampling (several persons can be appointed)
- Personnel involved in sampling groundwater (several persons can be appointed)

CV's for all staff members **must** be submitted (max. 15 CVs in total). Each CV **must** not exceed 3 pages.

It **must** be verified that the staff possess the required experience, scientific, technical and practical skills in order to ensure successful implementation of the demonstration experiments.

1.2 Project organisation

A detailed description of the bidder's project organisation defining roles and responsibilities **must** be given in the proposal.

This involves - but is not limited to - defining:

- The bidder's internal project organisation
- The organisation of subcontractors involved in the project

1.3 Project management

Communication: The bidder **must** provide a description of how internal communication and communication with contractors or external partners will be carried out. The project manager should be the primary contact person for all communication between the bidder and Region Midtjylland.

Client contact: The bidder should provide a description of how the bidder will maintain close contact to the client. This contact **must** include brief monthly status reports regarding progress and economic status of the project.

Quality assurance: The bidder **must** provide a description of how the quality of the specific project can be assured and documented in accordance to the requirements of the project. The most important specific project risks should be identified.

The pricing **must** include internal organisation, communication and quality assurance and all other costs involved in project management, not covered in section 2-8.

1.4 Data management

Database setup: A GeoGis database has been set up by Region Midtjylland to store the results from the project. The database will be maintained by Region Midtjylland on the internet to make the results available to all in the project group.

A geological model for the test site has been established by Region Midtjylland in the software GeoScene3D. If required, the winning bidder will be granted access to the GeoScene3D project for the test site.

The bidder **must** be responsible for entering the following data into the GeoGis database:

- well lithology
- well construction
- analytical results of sediment samples
- analytical results of groundwater samples
- water level measurements

Data **must** be entered within two weeks after it has been produced.

The pricing **must** include entering of the above mentioned data into Region Midtjyllands GeoGis database and the associated quality assurance involved.

2 Meetings

2.1 Technical meetings

It is envisioned that there will be a need for approximately 12 technical meetings. The location for the technical meetings is Regionshuset, Skottenborg 26, 8800 Viborg.

The price pr. meeting to be given in the tender list **must** be based on two participants for a length of approximately five meeting hours including time and expense for travel, meeting preparation and completion of minutes following the meeting.

2.2 Status meetings with the steering committee

It is envisioned that there will be a need for approximately 6 status meetings with the NorthPestClean steering committee. The Steering Committee consists of members from Region Midtjylland and The Danish Environmental Protection Agency. The location for the status meetings is Regionshuset, Skottenborg 26, 8800 Viborg.

The price pr. meeting to be given in the tender list **must** be based on two participants for a length of approximately five meeting hours including time and expense for travel and meeting preparation. The minutes from these meeting will be completed by Region Midtjylland.

2.3 Web meetings

It is envisioned that there will be a need for approximately 12 web meetings or telephone conferences. The price pr. meeting to be given in the tender list **must** be based on two participants for a length of approximately one hour and meeting preparation and completion of minutes following the meeting.

3 Preliminary tasks

3.1 Surfactant/co-solvent experiments

In test cell 2 enhancement by addition of a surfactant/co-solvent mixture **must** be tested. Short-term laboratory tests should be carried out to identify the most suitable surfactant mixture and the correct concentration for field testing in a test cell. A surfactant mixture is considered any surfactant or mixture of surfactants and co-solvents. The tests should compare a minimum of three different surfactant mixtures. One of the surfactant mixtures included in the testing **must** be a reference mixture provided by Region Midtjylland, who has requested Surbec Environmental, Norman, Oklahoma to formulate a site-specific mixture. The final two surfactant mixtures **must** be selected by the bidder.

Criteria for selection of the most suitable surfactant mixture for field testing include effect, price (while taking the required concentration into consideration) and ease of handling (including toxicity).

The proposal **must** include a description of the laboratory tests.

3.2 Initial characterisation of test areas

Each pilot test cell and each test pipe **must** be characterised in detail regarding geology and contamination distribution before the demonstration experiments are initiated. The following activities are included.

3.2.1 Characterisation wells

The purpose of the characterisation wells is:

1) The collection of discrete depth soil samples.

2) Establishment of permanent screens for repeated collection of groundwater samples and measurement of water levels. Screens should be established so it is possible to collect water samples from three discrete depths in <u>each</u> characterisation well.

3) Some wells may have an additional use in the circulation of groundwater or in other enhancements.

Characterisation wells should be constructed in each test cell and test pipe using direct push (Sonic or Geoprobe), bucket/hollow stem auger or other appropriate method as long as the purpose of the wells are met.

In each test cell and test pipe, the number of characterization wells **must** be a minimum of ten and two, respectively, for a total of 36 wells. The wells should be sunk to the top of the silt layer, and are therefore not expected to be deeper than 10 meters. The grain size of the sand is quite fine. Therefore, screen slots larger than 0.3 mm should not be used. HDPE is an acceptable material.

When installing screens at three different depths, well clusters may be used to avoid risk of short circuiting between multiple screens in the same borehole. In that case ten and two well clusters are needed for each test cell and test pipe, respectively. The total number of screens is 36x3=108.

In the proposal, the bidder **must** describe details including drilling method, well diameter, screen length, screen diameter, screen depth, slot size, grain size of filter pack, etc. and state the reasons for the choices where relevant.

Beware that the construction of the wells should not compromise the function of the test cell covering (i.e. the bentonite mat) by allowing rainwater to infiltrate.

All wells **must** be marked with a unique DGU number and completed with locked plastic well coverings similar to existing wells at the site. Excess contaminated sediments **must** be removed from the site and disposed of properly at the bidder's expense.

Due to the iterative nature of pilot scale work, changes in the number of wells and details of construction may alter during the project.

The bidder **must** be responsible for siting the individual wells, full-time supervision of the drilling and well-construction process, preparing lithologic and well-construction logs and entering this information into the project's GeoGis database. Health and safety requirements are found in section 7.2.

3.2.2 Sediment sampling

Sediment samples **must** be collected every ½ meter between elevation 0.0 and the silt layer from each characterisation well. For the purpose of calculating costs, seven samples per well **must** be assumed. For the initial characterisation this makes a total of 70 samples per test cell and 14 samples per test pipe. In total 252 soil samples.

Collection and preservation of sediment samples **must** follow a method involving composite sampling, neutralisation and extraction as described in the field instructions found in appendix 15 in /3/ or a similar method. This sampling method improves reproducibility, reduces risk for laboratory personnel contact with the contamination in the laboratory, and prevents further hydrolysis from occurring in the interval between sample collection and sample analysis.

The bidder **must** consider these requirements when pricing this activity as they are somewhat more involved than typical sampling. Previous experience has shown that two full-time field persons are needed to carry out supervision and sediment sampling activities.

The minimum number of samples, the parameters to be analyzed and the methods of chemical analyses are summarised in section 7.

All analysis of soil samples (except for mercury) are performed free of charge by Cheminova. Analysis for mercury in soil samples should be done by a commercial laboratory.

3.2.3 Groundwater sampling

In the initial characterisation of the test cells and test pipes groundwater samples **must** be collected from three depths from each of the 36 characterisation wells. This makes at total of 108 samples.

Collection of groundwater samples may be carried out using 12V submersible pumps or other methods. Preservation of the samples **must** follow a method involving neutralisation as described in the field instructions found in appendix 15 in /3/ or a similar method. The bidder **must** consider these requirements when pricing this activity as they are somewhat more involved than typical sampling. This treatment prevents further hydrolysis from occurring in the interval between sample collection and sample analysis. This method is not required for the initial characterisation samples, but only for water samples, with elevated pH-values due to presence of caustic soda, collected at later phases of the work.

In earlier studies, some groundwater samples showed a concentration of parathion greatly exceeding its water solubility. This was likely caused by release of DNAPL droplets during the sampling process and is not representative of groundwater concentrations. Documented methods for avoiding this problem are welcome to be used.

All analysis of groundwater samples (except for mercury) are performed free of charge by Cheminova. Analysis for mercury in groundwater samples should be done by a commercial laboratory.

The minimum number of samples, the parameters to be analyzed and the methods of chemical analyses are summarised in section 7.

In the pricing the bidder **must** take into account a meeting with the staff at Cheminovas analytical laboratory prior to the initiation of the groundwater and soil sampling. The meeting **must** be based on two participants from the bidder for a length of approximately three meeting hours. The location for the meeting will be at Cheminova A/S, Thyborønvej 76-78, Harboøre.

3.3 Revision of detailed experimental design

A preliminary design of the pilot scale experiments including the enhancement technologies **must** be included in the proposal. Region Midtjylland will comment and discuss the preliminary design with the winning bidder at the start of the contract period. The bidder **must** then prepare a detailed pilot scale design, taking these discussions and comments into consideration.

3.4 Initial draining and re-infiltration

As much of the groundwater as possible should be drained from each test cell and test pipe 2 and 3 down to the silt layer and re-infiltrated just outside the test area. Test pipe 1 (blank 1) is not to be drained.

3.4.1 Draining

Draining may be carried out by any method deemed appropriate. The bidder **must** provide a description of the planned draining method.

It is important that the water table is lowered as close as possible to the top of the silt layer. This will ensure a better contact between the caustic soda (which will be added in a subsequent step) and the highly contaminated sand just above the silt layer. Please note that the elevation of the top of the silt layer varies within short distances.

Water samples **must** be collected and analyzed during the draining and re-infiltration process. These samples may be collected as discrete samples or as flow-proportional samples. No matter what collection method is used, a minimum of 10 samples **must** be collected at equal volume intervals, during draining of each test cell and test pipe.

The number of samples, the parameters to be analyzed and the methods of chemical analyses are summarised in section 7.

The draining process presents several challenges in regard to equipment. Firstly, the groundwater quality is challenging. It contains organic solvents, a wide range of pH-values, particulates and has the potential for bacteria growth and precipitation of iron (and silicic acid during later draining steps after caustic soda has been added). Corrosion and clogging may therefore present problems. Secondly, the possible flow of groundwater from a test cell will have an extreme range from “ordinary” the first days and to extremely slow as the water table approaches the silt layer. The draining method selected should be able to accommodate this large variation. Empirical and modelling studies of water retention during draining have previously been carried out /3/. Thirdly, the groundwater must be lifted to a height that slightly exceeds the capacity of suction pumps.

The success of the draining process **must** be documented. The drained water volume **must** be measured for each test cell/test pipe separately. In addition, the water level in each test cell and test pipe **must** be measured as a function of time during the draining period.

3.4.2 Re-infiltration

The drained, contaminated groundwater should be re-infiltrated outside the test area but within the 20,000 m^2 area which is enclosed by sheet piling. Re-infiltration should take place at a depth below the top membrane and above the silt layer. The selection of location for re-infiltration **must** be made in dialogue with Region Midtjylland.

Re-infiltration may be carried out by any method deemed appropriate by the bidder. The method of re-infiltration **must** be described in the proposal. During re-infiltration, well screens may become clogged. It is the responsibility of the bidder to overcome this potential problem through extra infiltration well capacity, water treatment or other methods.

The groundwater from the initial draining is expected to have approximately the same level of contamination as the groundwater in the re-infiltration area. In subsequent re-infiltrations (after the 1st, 2nd and 3rd hydrolysis cycle), however, the groundwater will have a higher pH-value and greater amounts of hydrolysis products and possibly mercury. Infiltration of contaminated water into the subsurface requires a permit under the Danish Environmental Law (§ 19) from the local municipality (Lemvig Municipality). Application for the infiltration permit is the responsibility of Region Midtjylland.

4 Cycle 1

The purpose of cycle 1 is to determine the rate of hydrolysis in the various test cells and test pipes using no methods for enhancing contact between contamination and caustic soda and using only a simple method for adding caustic soda.

This will 1) allow comparison of variations in levels of contamination between test cells and test pipes, 2) provide a basis for the determination of the effect of improved delivery methods for caustic soda to be used in later cycles and 3) enable us to determine the effect of various enhancements.

4.1 Gravity infiltration of caustic soda / water

Following the initial draining, diluted caustic soda **must** be added by gravitation in a single well in each test cell and test pipe 3. Test pipe 2 **must** be infiltrated with water only.

Caustic soda may be purchased in the dissolved form of a 27 % solution. In connection with infiltration, the 27 % caustic soda solution should be diluted approximately 1:20. The resulting solution should therefore have a concentration of about 0.44 M.

$$\frac{27gNaOH}{100g\_conc.solution} \cdot \frac{1300g\_conc.solution}{l\_conc.solution} \cdot \frac{molNaOH}{40gNaOH} \cdot \frac{1l\_conc.solution}{20l\_dil.solution} \cdot = \frac{0.44mol}{l\_dil.solution}$$

The precise dilution **must** be discussed with Region Midtjylland prior to the start of cycle 1.

The expected pH-value for this dilution is between 13 and 14 when calculated with activities instead of concentrations. This value is so high that correct measurements with the use of normal pH-electrodes is difficult, due to the so-called alkaline error. To minimize this problem, it is required that pH-measurements be carried out using a special H-glass electrode. More information about pH measurements and calculations is found in appendix 4 of /3/.

During the infiltration period, the volume of caustic soda and the water level in the test cell/test pipe **must** be monitored continuously. In addition the actual dilution factor **must** be documented.

4.2 Alkaline hydrolysis (groundwater monitoring)

After infiltration, the caustic soda should be left undisturbed in the test cells and test pipes for a period of 6-12 months. The exact period depends on the hydrolysis progress.

To follow the hydrolysis progress during this period, groundwater samples will be collected and analyzed. The parameters to be analyzed and the methods of chemical analyses are summarised in section 7.

Samples **must** be collected for a minimum of four sampling rounds during the hydrolysis period. In each sampling round groundwater is sampled at three depths in each of the 10 characterisation wells per test cell and the two characterisation wells per test pipe. A total of 432 groundwater samples **must** therefore be collected and analysed in the alkaline hydrolysis step of cycle 1.

The progress of the alkaline hydrolysis **must** be calculated after each sampling round based on the analytical results.

4.3 Draining and re-infiltration

Following the hydrolysis period, the groundwater in each test cell and test pipe 2 and 3 **must** be drained. As with the initial draining, this groundwater should be re-infiltrated in an area adjacent to the test area. Monitoring **must** include the same parameters as the initial draining. It should be noted that draining at the conclusion of the 1st (and 2nd and 3rd) cycle involves water with a much higher content of the hydrolysis products and a higher pH than the initial draining.

During draining, water samples **must** be collected for analysis, with the aim of calculating the clean-up effect (mass removal) of the 1st completed cycle. The water samples may be collected as discrete samples or as flow-proportional samples. A minimum of 10 samples **must** be collected at equal volume intervals during the draining of each test cell and test pipe 2 and 3.

The parameters to be analyzed and the methods of chemical analyses are summarised in section 7.

The determination of mass removal will be based on mathematical calculations on the basis of flow, time and the concentration of hydrolysis products in the water that is drained from the cell.

During sampling of groundwater drained from the test cells/test pipes, one should be aware of the possible inclusion of DNAPL droplets caused by the pumping process. Since the pH in the groundwater is very high, continued hydrolysis during sample storage and prior to analysis may occur. Therefore, procedures described earlier to neutralize the samples in the field **must** be used, refer to section 3.2.3 and appendix 15 in /3/

4.4 Sediment sample control

To document the effect of the hydrolysis period on the concentration of parathion and other organophosphorous pesticides in the sediment, control boreholes **must** be carried out with the purpose of collecting soil samples. A total of four boreholes in each of the three test cells and two boreholes in each of three test pipes **must** be sampled at minimum of seven depths. Sediment sample neutralization and preservation **must** be carried out as described earlier in section 3.2.2. In total, 18 boreholes **must** be established and 126 soil samples **must** be collected during this step of cycle 1.

5 Cycle 2

Cycle 2 activities include delivery of caustic soda, alkaline hydrolysis with enhancements, draining and re-infiltration as well as sediment sample control. Several of these activities are identical or nearly identical to activities in cycle 1. In the following sections, activities which are different in cycle 2 are described.

5.1 Delivery of caustic soda / water

In this activity, the test cells and test pipe 3 **must** be filled with caustic soda for the second time and test pipe 2 **must** be filled with water only.

For cycle 2, there should be focus on the delivery form. As opposed to cycle 1 in which gravitation in a single well was used, delivery in cycle 2 may include multiple injection points, use of pressure, use of pressure pulsations, or another method. The bidder **must** describe the recommended method for delivery (pressure, flow, injection points, etc.) and explain why the method is expected to improve contact between caustic soda and the contamination.

5.2 Alkaline hydrolysis (groundwater monitoring)

Initial period:

An initial period of one month will be used to monitor whether the improved delivery increases the rate of hydrolysis. The period **must** include two rounds of groundwater sampling to determine the effect of improved delivery.

The parameters to be analyzed and the methods of chemical analyses are summarised in section 7.

In both sampling rounds, groundwater is to be sampled at three depths in each of the 10 characterisation wells per test cell and the two characterisation wells per test pipe. A total of 216 groundwater samples **must** be collected and analysed within the initial 1 month monitoring period.

After the initial period:
After the initial 1 month monitoring period, different enhancement technologies **must** be tested in each test cell for the remaining 5-11 months of the hydrolysis period. The exact period depends on the hydrolysis progress.

To follow the hydrolysis progress during the period where the enhancement methods are implemented, groundwater samples **must** be collected and analyzed.

Samples **must** be collected for a minimum of four sampling rounds. In each sampling round, groundwater **must** be sampled at three depths in each of the 10 characterisation wells per test cell and the two characterisation wells per test pipe during the hydrolysis period. A total of 432 groundwater samples **must** be collected and analysed during this step of cycle 2.

Below, the various enhancements are described:

5.3 Test cell 1: Implementation of enhancement no. 1, "Recirculation"

Recirculation of groundwater was previously identified as a potential method for enhancing *in situ* alkaline hydrolysis /3/. Modelled results of the spread of caustic soda during simple recirculation can be found in /4/. In this reference, the software package FEFLOW was used to describe the flow of groundwater under the influence of density flow in a 10 x 10 m test cell with one pumping well and one injection well.

The method or methods of recirculation selected by the bidder **must** be described in the bidder's proposal. In addition, details regarding the flow, the number of withdrawal and injection points, possible use of alternating recirculation, and other information **must** be described by the bidder. Finally, the bidder **must** describe any methods planned to document the resulting recirculation. These documentation methods may include - but are not limited to - any of the following: heat pulse groundwater flow measurement, empirical tracer studies or mathematical modelling.

During recirculation, a "recirculation log" **must** be maintained to document the process.

5.4 Test cell 2: Implementation of enhancement no. 2, "Surfactant/co-solvent"

The use of surfactants, co-solvents or mixtures was previously identified as a potential method for enhancing *in situ* alkaline hydrolysis /3/. Surfactant type(s) and concentration determined in the preliminary work (see section 3.1) should be used. The surfactant may be used in combination with recirculation if this is deemed suitable.

The method for using surfactants **must** be described by the bidder. Finally, the bidder **must** describe any methods planned to document the effect of using surfactants.

5.5 Test cell 3: Implementation of enhancement no. 3, "Vibration"

Use of vibration (acoustic) technologies was previously identified as a potential method for enhancing *in situ* alkaline hydrolysis /3/. Vibration may be used in combination with recirculation or other enhancements if this is deemed suitable.

The method of vibration selected by the bidder **must** be described in the bidder's proposal. In addition, details regarding the frequency, equipment, number of treatments and other information should be described by the bidder. Finally, the bidder **must** describe any methods planned to document the resulting vibrations. These methods may include - but are not limited to - use of geophones.

5.6 Draining and re-infiltration

See section 4.3.

5.7 Sediment sample control

See section 4.4.

6 Cycle 3

6.1 Delivery of caustic soda/water

See section 5.1.

6.2 Alkaline hydrolysis

No “initial period” before starting the enhancements, as in cycle 2, is required in cycle 3. The enhancement methods should be implemented immediately after delivery of caustic soda.

To follow the hydrolysis progress during the period where the enhancements are implemented, groundwater samples **must** be collected and analyzed. Samples **must** be collected for a minimum of four sampling rounds. In each sampling round, groundwater **must** be sampled at three depths in each of the 10 characterisation wells per test cell and the two characterisation wells per test pipe. A total of 432 groundwater samples **must** be collected and analysed during this step of cycle 3.

6.3 Test cell 1: Implementation of enhancement no. 1, “Recirculation”

See section 5.3.

6.4 Test cell 2: Implementation of enhancement no. 2, ”Surfactant/co-solvent”

See section 5.4.

6.5 Test cell 3: Implementation of enhancement no. 3, ”Vibration”

See section 5.5.

6.6 Draining and re-infiltration

See section 4.3. The only additional action in this final draining step is that test pipe 1 (the blank) **must** also be drained.

6.7 Sediment sample control after cycle 3 (final documentation)

To document the effect of the hydrolysis on the concentration of parathion and other organophosphorous pesticides in sediment, control boreholes with the purpose of collecting soil samples **must** be carried out after the three completed cycles.

A total of 10 control boreholes per test cell and two boreholes per test pipe **must** be sampled at minimum of seven depths. Composite sediment sampling, neutralization and preservation **must** be carried out where required as described earlier in section 3.2.2. In total, 36 boreholes **must** be established and 252 soil samples **must** be collected.

7 Additional tasks

This chapter describes chemical analyses as well as health and safety aspects of the project.

7.1 Chemical analyses

In this section, analysis parameters, analytical methods and an overview of the number of sediment and groundwater samples to be analyzed during the various activities of the project, is given.

Please note that considerable preparation for the analysis of samples **must** take place in the field; please refer to appendix 15 in /3/.

7.1.1 Parameter groups

The following parameter groups were defined in appendix 15 in /3/:

Parameter group	Group	Number	Group members
organophosphorous pesticides	OPP	7	Ethyl parathion (EP3), Methyl parathion (MP3) E-amino-parathion (E-amino-P3) paroxon Malathion (FYF), Ethyl Sulfotep
tri-esters, basic	TRI	4	O,O,O-triethyl-thiofosforsyre (E-OOOPS) O,O,S-trimethyl-dithiofosforsyre (M-OOSPS) O,O-diethyl-S-methyl-dithiofosforsyre (EEM-OOSPS) O,O,S-triethyl-dithiofosforsyre (E-OOSPS)
tri-esters, extended	TRIX	7	TRI plus O,O-diethyl-O-methyl-thiofosforsyre (EEM-OOOPS) O,O-diethyl-S-methyl-thiofosforsyre (EEM-OOSPO) O,O,S-triethyl-thiofosforsyre (E-OOSPO)
P1/P2-acids	P1P2	4	O,O-diethyldithiofosforsyre (EP1-acid), O,O,diethylthiofosforsyre (EP2-acid) O,O-dimethyldithiofosforsyre (MP1-acid) O,O,dimethyl-thiofosforsyre (MP2-acid)
PNP	PNP	1	*para*-nitrophenol (PNP)
Miscellaneous	MISC	9	pH, Hg, Si, chlorocresols, chlorophenols, MCPA, chlorinated solvents, total phosphorous, ortho-phosphorous

Table 7-1 Parameter groups.

The minimum analysis program for sediment and groundwater samples is shown in Table 7-2. If other parameters are of value for the specific activity, they should be included.

Sample medium	Parameters for analysis
Sediment	OPP, TRI
Groundwater	OPP, TRI, P1P2, PNP

Table 7-2 Minimum analysis program for sediment and groundwater samples.

In all groundwater samples, pH **must** be measured in the field.

Mercury **must** be analysed for in a limited number of soil and groundwater samples, see Table 7-4.

7.1.2 Methods of analysis

Analysis of organic contaminants in Table 7-2 will be carried out free of charge by Cheminovas analytical laboratory. In return for this service, the bidder **must** continually keep Cheminova informed of coming sampling events and respect the laboratory's work load when planning sampling.

The analytical methods employed by Cheminova include gas chromatography (GC) and liquid chromatography (HPLC). The detector used on GC analyses depends on the required detection limit.

Analysis of other parameters (such as mercury) should be carried out by a commercial laboratory. In previous work, Milana A/S was used (atomic absorption spectrophotometry, hydride method), but other laboratories may also be used. In preparing prices, however, the bidder should be aware that some laboratories may require extra payment or simply not accept the samples, when made aware of the associated toxicity and odour problems.

Sediment samples for the analysis of mercury may be digested according to method DS 2210. To ensure representative results, some method for overcoming the inhomogeneous distribution of mercury in sediments should be included. One method is to increase the size of the sample to be digested in the laboratory to a minimum of 15 g and to combine increment samples to a composite sample in the field.

7.1.3 Number of samples

An overview of the minimum number of samples to be analysed for organic contaminants for various activities in this project is shown in Table 7-3.

Activity	**wells/ cell**	**wells/ pipe**	**depths/ well**	**samples/ cell**	**samples/ pipe**	**Sample rounds**	**Total number of samples**
Sediment samples							
Initial characterisation	10	2	7	70	14	1	252
Cycle 1	4	2	7	28	14	1	126
Cycle 2	4	2	7	28	14	1	126
Final documentation	10	2	7	70	14	1	252
Groundwater samples							
Initial characterisation	10	2	3	30	6	1	108
Draining 1 (initial)	-	-	-	10	10	1	min. 50*
Cycle 1	10	2	3	30	6	4	432
Draining 2	-	-	-	10	10	1	min. 50*
Cycle 2	10	2	3	30	6	6	648
Draining 3	-	-	-	10	10	1	min. 50*
Cycle 3	10	2	3	30	6	4	432

*The samples may be collected as discrete samples or as flow proportional samples

Table 7-3 Overview of the number of samples for various activities (calculated for 3 test cells and 3 test pipes)

An overview of the number of samples to be analysed for mercury for various activities in this project is shown in Tale 7-4.

Activity	Number of soil samples analysed for mercury	Number of water samples analysed for mercury*
Initial characterisation	42	25
End of cycle 1 (draining)	0	25
End of cycle 2 (draining)	0	25
End of cycle 3 (draining)	42	30

* All samples **must** be taken during the draining process

Table 7-4 Overview of the number of mercury samples to be analysed.

In the tender list under point 7.1.3, only pricing for the mercury analysis **must** be given. The cost for the soil and groundwater sampling activities **must** be given under the respective actions (i.e. initial characterisation, cycle 1, cycle 2 etc).

7.2 Health and safety

According to Danish law, a plan for health and safety must be provided for the project. Region Midtjylland will prepare a health and safety plan and coordinate the overall safety work at the site. The plan for health and safety will contain a division of the test area into different risks zones and a division of responsibilities for the different fields.

As a part of the plan for health and safety, the bidder **must** provide written safety instructions for the various types of process involved in the implementation of the project for example drilling, soil and groundwater sampling, infiltration of caustic soda etc. The instructions **must** contain (but not be limited to); description of the processes, risks involved and protective equipment required.

A preliminary safety meeting **must** be held. There will be informed about the necessary security measures and what Region Midtjyllands' expectations to the bidder will be in that regard.

Region Midtjylland will by inspection throughout the project ensure that all agreements about the use of safety equipment etc. are obeyed.

7.2.1 Substances

The substances mentioned below are the most abundant compounds of the more than hundred substances found at the site. These substances are also viewed as the most important compounds due their significance in quantity and toxicity. The bidder's attention **must** be high on the health and safety issue towards these substances.

- Parathion
- Methyl-parathion
- Ethylsulfotep
- Malathion
- Mercury (Hg(0), Hg^{2+})
- Methyl-Hg (19 µg/l has been detected in one groundwater sample. Dimethyl-Hg, ethyl-Hg and diethyl-Hg has not been detected in the two

groundwater samples analysed, but the presence of these compounds in low quantities can not be ruled out)

- EP1-acid and EP2-acid
- Residual Dense NonAqueous Phase Liquid (DNAPL) is widespread in hot-spots, but very little is found as a mobile separate phase.
- Methane (has been detected in concentrations up to 70% in pore gas in hot spot areas)
- Caustic soda
- Volatile chlorinated solvents (TCE has been detected in the groundwater in concentration up to ca. 2 mg/l)
- BTEX (benzene has been detected in the groundwater in concentration up to ca. 7 mg/l, toluene up to 20 mg/l, ethylbenzene up to 3 mg/l, xy-lene up to 6 mg/l, naphthalene up to 7 mg/l)

The concentration level of the organophosphorous compounds in soil and groundwater can be found in reference /3/.

7.2.2 Protective equipment

The plan for health and safety will contain recommendations for protective eq-uipment. It is the bidder’s responsibility to acquire and instruct their own per-sonnel in the correct use of all types relevant protective equipment. The bidder **must** also be responsible for the health and safety of all subcontractors that throughout the project access the site.

To avoid risk of direct contact with contaminants, the recommended protective equipment should involve;

- Safety glasses or a mask regarding concentration level
- Respiratory protection may be required during some processes
- Chemical resistant gloves
- Chemical resistant one-piece protective suit
- Chemical resistant safety boots

All protective equipment must be chosen with care. They must be resistant to high concentrations of the above mentioned substances (several of the sub-stances may occur as a separate phase in DNAPL). Additionally, the equipment must be the resistant to acidic and alkaline conditions that may occur while handling caustic soda and when using acid to neutralise soil and groundwater samples.

The pricing **must** include the cost for personal protective equipment and other measures to ensure adequate safety precautions. In addition, the pricing **must** include cost for preparing written safety instructions and participation in one safety meeting.

8 Reporting

All reports described in 8.1-8.3 **must** be written in English. The report described in 8.4 **must** be written in Danish.

8.1 Preliminary activities

Preliminary tasks are to be reported in a series of three separate reports:

1. surfactant/co-solvent experiments
2. initial characterisation and initial draining/re-infiltration
3. detailed experimental design

Each report should include well logs, analytical results, drawings and calculations as relevant.

8.2 Status reports

A total of three status reports **must** be prepared, one for each cycle. The status report is due approximately 6 month after initiation of each cycle (section 10). It is intended that these reports should be largely data reports with limited text. The status reports **must** include - but are not limited to - information regarding each test cell/test pipe for the following subjects:

- Documentation of the amount and method of added caustic soda.
- Time series showing the increase of hydrolysis products and other contaminants in samples collected from monitoring wells during the alkaline hydrolysis interval.
- Calculation of hydrolysis rates.
- Results of the drainage including water levels, amount of water and concentrations of contaminants.

- Calculation of the mass of contaminants removed with the groundwater during draining compared to the original mass of contaminants in the test cell/test pipe.
- Results of sediment sample control and comparison to the contaminant level in sediment samples collected from the characterisation wells.
- Evaluation of the effect of the enhancement method
- Recommendation on how the demonstration experiments should be progress in the subsequent cycle.

As attachments, the status reports should at a minimum include the normal well logs, sampling logs, water levels and results of chemical analyses.

8.3 Final report

The final report **must** as a minimum include:

- Description of the demonstration experiments
- Summarisation of all the results
- Evaluation of results
- Comparison of the efficacy of *in situ* alkaline hydrolysis in all demonstration experiments
- Evaluation and comparison of the success of the enhancement methods
- Description of challenges and problems encountered
- Conclusions and perspectives
- Recommendations for the future work

8.4 Preliminary design report for full scale remediation

This report **must** include a preliminary design of full-scale remediation, calculations for up-scaling to full-size and expected costs. This report **must** be similar in content to a so-called “projektforslag” as given in /5/.

9 Alternative proposals

Bidder’s are encouraged to present alternative proposals, although this is not obligatory.

An alternative proposal could be an enhancement method different from the three methods described in section 5.3-5.5. A number of additional technologies for enhancing *in situ* alkaline hydrolysis were previously identified /3/. These include air sparging, recirculation wells, pulsating injection, fracturing and soil mixing. Increasing groundwater temperatures may also enhance hydrolysis. The bidder is encouraged to describe one or more alternative enhancement methods.

In the current project description the efficacy of *in situ* alkaline hydrolysis must be documented on the basis of chemical analysis of parent compounds and hydrolysis products in soil and groundwater samples, before and after hydrolysis. An alternative proposal may describe an alternative way of determining the efficacy of *in situ* alkaline hydrolysis during the demonstration experiments. The bidder is encouraged to propose alternative ways of documenting the efficacy of the method.

If one or more of the alternative methods is found to be an improvement to the project, Region Midtjylland may select it and incorporate it into the project.

The alternative methods proposed by the bidder **must** be described in detail in the bidder's proposal. In addition, the bidder **must** describe any methods planned to document the alternative method.

The alternative proposals **must** not compromise the overall objectives of the project (section 0.1) and should be conducted within the framework of the existing project (section 0.5-0.6). The alternative proposals **must** provide documentation on the effectiveness of *in situ* alkaline hydrolysis to at least the same extent as described in section 3-7.

10 Time schedule

The bidder's proposal **must** contain a detailed time schedule including all significant actions involved in the implementation of the project.

A preliminary time schedule for the project is given below:

Activity	2011				2012				2013			
	1Q	2Q	3Q	4Q	1Q	2Q	3Q	4Q	1Q	2Q	3Q	4Q
Detailed experimental design	■	■										
Selection of surfactant/co-solvent		■	■	■	■							
Initial characterisation		■										
Initial draining		■										
Cycle 1		■	■	■	■							
Status report 1				■								
Cycle 2						■	■	■	■			
Status report 2								■				
Cycle 3										■	■	■
Status report 3												■
Final report												■
Preliminary design report												■

The following deadlines are set for reporting:

- Report on detailed experimental design: May 15, 2011
- Report on surfactant/co-solvent: February 1, 2012
- Report on initial characterisation and draining: July 1, 2011
- Status report 1: November 15, 2011
- Status report 2: November 1, 2012
- Status report 3: November 15, 2013
- Final report: November 15, 2013
- Preliminary design report: November 15, 2013

References:

(All references are available on the website: www.northpestclean.dk)

/1/ Bondgaard, M., B. Hvidberg & L. Ramsay, 2010. Remediation of pesticide contamination by in situ alkaline hydrolysis - a new soil remediation technology. 11th International conference on management of soil, groundwater and sediment (CONSOIL), September 22-24, Salzburg, Austria.

/2/ NIRAS, 2005. Beregning af forureningsmasse. Høfde 42, Harboøre Tange.

/3/ ALECTIA, 2010. Forundersøgelser af basisk hydrolyse og biologisk nedbrydning ved Høfde 42. Samlerapport. (Udkast)

/4/ Erbs Poulsen, S. & S. Christensen, 2010. Hydrauliske beregninger vedrørende oprensning af et forsøgsvolumen.

/5/ Videncenter for jordforurening, 2007. Projektlederhåndbog, 4. udgave.