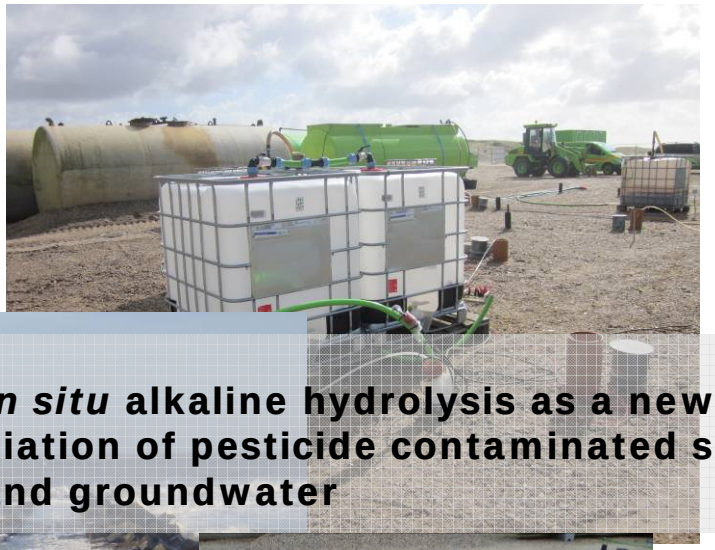
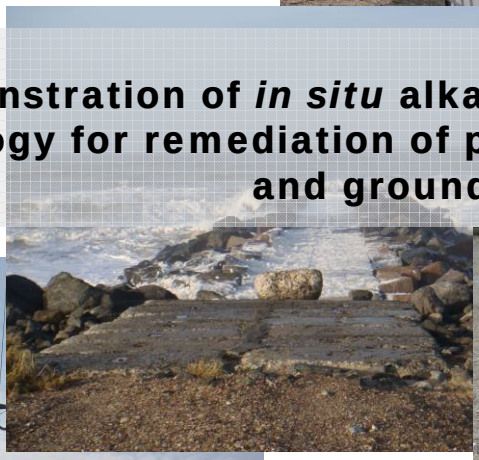
NorthPestClean
Pesticide Remediation

midt
Central Denmark Region



Demonstration of *in situ* alkaline hydrolysis as a new technology for remediation of pesticide contaminated soil and groundwater



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Publisher	Central Denmark Region Skottenborg 26 DK-8800 Viborg Tel. ++45 7841 0000
Department	Environment
Project	NorthPestClean
Publishing year	2013
Titel	Demonstration of in situ alkaline hydrolysis as a new technology for remediation of pesticide contaminated soil and groundwater
Editor	NorthPestClean
Pictures and graphics	NorthPestClean
Page numbers	12
Enquiries and comments to: mail phone	 miljoe@ru.rm.dk ++45 7841 1999
Read more about NorthPestClean	www.northpestclean.dk

Updated technical pamphlet
issued on 2013-03-27
a deliverable under action 7

Projekt nr.:
Life09/ENV/DK368

The project is supported through LIFE+, a program of the European Union. Since 1992, LIFE has co-financed some 3104 projects across the EU, contributing approximately €2.2 billion to the protection of the environment.

Introduction

In September 2010 a large European Commission funded demonstration project, NorthPestClean, was initiated. The primary objective was to determine the efficiency of the soil remediation method "*in situ* alkaline hydrolysis" and to demonstrate, in side-by-side field experiments, various techniques to enhance delivery and contact between the reagent (caustic soda) and the contaminants in the subsurface.

For this purpose there were in 2011 established three "test-cells". The pilot experiments are designed in order to determine the optimal remediation conditions allowing removal of as much contamination as possible.

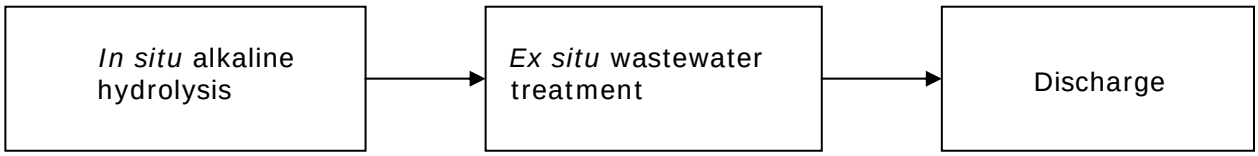


Figure 1: Conceptual model for treatment train of envisioned remediation at the site. The NorthPestClean project focuses on the in situ *alkaline hydrolysis*

The main objectives of the project are to;

- Document the efficiency of *in situ* alkaline hydrolysis
- Test and compare "enhancement" technologies (delivery and contact)
- Risk assessment-based "stop-criteria" for clean-up

The results from the pilot testing will be used to design a full-scale remediation at the site and calculate the economical feasibility.

Two years into the project, this pamphlet will give an overview of the first results available.

History of the test site – Groyne 42

"Groyne 42" is an old chemical dumpsite, located in the sand dunes at the west coast of Denmark. The waste was mainly sewage and solid waste products from the manufacturing of pesticides at a nearby chemical production plant. In the early 1960'ies the Danish State dumped an additional 40 tons of chemical waste at the site. After several attempts of remediation in the 1970'ies and 1980'ies, there are still approximately 100 tons of highly toxic compounds left in the saturated zone of the dumpsite. The main contaminant is the insecticide ethyl-parathion. In 2006, a 14 m deep iron sheet piling was set up surrounding the 20.000 m² pesticide contaminated area. Subsequently it was covered with a plastic membrane and the coast side was strengthened by a solid stone protection wall. Inside the enclosed area, the water table is currently maintained at a level below the sea-water level in order to prevent any leakage of contaminants to the North Sea.

With the encapsulation in place and the contamination under control, the Danish Environmental Authorities have since 2006 tried to find an effective and sustainable method for remediation of the site.

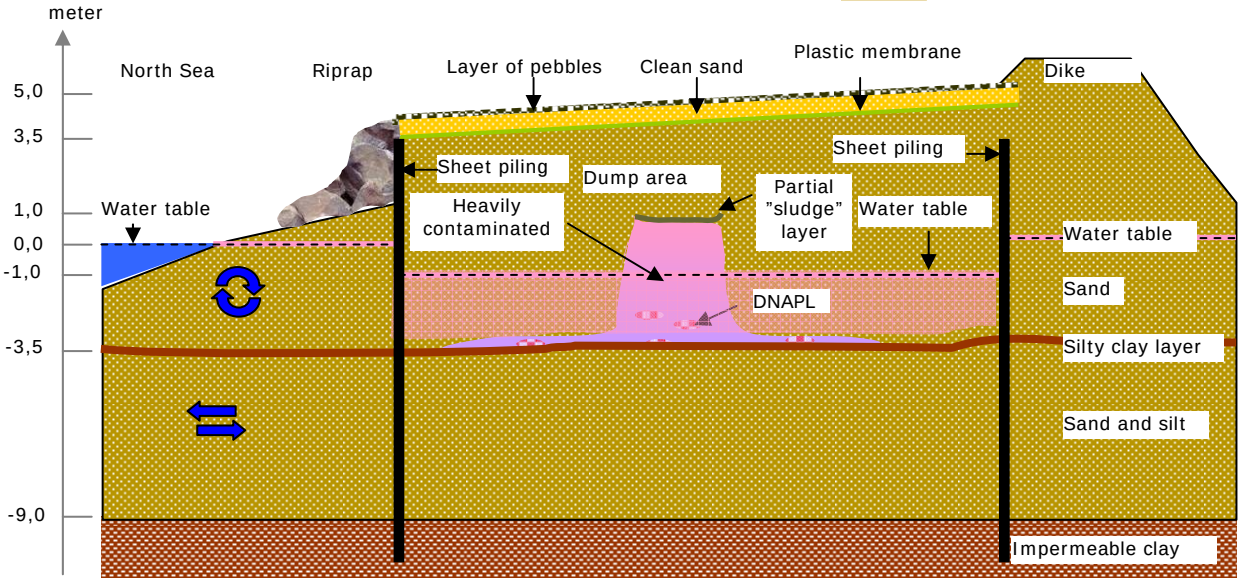


Figure 2: Principal sketch of Groyne 42.

In parallel to the enclosure of the site, feasibility studies and laboratory tests for six different remediation technologies were conducted in 2005 and 2006. The main result from these initial treat ability studies was that all technologies could probably be applied for the final remediation, but with a large variability in cost effectiveness and time-frame. Based on this technology screening, *in situ* alkaline hydrolysis was chosen for further experimental testing.

It is fair to say the site "Groyne 42" is one of the most studied and well characterised pesticide dumpsites in the world. In that regard, the site is considered ideal for testing the proposed new remediation technology.

Alkaline hydrolysis as a novel remediation technology

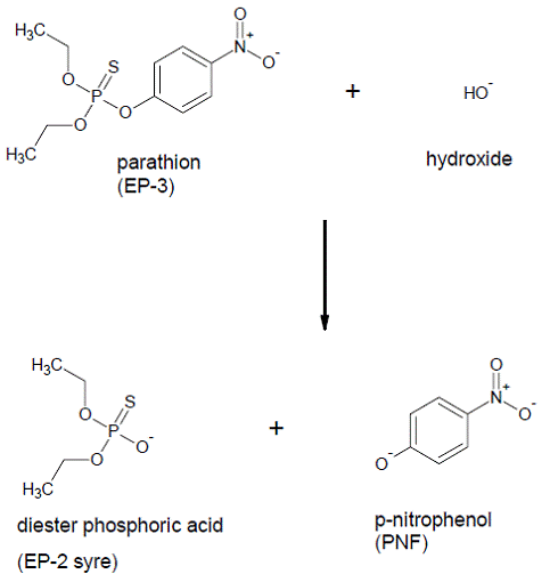


Figure 3: Degradation of parathion by nucleophilic substitution.

It is well described in the scientific literature that alkaline hydrolysis can be used to degrade organophosphorous insecticides such as ethyl-parathion (EP3), methyl-parathion (MP3), sulfotep and malathion to less toxic and water-soluble metabolites. The method has been used for many years by agrochemical companies that produce organophosphorous pesticides to neutralise the compounds upon accidental spills, but also as a pre-treatment of wastewater containing organophosphates before it is led to the biological wastewater treatment plant.

In situ alkaline hydrolysis has not previously been used as a technology to remediate soil and groundwater contaminated with organophosphorous insecticides. In 2005-2008, *in situ* alkaline hydrolysis as a soil remediation technology was tested in laboratory experiments and a small-scale field trial and the results were promising. Testing the novel technology in large-scale pilot experiments at a heavily contaminated site in the field was the next step in demonstrating the efficiency of this technology in soil remediation.

Design of test site

The objective of establishing a test site is to create the physical framework for large scale demonstration of "*in-situ* alkaline hydrolysis".
The test site consists of 3 test cells and 3 test pipes. In each of the 3 test cells separate technologies (acoustic vibration, re-circulation and addition of surfactants) will be employed to enhance contact between the contamination and the reagent. Every scientific experiment needs blinds or controls in this project test pipes are used as controls.

Pilot test cells

Each test cell measures 100 m^2 (10 m x 10 m) mimicking the large contaminated site "Groyne 42" enclosed by deep steel sheet piling. All of the test cells are placed within the most heavily contaminated area of Groyne 42.
Each test cell has 9 monitoring wells installed with screens in 3 depths for monitoring the progress of hydrolyses.

Blind tests – controls (test pipes)

The controls are designed as blind tests and constructed as mini-test cells composed by large-diameter iron piping (Ø 2m) with a depth of 14 meters. The test pipes are placed immediate next to the test cells. Each test pipe has 2 monitoring wells installed with screens in 3 depths for extraction of water samples.

Blind 1: Untreated for the whole period

Blind 2: The test-pipe is drained similar to the test cells, but is refilled with tap water (without caustic soda). This is to address a conceivably effect caused by the draining/refilling activity.

Blind 3: This test-pipe is drained, filled with caustic soda, drained again, etc. in three cycles precisely mimicking the procedures in the three test cells with the exception of the use of contact enhancement methods.

The data from the blind test will be compared with the results of the treated cells and thereby provide a solid foundation for evaluating the efficacy of the remediation methods.

Figure 4: Location of the test cells and test pipes within the encapsulated area of Groyne 42.

Initial characterisation of the three test-cells

Before the start of the experiments each pilot test cell is characterised in detail regarding geology and initial contamination distribution.

In the three test cells and the three blinds there were installed a total of 35 wells and taken 410 soil samples and 105 water samples throughout the initial characterisation.

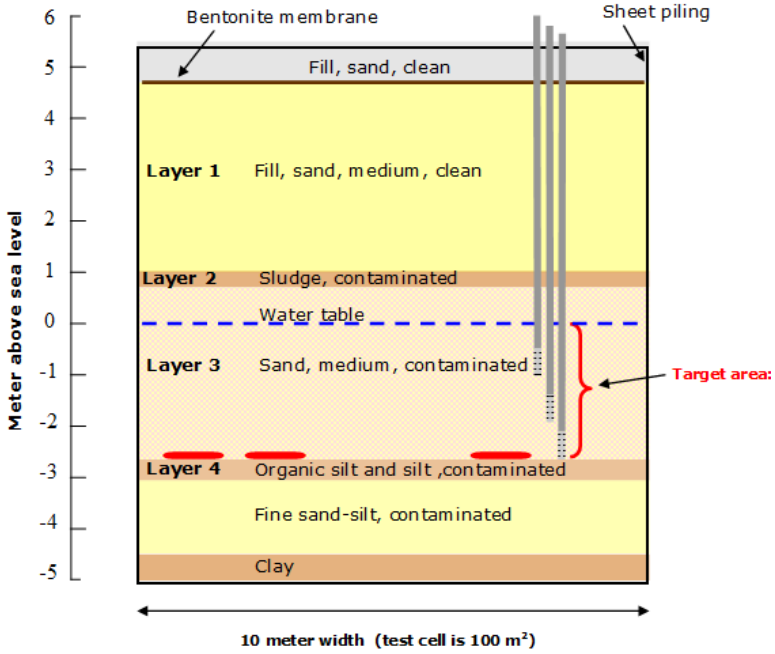
Sampling

All the soil samples were analysed for the main contaminants; organophosphorus pesticides (OPP), tri-esters (TRI) and 4-chloro-creosol (4-Cl-creosol).

Some of the samples were also selected for mercury analysis.

Figure 5: Samples are taken the spring 2011 drilling campaign

Geology



The characterisation shows that the geology at the site is relatively uniform to the investigated depth of elevation -2,8 m. The geology is characterised by the following layers:

- Sand, medium, stony fill sand
- Sand, medium, light/grey, well sorted
- Sand with areas with a sludge horizon
- Sand, medium, well sorted, intact, locally more fine- or coarse-grained layers
- Organic silt (green) and silt (grey).
- Alternating layers of silt and fine grained sand.

Figure 6: Schematic overview of geology in a test cell

Soil contamination

The soil samples were analysed for the mentioned main contaminants. Analyses of the results showed an almost even distribution of high concentrations of contaminants from about elevation 1 m to – 2,8 m. Results from the soil samples also showed great variation between the individual samples.
The results were processed in a 3 D model to visualise the distribution of soil contamination in the test cells.

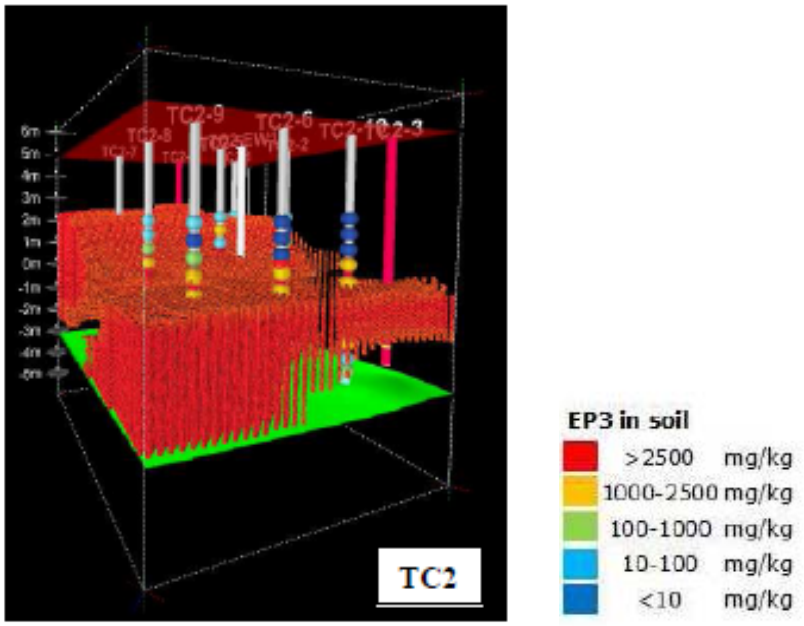


Figure 7: Distribution of EP3 concentrations above 2000 mg/kg in the test cell 2 (TC2).

Mercury analyses showed very high mercury concentrations (2.600-4.900 mg/kg) in the sludge layer in Test Cell 2 at an elevation of +1 m (in the unsaturated zone).

Groundwater contamination

Groundwater samples were analysed for the water soluble contaminants and pH was measured in the field during sample collection.

Table 1: Simple overview of average concentrations and pH in the groundwater (before treatment)

	TC1	TC2	TC3	TP1	TP2	TP3
pH	6.0	4.5	4.8	5,9	2,8	3,6
OPP, sum (mg/l)	10	33	23	15	12	20
TRI, sum (mg/l)	27	32	36	5	7	11
P1P2, sum (mg/l)	219	40	109	76	66	61
PNP (mg/l)	17	16	27	5	5	17

It is evident that the group of water soluble hydrolysis products (P1 and P2 acids) is found in the highest concentrations. Concentrations and pH vary greatly within each test cell/pipe. Data analyses also showed that the concentration of EP2 acid increases significantly with depth from the medium screens to the deep screens in all test cells.

DNAPL observations

Figure 8: Free phase on top of a narrow fine-grained horizon in TC2-4

The presence of free mobile organic phase was observed on top of the silt layer in approximately every 3rd well in the test cells. In addition, residual free phase (dark NAPL not flowing freely from the soil sample) was observed in three wells.

The field observations indicate that the presence of free mobile and residual organic phase was dictated by the presence of layers with low hydraulic permeability.

Calculated contaminant mass

Calculations were carried out for soil and groundwater to estimate the total contaminant mass before the start of the experiments. The calculations for the test cells/pipes were based upon the results from soil and water samples collected and analysed from the characterisation wells.

Mass in Soil

The total mass of selected contaminants in soil was calculated for the saturated zone thickness extending from elevation 0.0 m down to the top of the silt layer (elev. -2,8 m). For each test cell there are more than 60 soil samples in total to do these calculations, which is about one analysis for every 8 ton of soil.

Calculations for the main contaminant EP3 (parathion) gave values of 575, 991 and 780 kg for the test cells TC1, TC2 and TC3 respectively.

Mass in water

In the same zone dissolved phase contaminant mass occurring in the groundwater was also calculated.

When comparing the masses in water and soil, it is seen that about 99.7 % of the EP3 mass is found in the soil. For the other compounds it is typically more than 97 %. This distribution is consistent with expectations because of the low water solubility of the compounds.

Summary of the initial characterisation

Based on the soil and groundwater sample results, the following conclusions can be drawn regarding the distribution and quantity of contaminants:

- All test cells had masses of EP3 between 500 – 1000 kg which was close to the expected. The cells represent an area with high contaminant levels. Contaminant within each test cell was distribution relatively homogenous.
- High concentrations of contaminants were also observed above elevation 0.0 to about +1.0 m.
- About 99.7% of the EP3 mass was found in the soil (sorbed or free phase).
- An estimated 100 kg of mercury was found in the soil of each test cell, but only about 1 g was dissolved in the water.
- All test cells and test pipes are located in the expected old depot/ leaching area of the site, except Test Pipe 1, where contamination is only present in the bottom.

Based upon the characterisation results it is evident that the contaminant masses and distribution as well as hydrogeologic properties in the test cells and test pipes are relatively similar, but vary for some properties. Geology and contaminant distribution within each test cell is much more homogeneous compared to the expected.

Implementation of the pilot experiments

The experiments in the NorthPestClean project focus on demonstrating the efficiency of *in-situ* remediation using various technologies for enhancing contact between the contaminants in the soil and a reagent (an alkaline solution) delivered to the sub-surface. The pilot experiments are designed in order to determine the optimal remediation conditions, allowing the maximum removal of contamination. Based on the preliminary experiment from 2007 and 2008, the emphasis in the experimental design is on delivery of reagent and contact between reagent and contaminants.

The demonstration experiments are divided into three cycles, each cycle have a duration of 6-9 months. One cycle consist of; draining of the test cell, re-infiltration of caustic soda, period of hydrolysis with or without enhancements and finally draining again. During the demonstration experiments the results will be compared with the results from the controls in the test pipes.

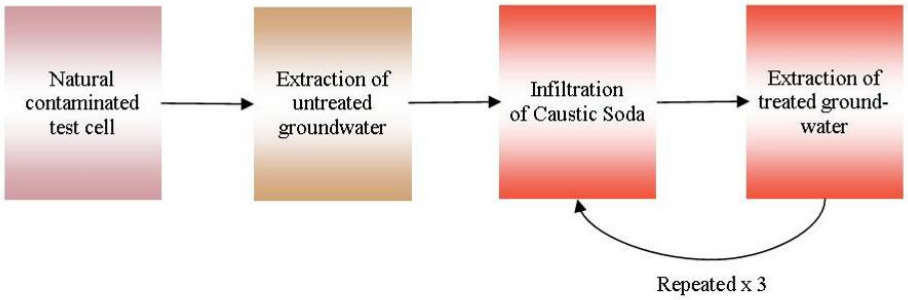


Figure 9: The experimental design of the pilot tests.

Cycle 1 - Drainage and infiltration by caustic soda

All test cells are treated in the same way. The groundwater in each of the three pilot test cells is drained to the silt layer about 8 m below the terrain. Approx. 150 m^3 of contaminated groundwater is removed from the three test cells.
When the test cells have been drained, diluted caustic soda is infiltrated via a central infiltration well by simple gravitation into each of the pilot test cells in order to increase the groundwater pH to about 13. The caustic soda solution is left undisturbed in the test cells for 6-9 months and the increase in hydrolysis products in the groundwater will be monitored over time to follow the hydrolysis progress. The experiments in cycle 1 comprise the baseline for the various contact enhancements conducted in the experiments of cycle 2 and 3.

Results of cycle 1

It was possible to extract approx. 50 m^3 of groundwater from each cell which is equivalent to 40% of the estimated total water content in a test cell. It is estimated that approx. 50% of the water in the test cell are drainable, e.i. approx. 80% of the "drainable water" was removed.
The infiltration of the caustic soda solution by gravitation was successful, however pH measurement showed that caustic soda was not fully distributed to the upper layers of the test cells.

Monitoring – water

More then 300 water samples have been collected and more than 11.000 chemical analyses have been conducted within the monitoring period of cycle 1.
The monitoring program included both "snap shot" events where water samples were collected from 27 screens at 3 depths in each test cell as well as "time series" events where more frequent monitoring is completed at a few selected locations and depths. The snap shot events have provided an assessment of the overall hydrolysis progress. The time series events have allowed for an assessment of the rate of the hydrolysis.

Example of a monitoring time series from test cell 1 is given in Figure 10. For simplicity only results from the primary hydrolysis products (PNF, MP2-acid and EP2-acid) are shown. Figure 11 shows the comparable results from the controls (blinds).

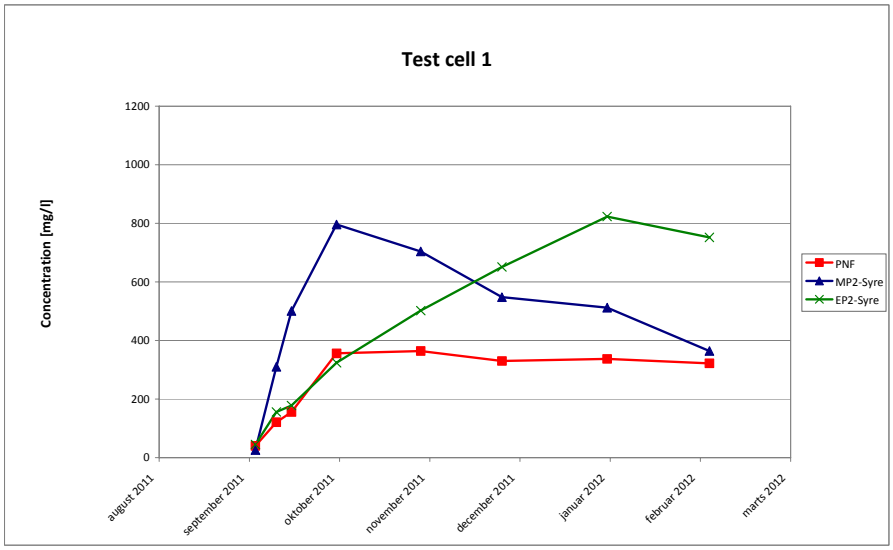


Figure 10: Time series from test cell 1, well 3 screen 1 (the bottom screen).

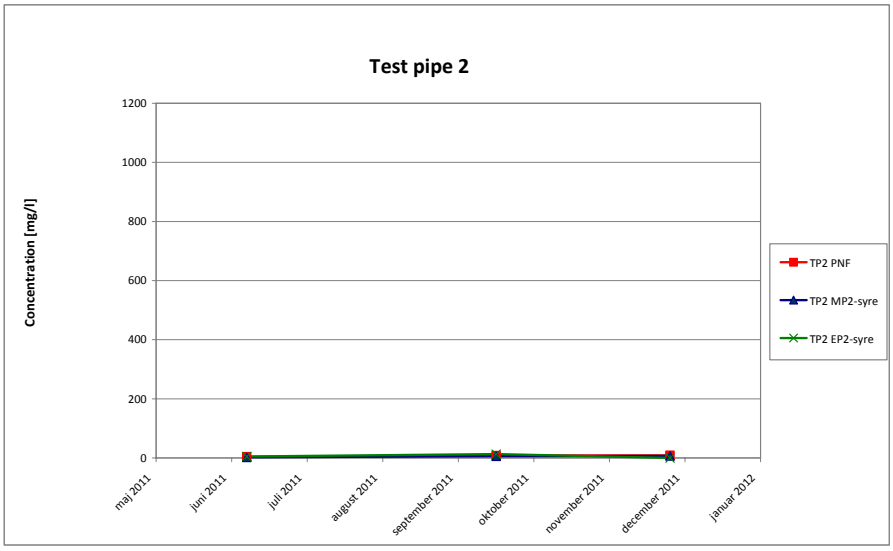


Figure 11: Monitoring results from test pipe 2 (control - water).

The progress of the hydrolysis of ethyl-parathion can be described as the rate of formation of the primary hydrolysis product (EP2-acid). The formation rate is given as the average EP2-acid concentration increase during a certain time span. The rate indicates how fast the degradation of the pesticide parathion is occurring. In the first 2,5 months after caustic soda infiltration EP2-acid formation rates of 167, 477 and 418 mg/litre/month are determined in test cell 1, 2 and 3 respectively. In the controls (test pipe 1 and 2) EP2-acid formation was insignificant (figure 2).

Draining

After 9 months, cycle 1 was completed and the test cells were drained. Several water samples were taken throughout the draining period.

Monitoring – soil

At the end of cycle 1 soil samples were collected for chemical analysis in each test cell from 6 new boreholes in order to evaluate contaminant mass removal. A range of about 8-10 soil samples were collected from each of the new boreholes. Lab result showed that the concentrations of the pesticides in soil had been significant reduced.

Mass removal

Mass removal estimations have been made based on both soil samples, water samples and monitoring- and drainage samples.

Table 2: Mass removal estimations. Removal is defined as the difference between the initial sum of measured contaminants in kg compared with the sum of measured contaminants in kg after cycle 1.

	E-sulfotep	MP3	Malathion	EP3	PNF	MP2	MP1	EP2	EP1	EP2+MP2+PNF	MP3+EP3+sulfotep	MP3+EP3 hydrolysed	Total
Dissolved mass at the end of cycle 1													
TC1	0.4	0.4	0.3	4.5	21	23	14	67	33	110			160
TC2	0.2	1.0	0.1	13	60	77	38	160	55	300			410
TC3	4.3	6.3	3.9	18	46	67	60	170	90	280			460
Drained mass at the end of cycle 1 (compensated for remaining water)													
TC1	0.5	0.7	01.	6.7	12	19	7.8	42	22	72			110
TC2	0.3	0.3	0.0	3.8	38	56	38	120	44	210			300
TC3	4.4	4.2	0.6	26	28	42	35	82	35	150			260
Mass reduction based on soil samples													
TC1	9	40	23	180							230		250
TC2	19	130	100	360							520		620
TC3	20	72	150	190							280		430
Mass reduction based on total-N measurements													
TC1												320	
TC2												480	
TC3												630	

The different ways of calculating the mass removal give comparable results within the same order of magnitude for each test cell. Estimations based on soil samples suggest that a relatively large mass of contaminants was removed from the soil during cycle 1: 300, 680 and 450 kg (sum of analysed contaminants) in TC1, TC2 and TC3, respectively, corresponding to 37%, 43% and 33% of the estimated baseline mass.

Cycle 2 - Tests of methods for contact enhancement

The main focus in cycle 2 will be the enhancement of contact between the contaminants and the reagent. Three methods for enhancement will be tested; acoustic vibration, re-circulation and surfactants.

Test cell 1

<u>*In situ* alkaline hydrolysis - contact enhancement by vibration</u>

The second cycle of test cell 1 involves; draining, delivery and enhancement consisting of vibration. Previous studies have shown that acoustic pressure waves have an effect on the dissolution and mobilisation of dense non-aqueous phase liquid (DNAPL). Prior to initiating cycle 2 a vibro seismic test was carried out in order to identify the optimal frequency and amplitude for the vibration experiment. Tests were made with both

an *ex situ* and an *in situ* vibration source. The results from sweep tests have been reviewed to assess the equipment, frequency, and amplitude that best transmit the vibration energy from a seismic source to the target area. The preliminary tests showed that vibration induced from the topsoil (*ex situ*) was just as efficient as an *in situ* source. As a result of the pre-test a device was constructed to deliver a frequency around 43 Hz and amplitude at approx. 30 kN.

Test cell 2

In situ alkaline hydrolysis - contact enhanced by recirculation of caustic soda
The second cycle of experiments in test cell 2 involves; draining, delivery and contact enhancement by recirculation of caustic soda. Preliminary calculations and modelling have been made on re-circulating a solution consisting of three extraction- and three infiltration wells. The recirculation flow from each extraction well is set on 100 l/h, which entails a complete distribution of diluted caustic soda in the entire cell within 20 days.
To improve the understanding of the effect of the circulation, numerical flow modelling and empirical tracer studies are carried out.

Test cell 3

In situ alkaline hydrolysis - contact enhancement by surfactants
The second cycle of test cell 3 involves; draining, delivery of caustic sodas. Several preliminary lab tests have been preformed in order to select a suitable surfactant that might raise remediation efficiency. 15-20 surfactants have been tested for their ability to enhance the solubility of DNAPL and the effect on alkaline hydrolysis. Several of the surfactants have shown promising result, and a final decision on which surfactant to test in large scale *in situ* will be made prior to cycle 3.

Cycle 3

A third cycle will be carried out. Based on the results and experiences gained throughout cycle 2, the different enhancement techniques will be further tested, possibly in combination with the aim to optimise the remediation efficiency.

Environmental risk assessment and remediation stop-criteria

The main objective of a full-scale remediation at “Groyne 42” is to ensure the residual contamination after remediation of soil will not pose an unacceptable risk to the aquatic environment in the North Sea.

Therefore in order to answer the question: “When is the site clean enough?” environmental risk assessment-based success-criteria (stop-criteria for remediation) will be established. By the end of the NorthPestClean project there will be done a comparison between the remediation potential of the new method (found in the pilot tests) and the risk assessment-based stop-criteria for the clean-up.

By establishing measurable stop-criteria and demonstrating the effectiveness of the new method, the decision makers are provided with crucial information that should allow them to make a decision on how to proceed with the full-scale remediation of the site.

More information and detailed reports on different aspects of the project are located on the web; www.northpestclean.dk.