MILJØMINISTERIET

Miljøstyrelsen

Updated layman report issued on 2014-06-30
a deliverable under action 7

Projekt nr.: Life09/ENV/DK368

NorthPestClean
Pesticide Remediation

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.

NorthPestClean

Demonstration of *in situ* alkaline hydrolysis as a novel soil remediation technique for a pesticide contamination

Introduction

According to the Danish law on soil contamination, all contaminated sites in the country must be registered. Contaminated soil posing a risk to human health or the environment must be decontaminated or in other ways neutralized. Denmark and the EU Commission continuously work on developing new soil remediation methods, to be able to decontaminate diverse contaminations more effectively for the benefit of environment and humanity.

The former chemical dumpsite "Groyne 42" is one of Denmark's most heavily contaminated sites. The contamination is situated at the coast facing the North Sea between the small towns of Harboøre and Thyborøn in the western part of Denmark. The area is heavily contaminated by more than 100 tons of toxic chemicals, mainly pesticides and mercury.

Central Denmark Region and the Danish Environmental Protection Agency (Danish EPA) have since 2007 been working on the development of an entirely new method, "*in situ* alkaline hydrolysis", to remediate the site. The preliminary experiments showed promising results and in 2010-2014, with economic support by the EU's LIFE^{+} programme, a large scale demonstration project was carried out. The project should demonstrate the effectiveness of the method and determine if the new method can be used to remediate the entire 20.000 m^2 sized dump site.

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Read more on www.northpestclean.dk

Surfactant
The word surfactant is a combination of the words surface and actant. Surfactants are substances like for example soaps that reduce the surface tension of hydrophobic substances (for example oily substances) and make them therefore more water soluble.

In a later phase a surfactant was added in the test cell with recirculation. The addition of a surfactant resulted in markedly higher concentrations of chemicals in the water phase (primarily parathion). This means the use of surfactant "moves" the contaminants that are bound on the soil, from the soil to the groundwater. The experiment did not show an increased degradation of the pesticides in the water, but the addition of surfactant did result in an increased overall removal of contaminants from the soil.

Perspectives

The project NorthPestClean has shown that it is possible to remediate soil contaminations with pesticides by using *in situ* alkaline hydrolysis. The results showed as well that the duration of the remediation will depend on the type and amount of chemicals in a given contamination.

The NorthPestClean project has successfully contributed to the development of the alkaline hydrolysis method and has paved the way for the future use of the method in both Europe and also in the rest of the world.

History of Groyne 42

From 1953 to 1962 Cheminova, an agrochemical manufacturing plant, deposited solid waste and wastewater from the production of pesticides (mainly the insecticide ethyl-parathion) and mercury between the sand dunes right at the coast to the North Sea. The deposit had been permitted by the Danish Authorities and the state itself used the site to deposit chemical waste in the 1960'ies.

With a first partially excavation in the early 1970'ies, about 1.250 m^3 contaminated sand and waste were removed and the site was covered with asphalt. In the following years the local citizens and the authorities became aware that the

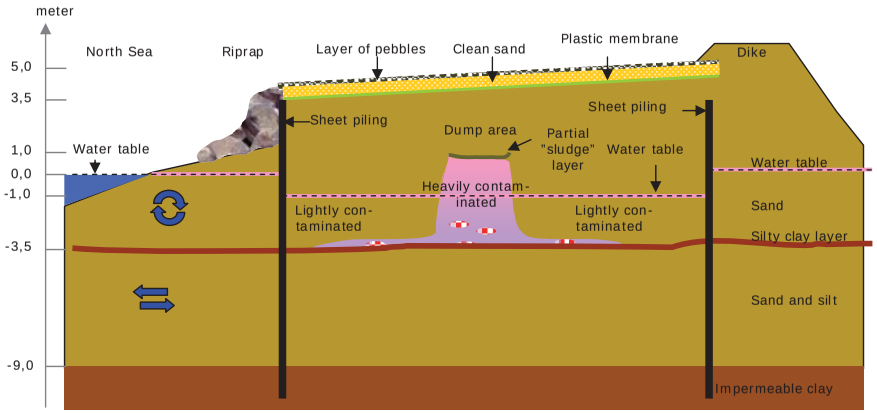
dumpsite still posed a considerable risk to the environment and the wildlife, since dead fish and diseased birds were observed.

In 1981 the Danish EPA financed another partial excavation of contaminated soil. During this remediation ca. 1.200 m^3 contaminated sand was removed and deposited in a salt mine in Germany. However, still more than 100 tons of toxic chemicals were remaining in the ground below the groundwater table.

The contamination today		
Parathion	68 tons	62 %
M-parathion	9 tons	9 %
Mercury	7 tons	7 %
E-Sulfotep	6 tons	5 %
Malathion	3 tons	3 %
Other contaminants	16 tons	14 %
Total	**110 tons**	**100 %**

In 2000 it was found that there still was considerable seepage of chemicals from the site into the Nord Sea. The former Ringkjøbing County and the Danish EPA agreed to share the costs of encapsulating the contaminated area.

A new site investigation showed that an area of approximately 20.000 m^2 was contaminated and the contaminants were situated 4-8 meters below ground. The encapsulation was established in 2006. A 600m long and 14m deep iron sheet piling encircles the contaminated area. The area is covered by a membrane and the water table is kept lower than outside the site to prevent seepage. The iron sheet piling is guaranteed to last to the year 2021 and is expected to last even longer.



The experiments also showed that a part of the mercury which is hard bound to the soil at “Groyne 42” is mobilized during the treatment with caustic soda. It is estimated that 10-20% of mercury is removed with a remediation using alkaline hydrolysis.

Is it possible to increase the efficiency of the method?

During the experiments three enhancement methods to improve contact between the contaminants and caustic soda were tested:

1. vibration of the soil
2. recirculation of caustic soda
3. addition of a ”surfactant” (a kind of liquid soap)

One of the test-cells was “treated” with vibration waves of different intensities. This method did not show a significant improvement of the overall degradation of the contamination.

In another test-cell the caustic soda solution was circulated in the cell. Recirculation did not show a direct improvement on the degradation of the contamination. However, recirculation did contribute to a better, even distribution of caustic soda over the entire test-cell.

Results

In the three years the experiments lasted, following was tested:

- Is it technical feasible to use the technology in the field and on a large scale?
- Can alkaline hydrolysis effectively degrade the contaminants in the soil?
- Is it possible to enhance the methods performance by improving the contact between the contaminants and caustic soda in the soil with help of "enhancements methods" (vibration, recirculation and surfactants)?

Large scale

A scale is usually used to compare things of different sizes. In an experimental context the term "small scale" is used when testing a method on a very small area which might be unrealistic to compare to "full scale", which here would be the same as the whole site. Testing a method on a large scale means that it is large enough to yield results that are comparable to "full scale" but still is significantly smaller (and cheaper) than a "full scale" experiment.

Is it technical feasible?

The experiments have shown that it is possible to use the method in a large scale. At the same time the experiments have provided valuable knowledge of the issues and problems that can arise when implementing the method and how they can be solved.

Can alkaline hydrolysis effectively degrade the contaminants in the soil?

By analyzing water and soil samples throughout the experiments the degradation of the contaminants was closely monitored.

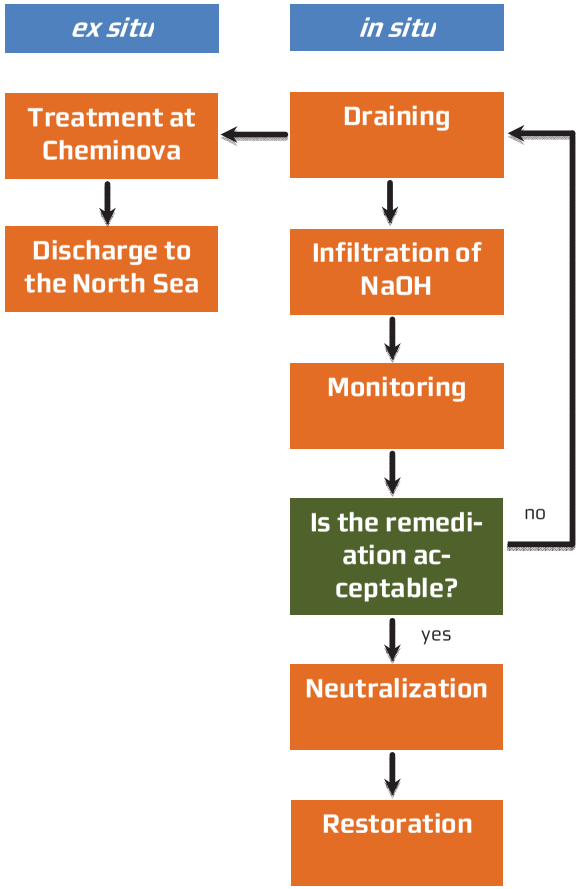
As expected from the theory the contaminants in the experiments were degraded in the soil, but at different rates. Up to 95% of the contaminants m-parathion, malathion and E-sulfotep were removed from the soil during the experiments. But for ethyl-parathion, which is the primary contaminant at the site, only 20-60% was removed during the experiments (2½ years).

The overall conclusion on the experiments is that the method *in situ* alkaline hydrolysis can be used to remediate soils contaminated by organophosphorus pesticides. If the method is to be used in full scale at "Groyne 42" it is estimated that the treatment with caustic soda has to be repeated up to 8 times to ensure that the contamination is sufficiently degraded and removed. A full scale remediation is estimated to take approximately 10 years and the cost will approximately be 13 mio. €.

The technology

It is well described in the scientific literature that alkaline hydrolysis can be used to degrade organophosphorus pesticides. The method has been used for many years by agrochemical companies producing organophosphorus pesticides to neutralise the compounds upon accidental spill, 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 organophosphorus pesticides. The concept for the use of the method on Groyne 42 is to degrade (e.g. parathion) under highly alkaline conditions to less toxic, water soluble break down products. Thus the contaminants, which are bound to the soil, will be transferred to the groundwater. The breakdown products can now be pumped up and treated in a biological wastewater plant. The treatment is repeated several times and the contaminants are gradually removed from the soil.



Objective of the project

A large scale pilot experiment using *in situ* alkaline hydrolysis (NorthPestClean) was conducted in 2010-2014.

The projects primary objectives were:

- Document the effectiveness of the new method and provide a political decision base for a full scale remediation at Groyne 42.
- Demonstrate the effect and usability of three different “contact enhancement” technologies (vibration, recirculation and surfactant addition).
- Provide stop criteria / success criteria for a future full scale remediation – How much of the contamination has to be removed to eliminate the risk for the North Sea and environment?

The experiments

The large scale pilot experiments were conducted in three test-cells (10x10 m) enclosed by a 14 m deep steel sheet piling. The test cells are constructed in the most contaminated area of the dump site to simulate a future full scale remediation. Prior to the start of the experiment a high resolution site characterization was made in order to determine the extent of contamination in each test cell.

The main process in the experiments was to drain the test cells for natural groundwater and replace it with an alkaline NaOH solution (caustic soda), with pH 13. Over a few months the contaminants are degraded to less toxic water soluble compounds, which can be pumped up. This process was repeated twice. During the experiments it was closely monitored how much of the contaminants was degraded and how much of the contamination was removed.