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Selection and Testing of Surfactants for Enhanced *In Situ* Alkaline Hydrolysis (S-ISAH) of Pesticide DNAPL

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**Background**

Groyne 42 is a 20,000 m² former chemical dump site in Denmark contaminated with 200-300 tons of organophosphorous pesticides (OPPs). The majority of contaminant mass is present as sorbed phase and residual DNAPL. The NorthPestClean project was established to determine the effectiveness of using *in situ* alkaline hydrolysis to treat the DNAPL (Fig. 1).

**Scope of study**

To test surfactants as a method for enhancing the solubility of OPPs and the rate of *in situ* alkaline hydrolysis and select a commercially available formulation for pilot scale site tests.

**Initial selection**

Previous work has identified non-ionic surfactants as the best performing type increasing OPP solubility. Ten candidate surfactants was identified based upon the following criteria:

- stability under alkaline conditions (pH of 12 or higher)
- acceptability for in situ use – not toxic to the environment
- readily biodegradable in the environment
- limited foaming

**Screening**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>SUM OPP</td>
<td>parathion (EP3), methyl-parathion (MP3), malathion, ethyl-sulfotep</td>
</tr>
<tr>
<td>SUM P2 acids</td>
<td>O,O-diethylthiophosphoric acid (EP2), O,O-dimethyliophosphoric acid (MP2)</td>
</tr>
<tr>
<td>PNP</td>
<td>para-nitrophenol</td>
</tr>
</tbody>
</table>

**Alcohol Ethoxylates**

- **Fig. 3:** The contaminated soil/surfactant water ratio used in this test was 4 g/mL. No extra DNAPL was added.

**Conclusion**

- **Fig. 4:** Results of batch tests with soil of four alcohol ethoxylates after 7 days of reaction at pH 13.

**Ecosurf EH-9** was best at increasing OPP solubility in the presence of soil due to higher soil adsorption of the other ethoxylates. Highest OPP removal from the soil was obtained with Rhodasurf CET25 (64%) and Ecosurf EH-9 (63%) compared to 40% of the reference alkaline tap water. Ecosurf EH-9 has higher biodegradability and lower costs.

**Ecosurf EH-9** was chosen for pilot scale tests at the Groyne 42 site at a concentration of 4%.

(Results of pilot scale test: Session H5 Tuesday by MacKinnon et al.)

Conducted in close collaboration with:

- COWI
- Rambøll
- Tufts University
- Geosyntec Consultants
- COWI

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**Fig. 1:** The alkaline hydrolysis of OPPs.

**Fig. 2:** Screening of ten surfactants at pH 13 after 7 days with a 10:1 surfactant:DNAPL volumetric ratio.

**Fig. 4:** Concentration in water samples (mg/L) for each of the four alcohol ethoxylates included in the test.

**Equilibrium DNAPl tests (30 g/L of surfactants)**

- SUM OPPs
- SUM P2 acids
- PNP

Batch equilibrium solubility tests showed that alcohol ethoxylate non-ionic surfactants was superior with respect to increasing OPP solubility compared to the alkaline tap water reference. The concentrations of hydrolysis products were on the same level as the reference and hence no significant enhancement of the hydrolysis rate was observed.