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Background/Objectives. Groyne 42 is a former organophosphorus pesticide manufacturing waste disposal site located on the west coast of Denmark. The Site covers an area of 20,000 m^2. Chemical wastes were disposed of at the Site from 1953 to 1962 between two sand dunes situated close to the North Sea. The organophosphorous pesticides and associated contaminants are present as dense nonaqueous-phase liquids (DNAPLs) in certain portions of the Site. Residual DNAPL is widespread in hot spots, but little contaminant mass exists as a mobile separate phase. The estimated total mass of organophosphorous pesticides present (DNAPL + sorbed phase) is between 200 to 300 tons. A European Commission-funded demonstration project (www.northpestclean.dk) was initiated in September 2010 with the objectives of (1) determining the efficiency of using in situ alkaline hydrolysis (ISAH) for treating the organophosphorus pesticide DNAPL, and (2) testing, in side-by-side field experiments, various techniques to enhance in situ delivery and contact between the reagent (caustic soda) and the contaminants. Surfactant flushing was one of the three enhancement methods to be tested.

Approach. Laboratory studies were completed to identify surfactants capable of enhancing the solubility of the pesticides under strongly alkaline (pH 12) conditions. Alcohol ethoxylates were found to be the most effective and were selected for the field experiments. The field demonstration project is being performed in three (10 m wide x 10 m long x 15 m deep) test cells. The test cells have been constructed using iron sheet piles to maximize hydraulic control. During the first stage of the project, ISAH was tested without enhancement (i.e., under static conditions) over a period of 8 months. In the second stage of treatment, recirculation was used in combination with ISAH in one of these test cells over a period of 12 months to evaluate any enhancement in reactivity due to mixing. In the final treatment stage, an alcohol ethoxylate surfactant was injected into the test cell at a target in situ concentration of 3% (wt.), for a final 8 month treatment period. Measurements of surface tension were used to evaluate the distribution of surfactant solution within the test cell. During each treatment stage, groundwater samples were collected to evaluate the progress of hydrolysis. Groundwater and soil sample analytical results were used to evaluate changes in the mass and distribution of pesticides through the three stages. The final stage of the pilot test will be complete in November 2013.

Results. The recirculation and surfactant flushing stages of the demonstration project were found to promote mixing of the pesticides and caustic soda in the test cell. Surface tension and contaminant measurements confirmed that the surfactant effectively increased the solubility of the pesticides to enhance the ISAH treatment. The results from the three stages of the demonstration project will be discussed in terms of the relative benefits and practical considerations for ISAH during static, recirculation and surfactant flushing conditions.

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Field Test of Surfactant and Acoustic Vibration as Enhancement Methods for ISAH of Organophosphorus Pesticide DNAPL

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NorthPestClean Pesticide Remediation

Life

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Kogsgaard

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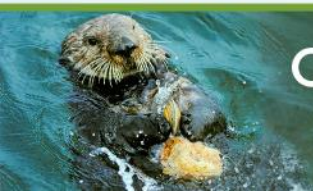

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Posters:

C5 – Tuesday - Comparison of Contaminated Mass Estimation Methods in a Large Field-Scale Experiments with In Situ Alkaline Hydrolysis.

H5 – Wednesday - In Situ Alkaline Hydrolysis (ISAH) of Insecticides—A Large-Scale Demonstration Project.

H5 – Wednesday - Selection and Testing of Surfactants for Enhanced In Situ Alkaline Hydrolysis (S-ISAH) of Pesticide DNAPL.

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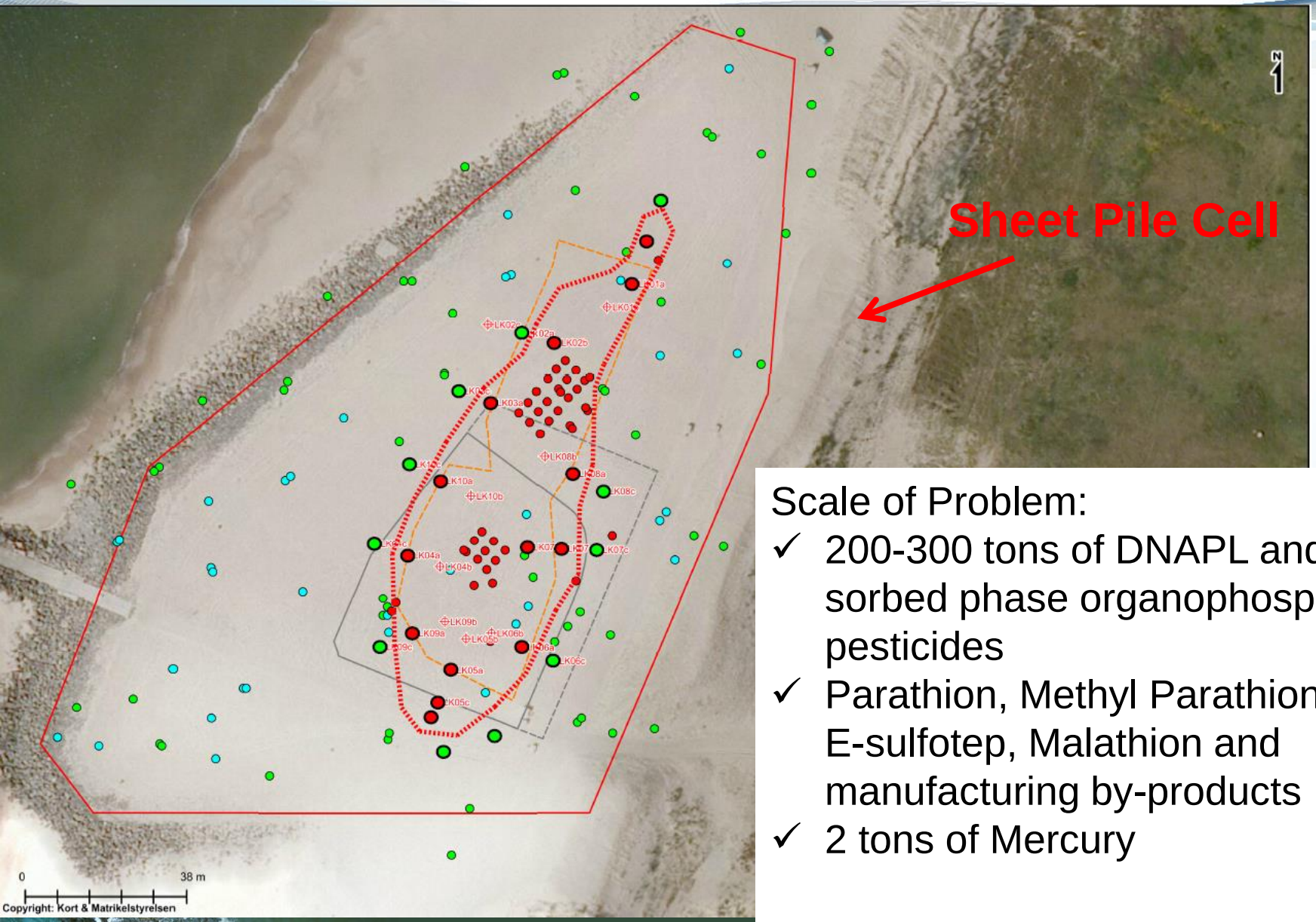
Outline

- The Høfde Site and COCs
- ISAH Technology
- Pilot Test Objectives and Program
- Approach and Results:
  - ISAH with no enhancement
  - ISAH with acoustic vibration
  - ISAH with recirculation
  - ISAH with surfactant
- Conclusions

Site Layout & OPPs

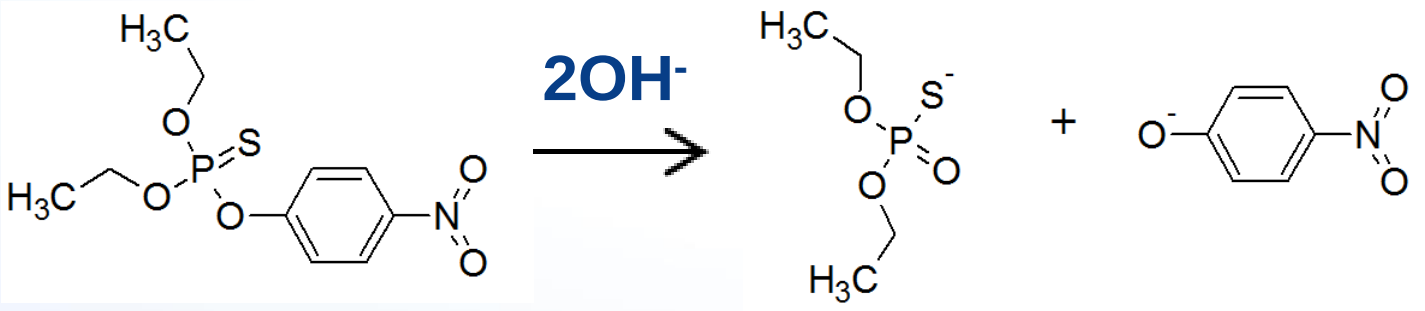


Scale of Problem:

- ✓ 200-300 tons of DNAPL and sorbed phase organophosphorus pesticides
- ✓ Parathion, Methyl Parathion, E-sulfotep, Malathion and manufacturing by-products
- ✓ 2 tons of Mercury

2011-2013 ISAH Pilot Tests

- ISAH products less toxic and more water soluble than parents
- Technology used at Cheminova site for wastewater treatment in sequence with a biolagoon



Parathion (EP3) → *Diester phosphoric + p-nitrophenol (PNF) acid (EP2 acid)*

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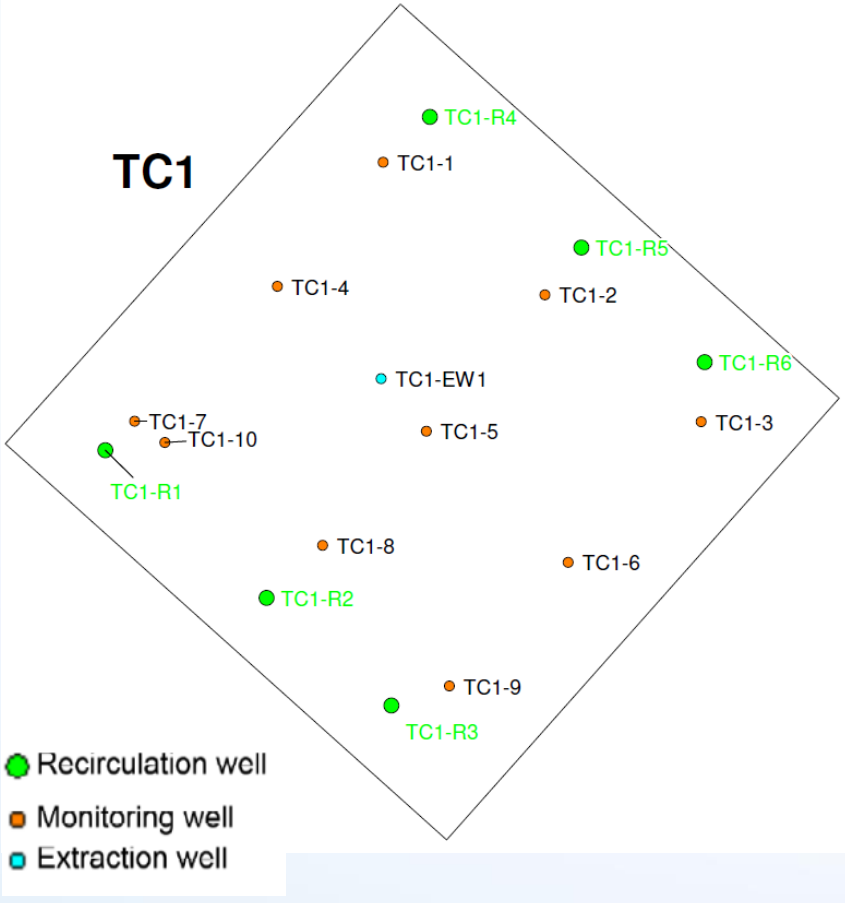
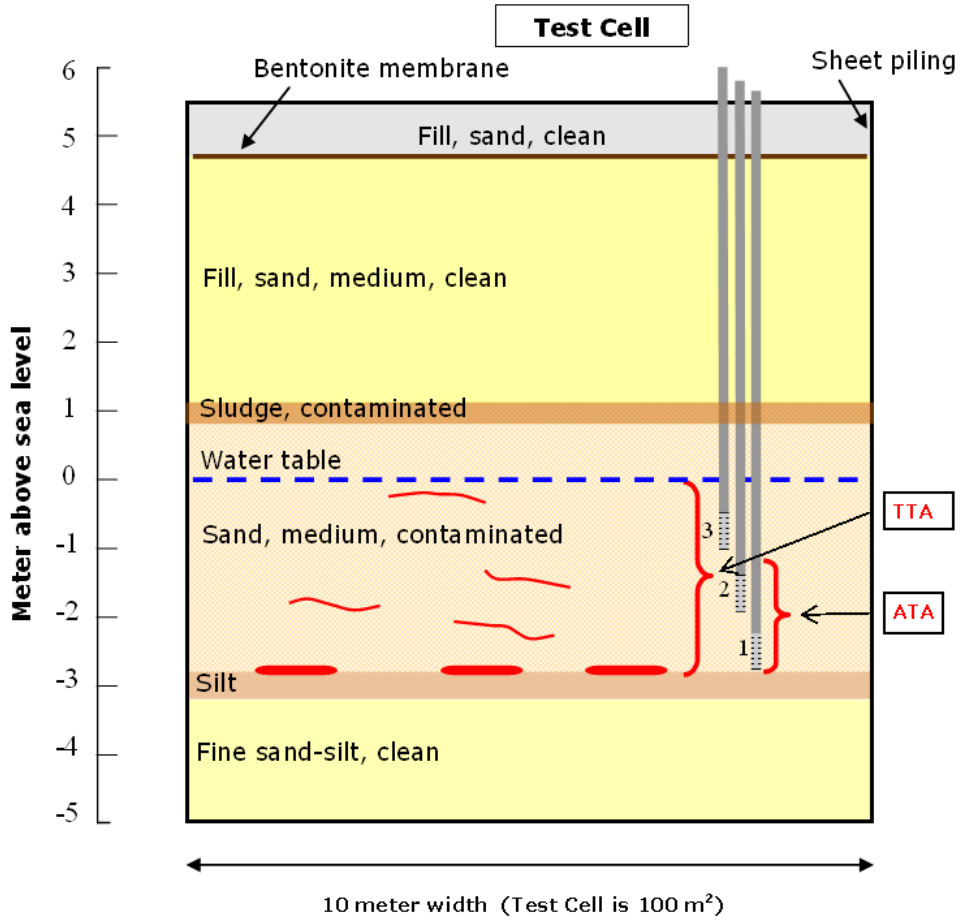
ISAH Pilot Test Objectives

- To demonstrate in a large-scale pilot experiment the efficiency of a novel remediation method that uses ISAH to treat organophosphorous pesticide (OPP) contaminated soil and groundwater
- To demonstrate, in side-by-side pilot experiments, the performance and usability of different "enhancement" technologies
    1. Groundwater Recirculation
    2. Surfactants
    3. Acoustic Vibration

Test Cell Layouts





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Pilot Test Program

	2011										2012												2013											
	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N
	Initial characterization						Cycle 1										Cycle 2												Cycle 3					
Operation																																		
Draining and NaOH infiltration																																		
TC 1 - Vibrations																																		
TC 2 - Recirculation																																		
TC 2 - Surfactant																																		
TC 3 - ISAH - no enhancement																																		
Monitoring																																		
Soil sampling																																		
Water sampling																																		

- 3 “Cycles” of operation between 2011 and 2013
- Lines of evidence for ISAH:
  - Groundwater → Changes in OPPs + hydrolysis products
  - Soil → Changes in OPPs

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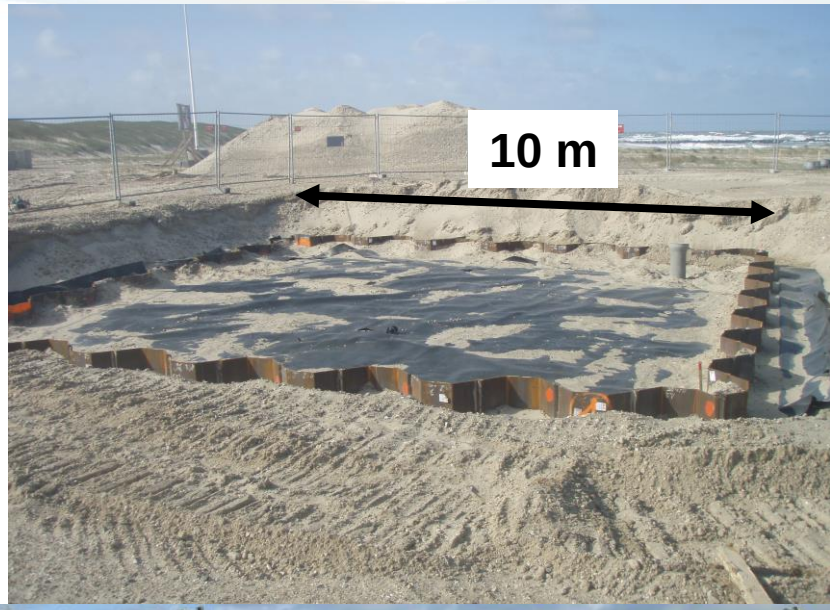
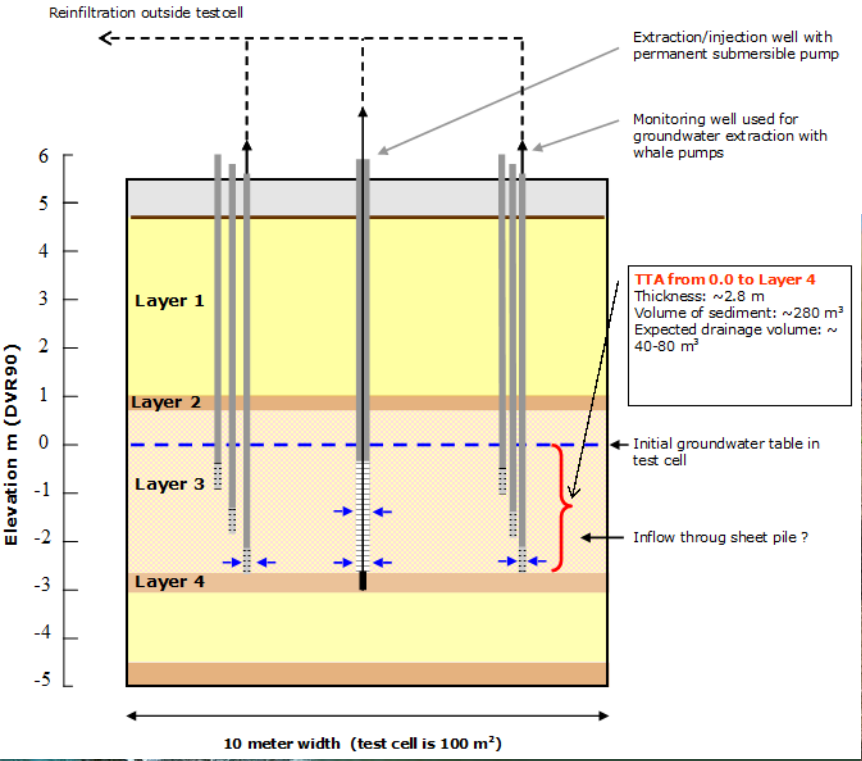
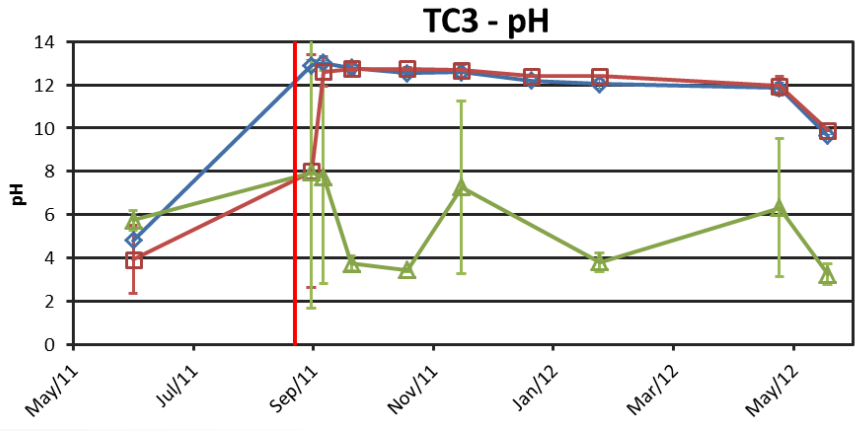
Cycle 1 Implementation: NaOH Injection

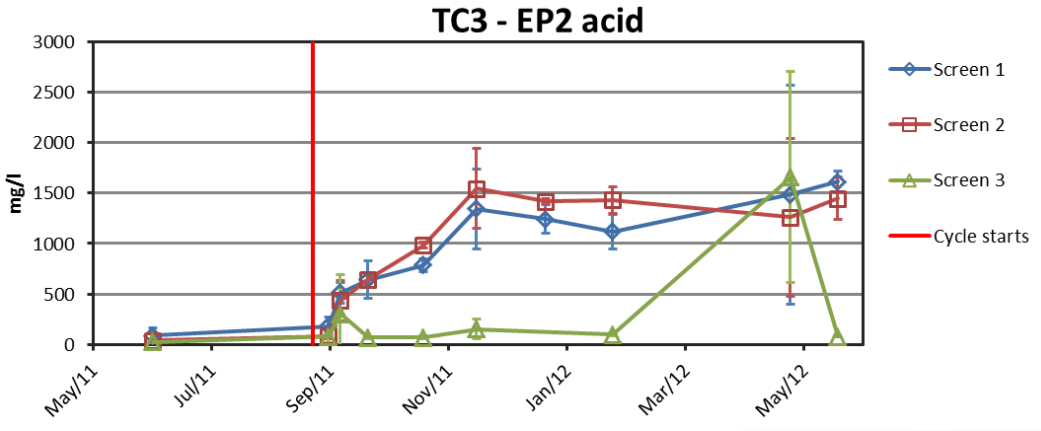
- Test cells drained in advance of NaOH Injection
- NaOH added at pH >12
- Monitoring for 8 months



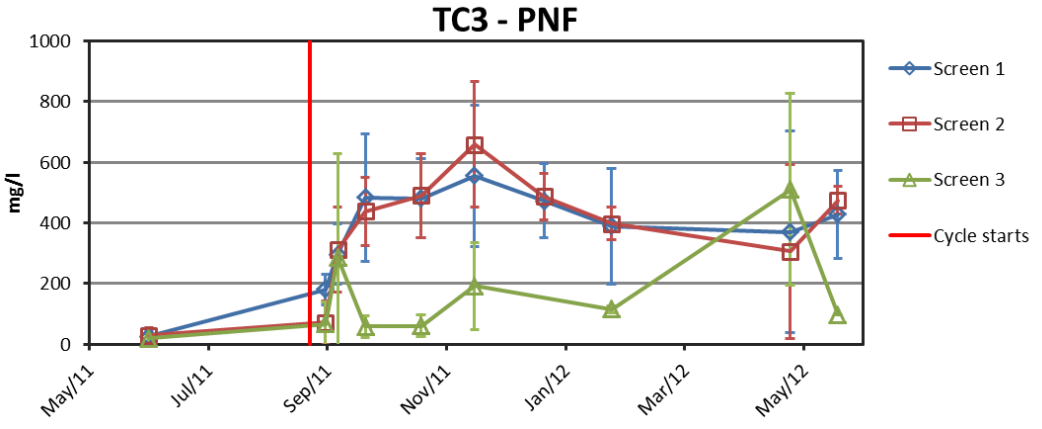


Cycle 1 Monitoring Results





- PNF & EP2 produced
- Plateau after a few months
  - pH decrease
  - Daughter products degrade over time



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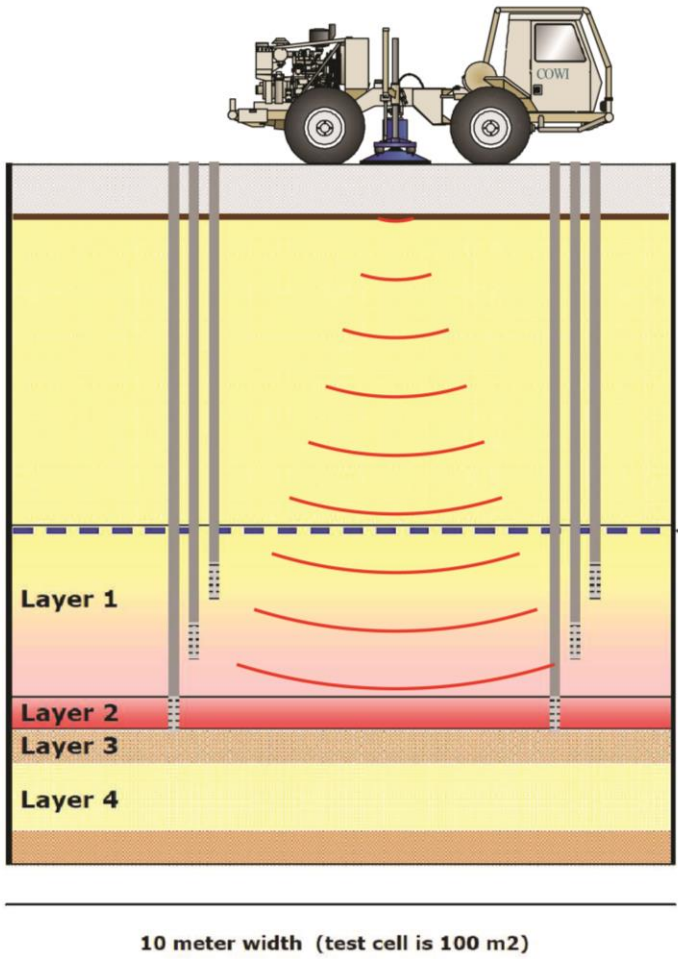
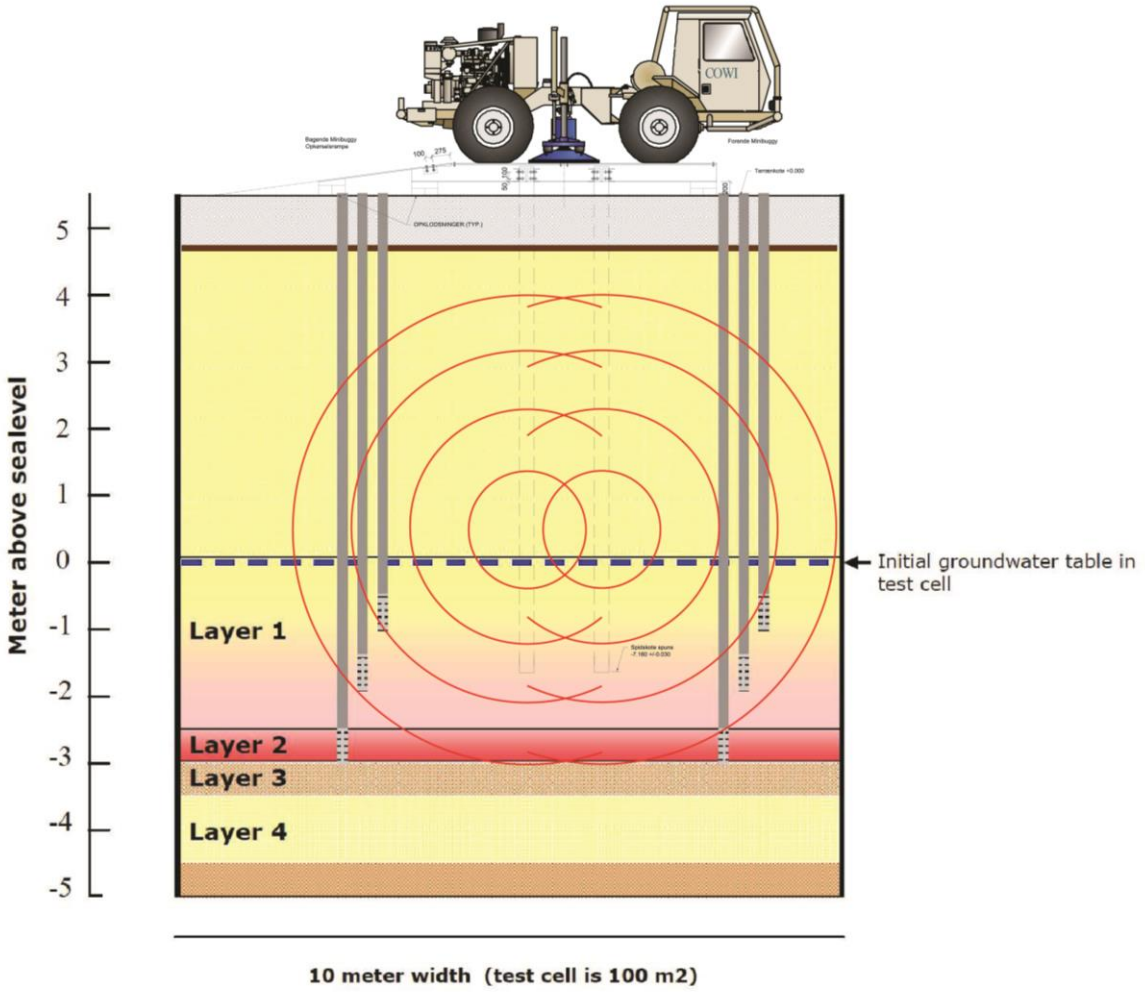
Cycle 2: ISAH with Vibration

Ex Situ vs. *In Situ* Sweep Test Equipment

Ex Situ



In Situ



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Stationary Vibration Device

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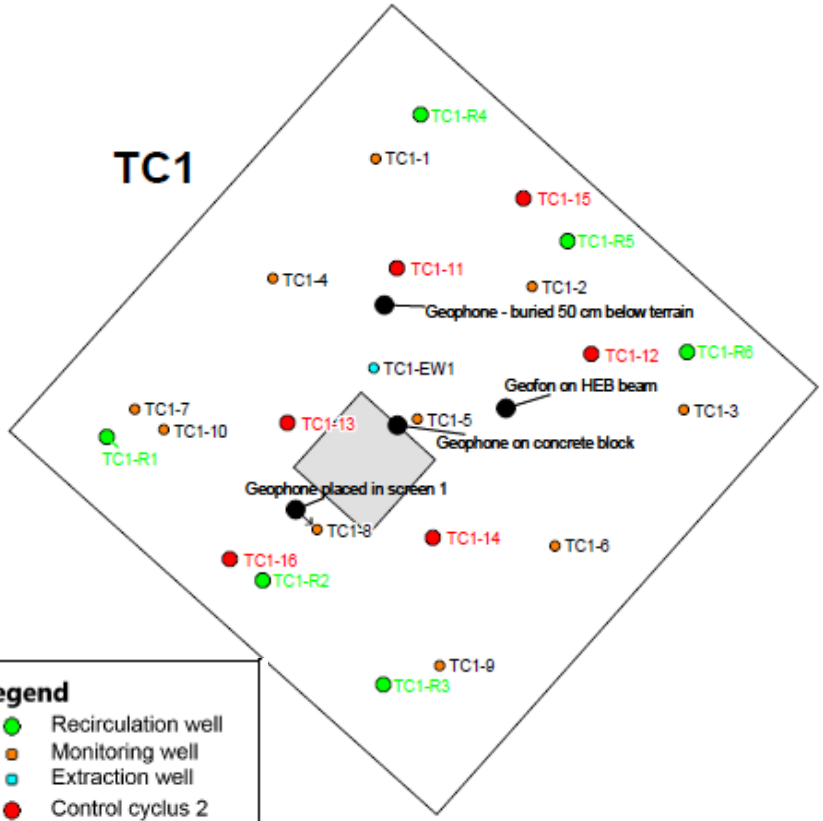
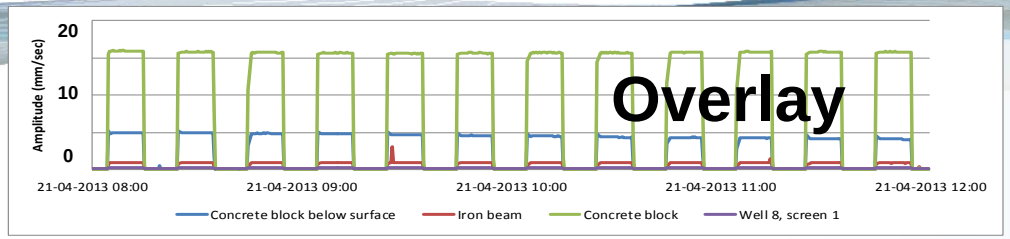
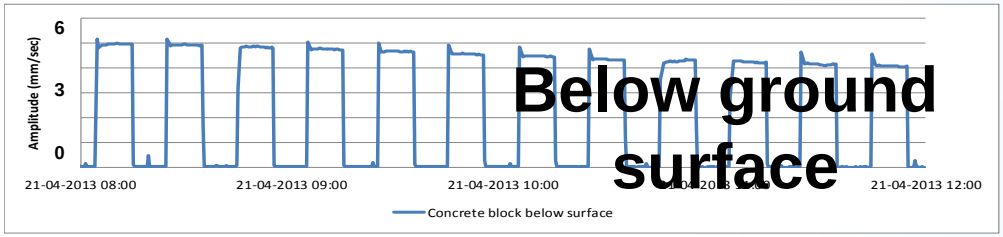
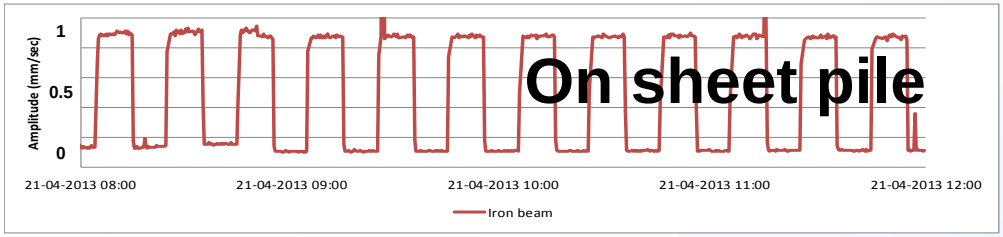
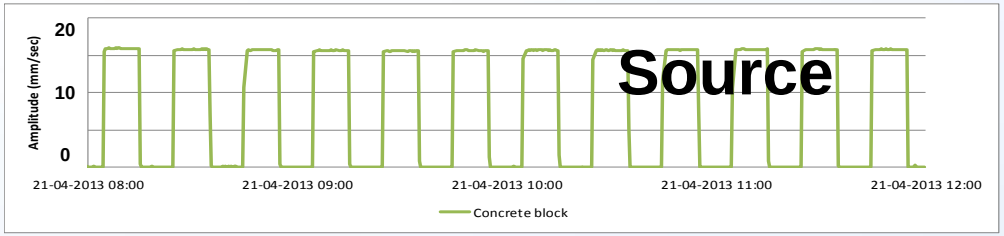
Propagation of Vibration

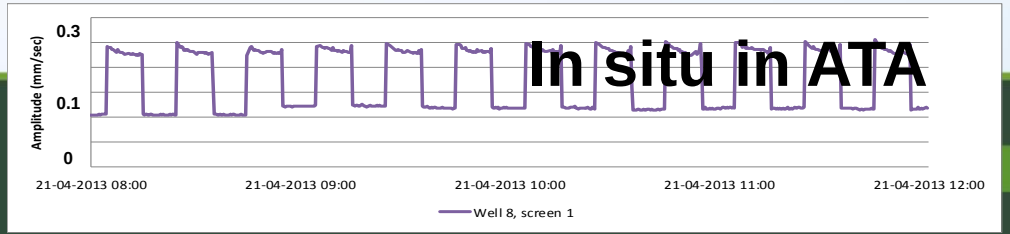












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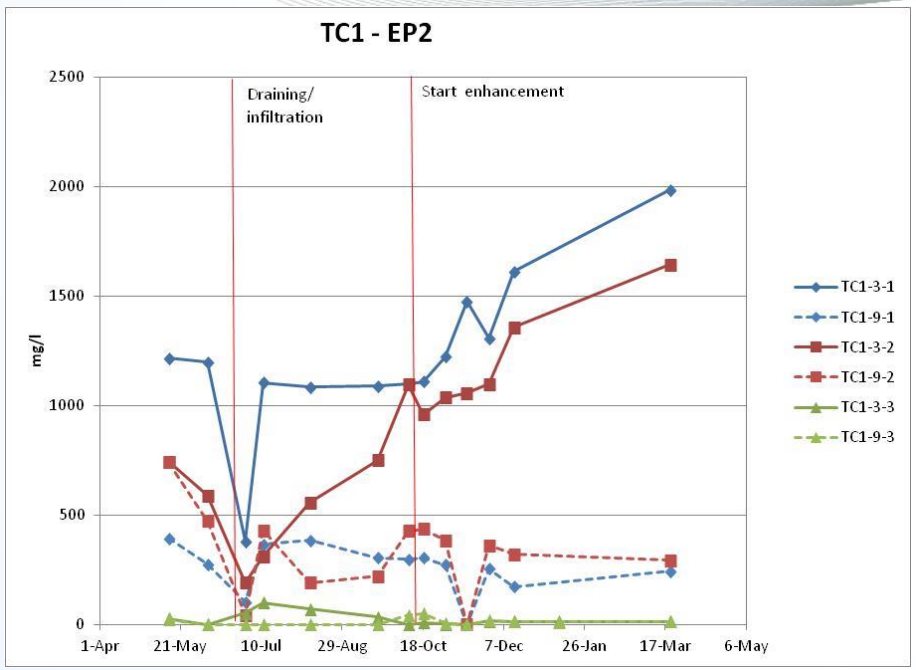
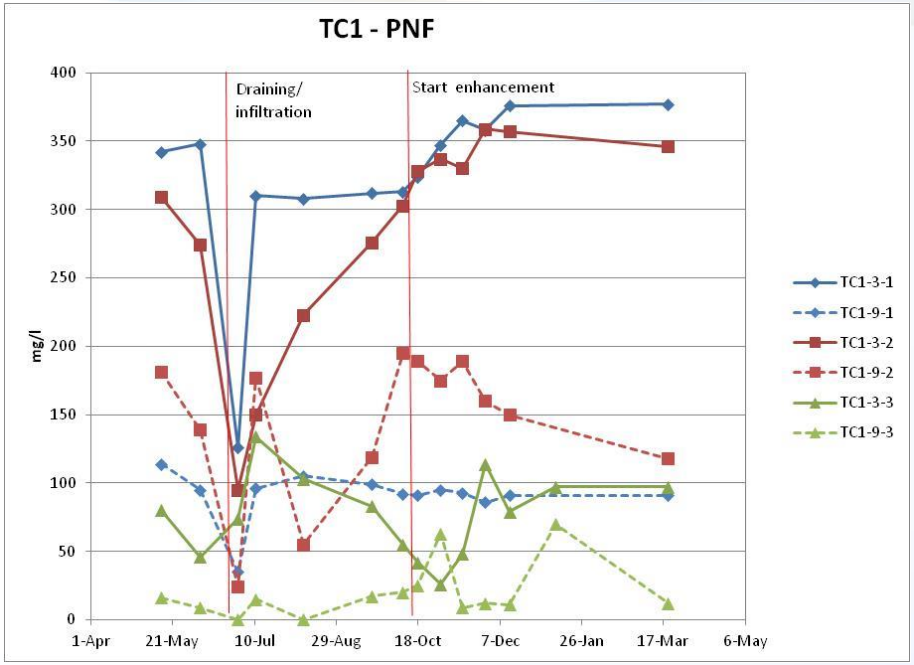
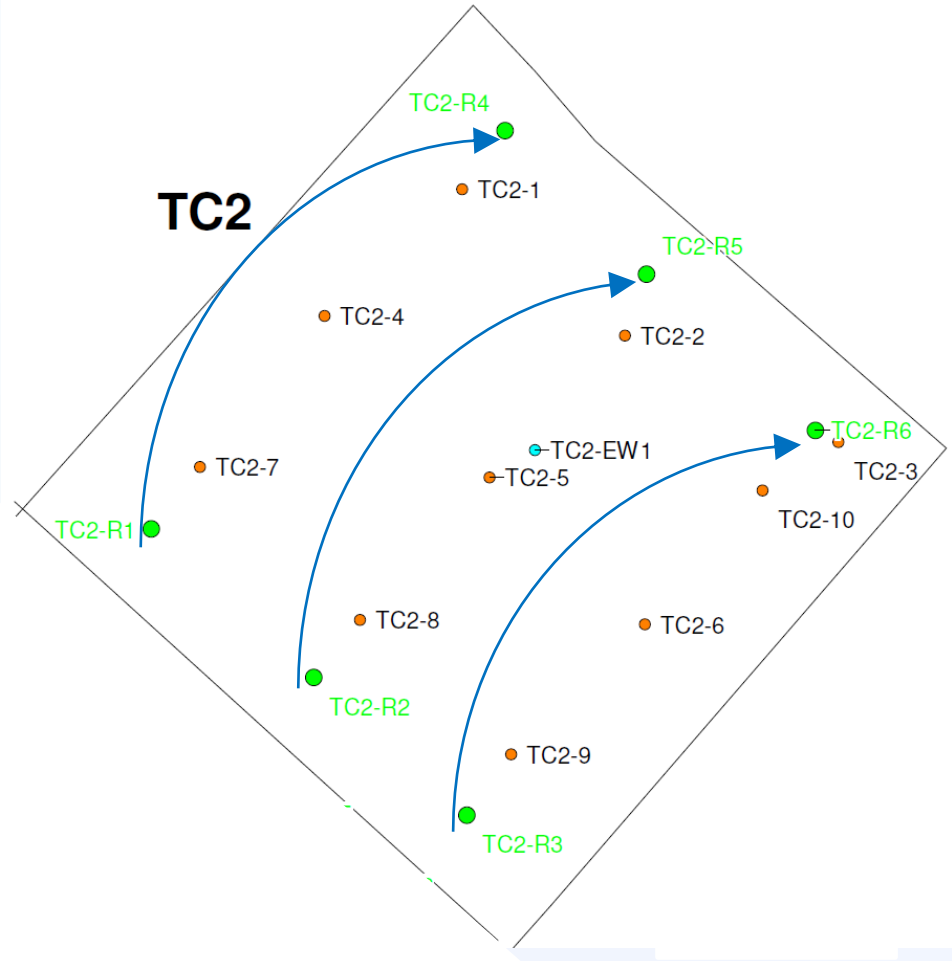
Vibration Results



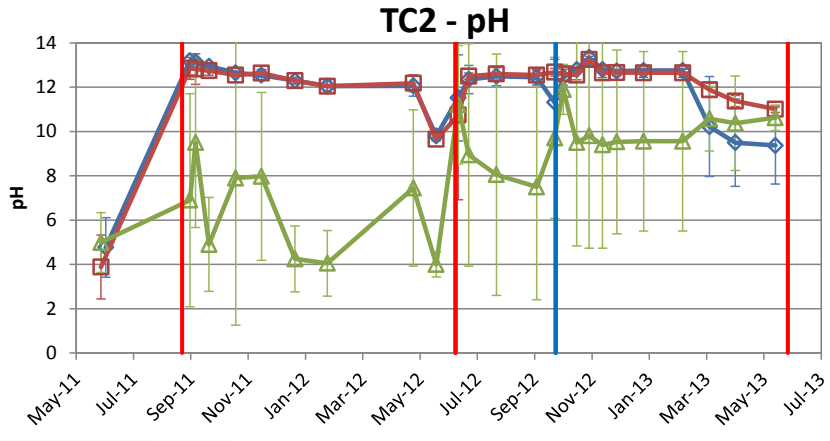


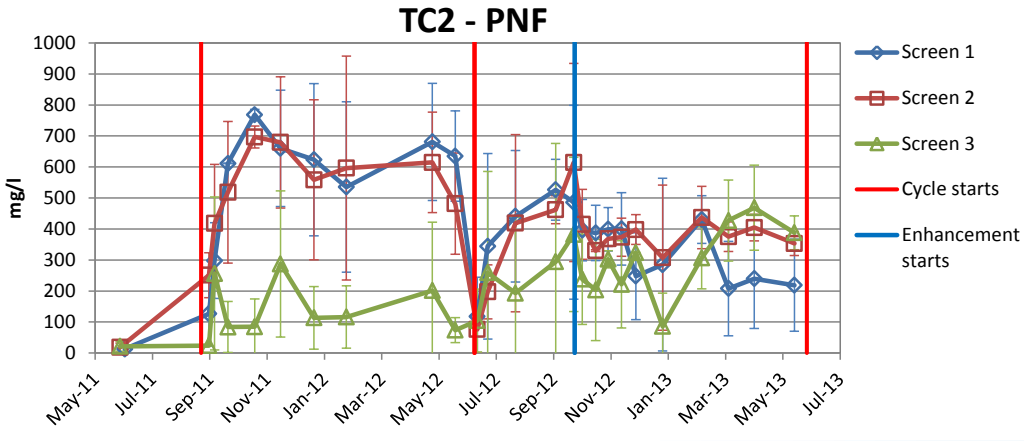
- ISAH lasted longer & at faster rates compared to Cycle 1
  - → mixing caused by vibration
  - → pH stayed in target range

Cycle 2: Recirculation

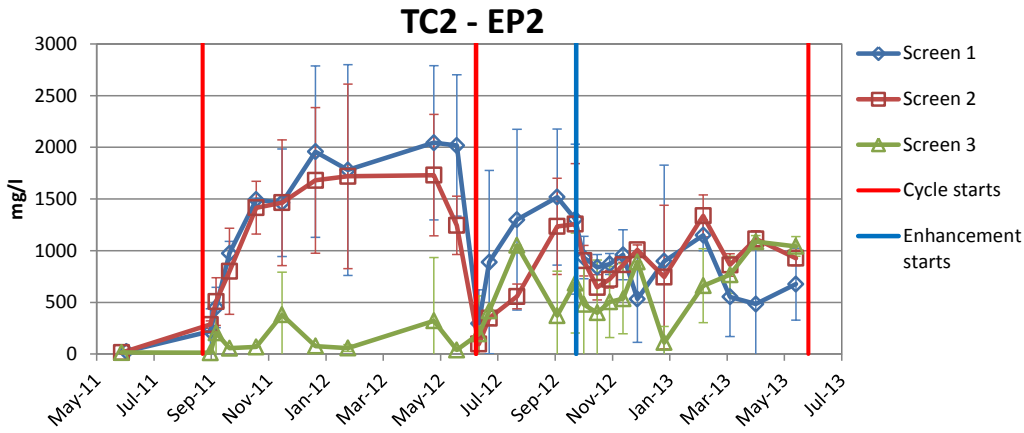


Recirculation Results

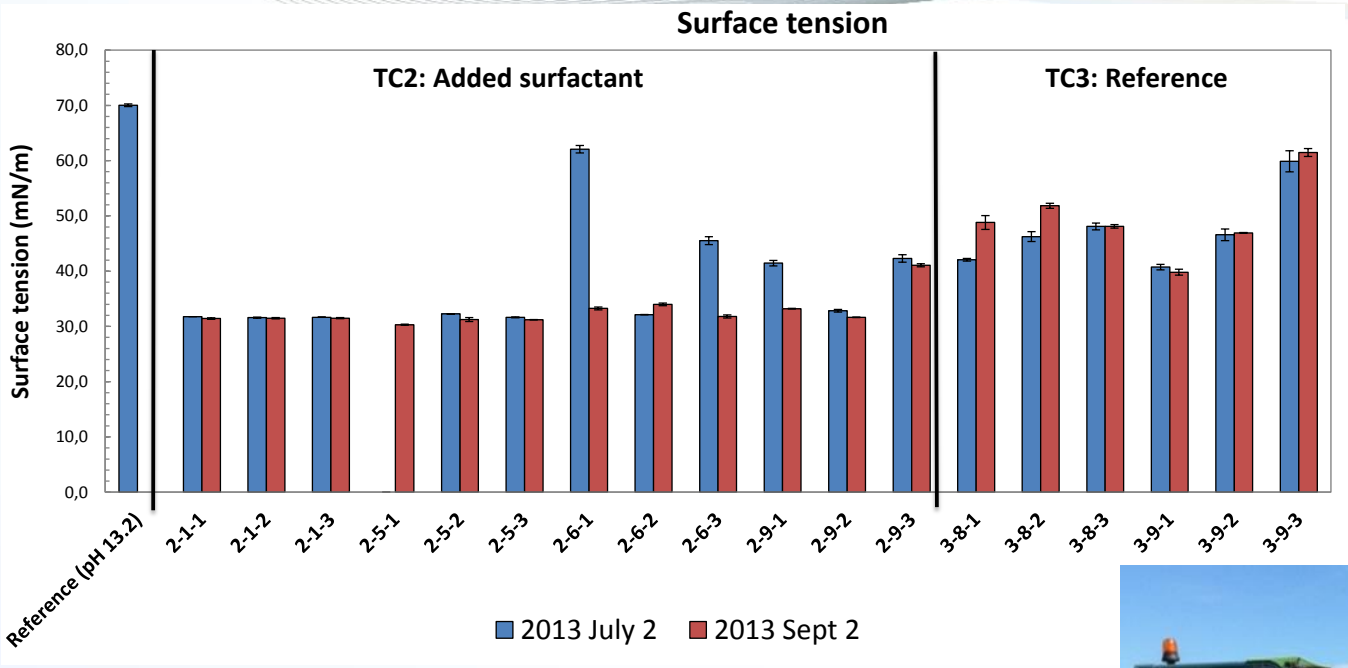




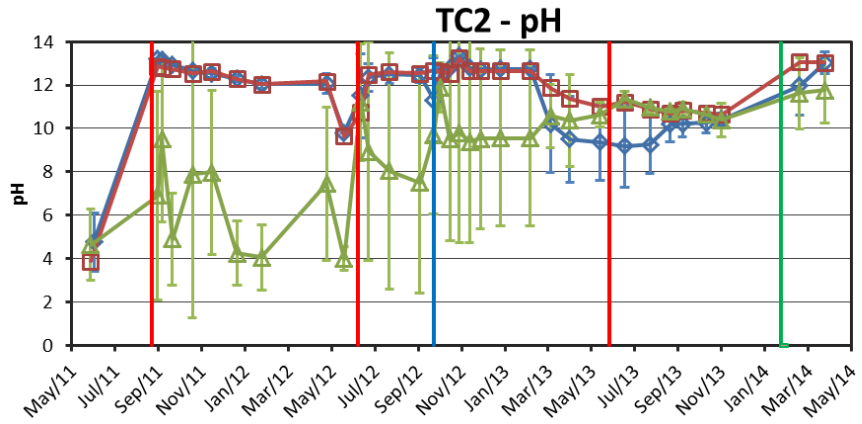
- NaOH, COC concentrations mix between depths
- pH decreases below target range

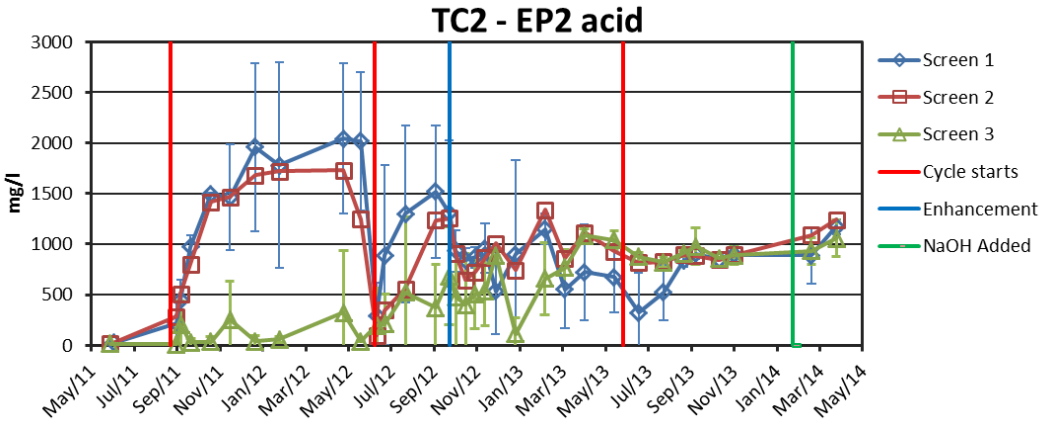


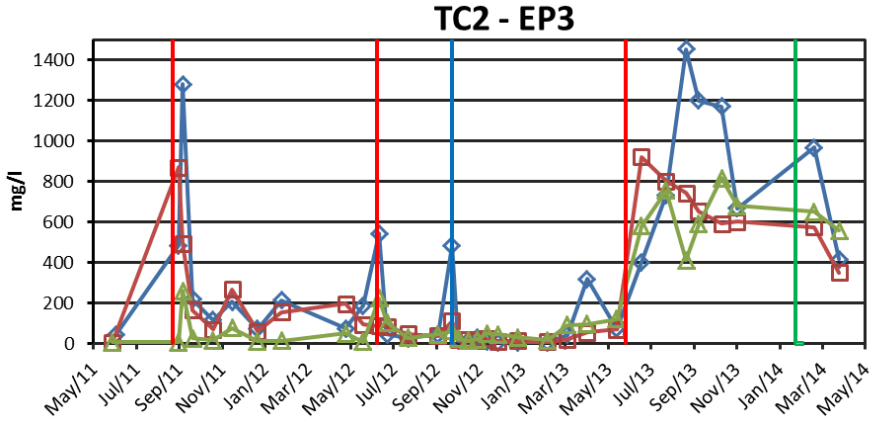
Cycle 3: Surfactant

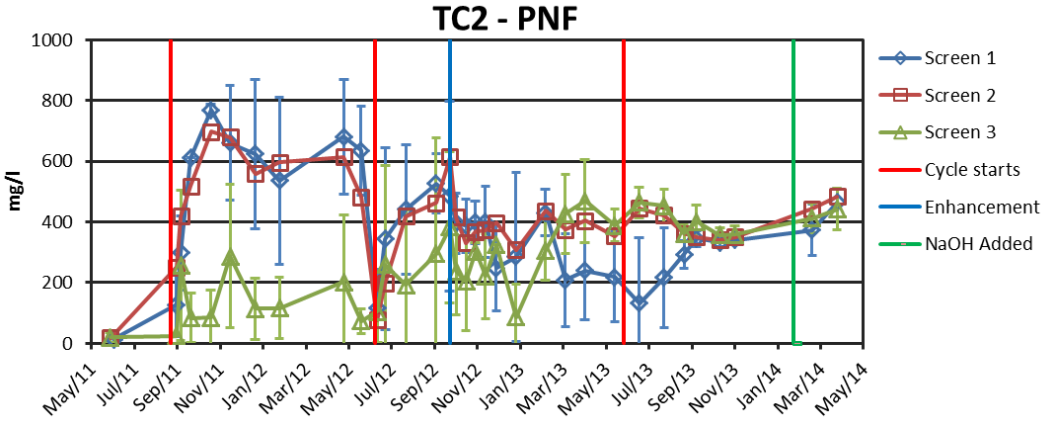


Surfactant - Results

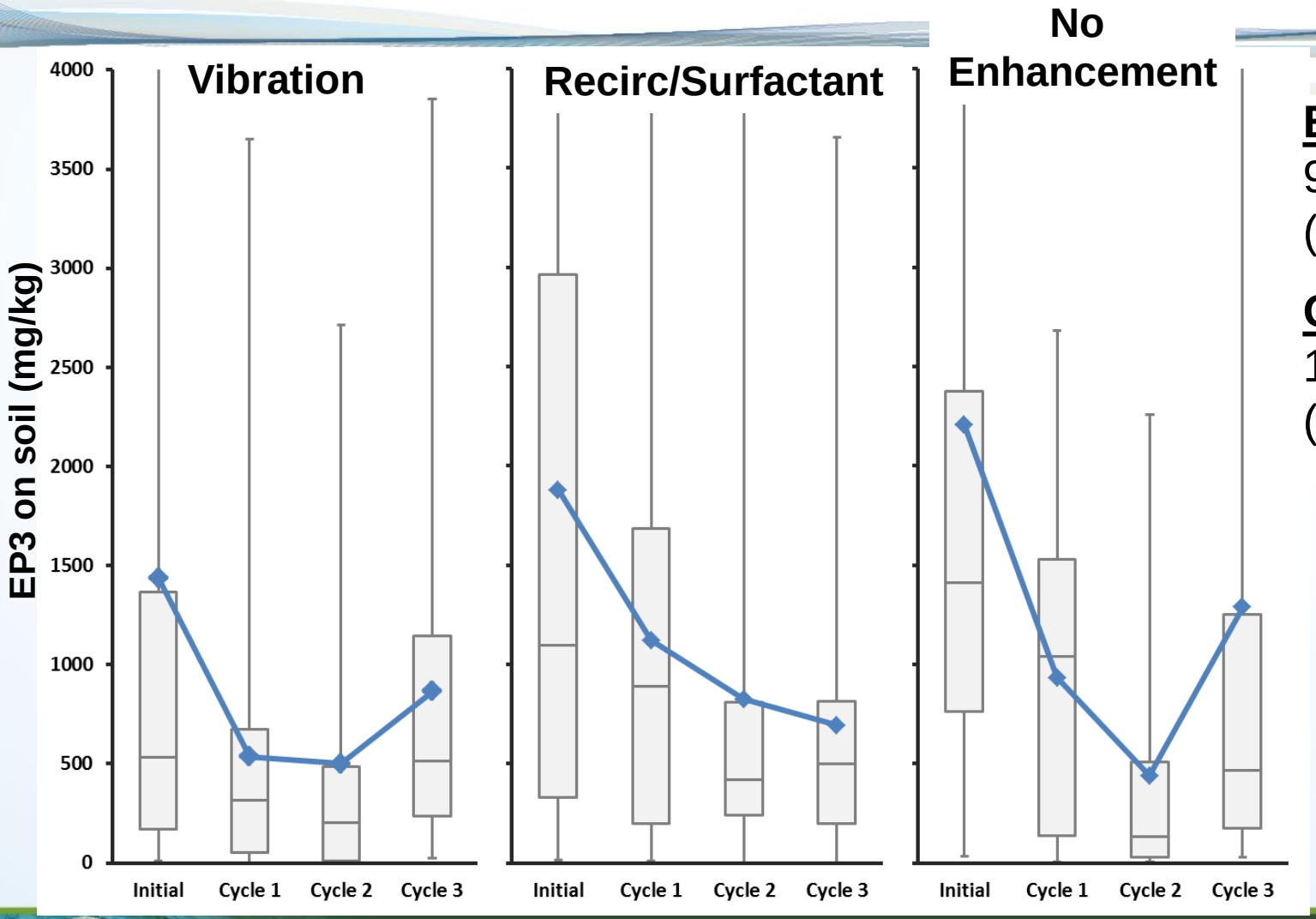








Mass estimates for EP3 in the ATA



EP3 Removed
99 to 309 kg
(20 to 60%)

OPP Removed:
179 to 497 kg
(41 to 68%)

Conclusions
Objective 1: ISAH Effectiveness

- Between 198 and 497 kg OPPs, (41% to 68%) of the estimated initial mass were removed over the three cycles by ISAH.

- Slower mass removal in later cycles, as most reactive OPPs and initial dissolved phase mass removed.

  →Mass transfer limitations.

Conclusions
Objective 2: Enhancement of ISAH

Vibration

- The vibration technology delivered vibration to the target depth & hydrolysis rates were enhanced over ISAH without enhancement.

Recirculation

- Recirculation provided mixing of NaOH and OPPs
- Rates limited due to pH less than target range

Recirculation and Surfactant

- Surfactant addition increased the dissolved concentration of the OPPs and reduced mass on soil
- Rates increase when pH increased to target range

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Questions?

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