INSURE

Innovative Sustainable Remediation

REPORT ABOUT SUITABILITY TESTS FOR PILOT AREAS

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EUROPEAN UNION
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Interreg
Central Baltic

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1. INTRODUCTION

Currently, the most commonly used treatment for contaminated areas is excavation, where contaminated masses are excavated and transported into landfills. Today there is a growing need to decrease the use of landfills. To minimize the transport of contaminated masses and to decrease costs and process-bound CO_2 emissions, sustainable *in situ* remediation alternatives have been developed.

The difficulty in analyzing the results from a field treatment is, that even if a control study has been conducted at similar conditions, and preferably still, at the same exact location, it is often difficult to determine whether the achieved effect can be attributed to the treatment alone. For a clearer perspective on the benefits, some key parameters can be modelled in laboratory or lycimeter scale test with sufficient amounts of replica and control treatments, in controlled environments. With these the effects of chosen parameters can in some cases be verified as being statistically significant, giving more credibility to phenomena seen on sites.

On the other hand, these test alone rarely give an exact picture of the situation in a pristine soil, since for example, carbon and oxygen availability are often greatly enhanced by the act of removing the soil from the source location. Similarly the scale itself is one parameter affecting the outcome of several phenomena, for example the Fenton's reaction, utilized in INSURE as a form of chemical oxidation. Generally, when an *in situ* application is studied, the technology itself can be tested only in proper scale, even when it is based on micro-scale phenomena. In optimal situation, a field study is therefore connected to piloting activity in different scales.

In project INSURE the methods studied by UHEL were

- Electrokinetic dispersal of biostimulation additives
- Hydrogen peroxide as a chemical and/or chemico-physical remediation method for volatile and non-volatile oil hydrocarbonds
- Methyl-β-cyclodextrin as a bioavailability enhancing product in biostimulation applications

2. ELECTROKINETIC REMEDIATION

Electrokinetic biostimulation was applied at three different INSURE sites, Villähde, Motala and Valmiera in different conditions in regards to the soil type and ground water level. During the later stages of these treatments, some of the phenomena seen at the site treatments were hoped to be accomplished also in the more controlled laboratory environment. These phenomena mostly concern movements of water and oil both in the non-saturated zone and below ground water level when electricity is applied.

2.1. Column tests with artificial dense soil in laboratory conditions

The intention of the tests was to simulate the situation underground and below the groundwater level in a situation similar to that of the Motala field test. The first simulation studies were executed by Johan Niemelä of the Lahti University of Applied Studies. The simulation was repeated during UHEL lab course in environmental biotechnology with modified procedure. Soil mixture containing 50% natural fine sand (0–4 mm) and 50% superfine clay type quartz sand was used. This sand was tested in short (ca. 20 cm) upright column and found to have a sufficiently low water permeability. The water level was found to ascend to the top of the sand column due to capillary forces when left standing in the water overnight. When a water column was added on top of the soil column, the water level sank by only 12 mm overnight.

Such dense soil mixture was used in tests, where elektrokinetic forces created by direct current (DC) electric field in the soil were used to pump water horizontally towards the cathode after adding water at the anode. Due to the low permeability of the soil, virtually no water movement takes place without elektrokinetic forces, but with DC electricity applied, the water readily travels towards the anode. In field conditions, the intention with this technique is to introduce nutrient rich water into the contaminated soil, but in Motala also movement of oil was observed. The working hypothesis with lab tests was that the water flow mobilized the oil adsorbed to the soil and pushed it in the direction of the water flow, that is, towards the cathode, while also moving towards the water surface. The hypohtesis was tested by comparing horizontal tubes with fluorescently labelled oil adsorbed to saw dust. DC was applied to one of these tubes while the other served as a control.

A 60 cm tube with an inner diameter of 54 mm was filled with the same soil mixture. The tube was capped with a fine membrane fabric attached to one end of the tube. The filled tube was left to stand in water to soak up water by capillary forces for two nights. The grey 90° bends were attached to the tube ends and these bends were filled with same soil mixture. Water was added to the bends and the tube was applied vertically. The left grey bend was filled with water and the other was partly drained, and the setup was left standing over night. During that time no water had been moving through the column.

Saw dust with oil and fluorescent oil stain was added through a hole in the middle of the tube. The same was done with saw dust stained with water soluble, non-fluorescent Sudan IV stain, and the setup was left to settle overnight. The tube was applied with the hole facing sideways, leaving the upper side of the tube free for inspection.

An electric field was then introduced: A 300 V (ca 5 V/cm) voltage resulted in a 4–6 mA current. Pictures were taken with and without UV light for showing the fluorescent and non-fluorescent dyes, respectively. Water motion was from left to right, towards the cathode. The overflow from the right grey bend was collected in a decanter, and more water was added to the left-side bend.

After a run of ca 40 hours, 250 mL of water had been collected in the decanter. During that time, the water-soluble dye (apparently negatively charged) had moved towards the anode, whereas the fluorescent dye had spread towards the cathode, at most ca 12 cm (Figure 2.1). The oil had also spread somewhat sideways into the column material. Thus, the simulation supported the explanation of the phenomena observed in the field experiment, that is, that oil does indeed travel with the water flow in the direction of the cathode. Due to its polarity, the water-soluble dye travelled according to its charge towards the anode and did not reflect the movement of water.

The column was shaken out from the tube, and the column material was sliced into 8 sectors. New picture was taken with and without UV light. The fluorescence was even brighter without the tube. Part of each sector was taken as a sample.

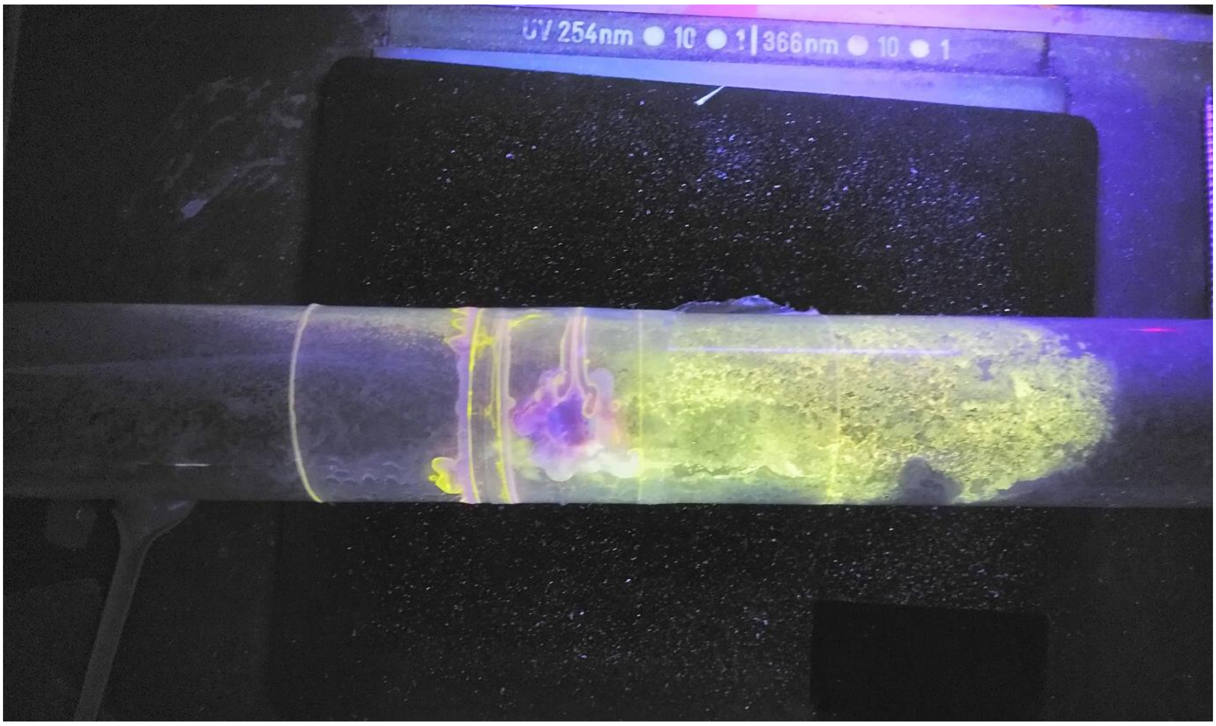

Figure 2.1. Oil dyed with fluorescent dye spreading towards the cathode (yellow), at most ca 12 cm. Point of addition of dye is the violet spot in the middle of the picture.

2.2. Tests using soil from Motala

A rectangular box was filled with oil-contaminated soil samples from the Motala site. Thin plastic hoses were attached to the holes at the both ends of the vessel, near the soil surface, to collect any water accumulated on the cathode side. The anode side was used as a control.

Fluorescein (1 g of dye, 15 ml of water) and diesel dyed with oil-soluble dye were absorbed into sawdust, which was added a few centimeters below the soil, in the middle of the vessel (25 cm from the ends). The soil was then irrigated with 2 mM phosphate buffer, with a volume of about 900 ml. The system was left to become soaked with water for a weekend. The experimental setup (electricity connected) is shown in Figure 2.2.

After the weekend, the soil had sunk a few centimeters, resulting in the holes in the top being exposed. Thus, new holes were drilled below the surface. Then the soil was examined under UV light. Fluorescein had slightly spread while the oil dye was approximately in the same shape and size as it was in the start of the experiment (Figure 2.3). The height of the contamination was about 5 cm and its length was 10 cm; 4 cm towards the anode and six cm towards the cathode. Less movement occurred vertically, however, dyed oil could be observed to move downwards and slightly upwards.

In addition, about 100 ml of water was accumulated in a beaker on the cathode side. This water was poured out and the test vessel was straightened with a spirit level. Electricity was connected in the afternoon, and with 20 V, five mA electric current was formed. One hour later, the electric current had remained unchanged, and about 50 ml of water had accumulated in a beaker on the cathode side. The next day, about 50 ml of water was still on the cathode side. Artificial pollution had spread in both directions; about 7 cm towards the anode and about 10 cm towards the cathode. In addition, small amounts of dyed oil were detected on top of the soil (Figure 2.4). 50 ml of water was added to the vessel evenly using a pipette to compensate the loss of water.

During the next three days, no significant changes in location of the contaminant were detected. Water was still accumulating on the cathode side and a total 100 ml of water was added. The experiment was finished after four days. At the end of the experiment, pH was measured using pH strips. On the anode side, pH was decreased to 3 while on the cathode pH was 9. Fluorescein was observed to have disappeared almost completely from the soil; small amounts were observed in water layer on the soil. Larger amounts of were found in beakers, particularly on the cathode side (Figure 2.5).

About 1.5 weeks later, the test was re-started. 900 ml of water was added to the vessel to soak the dry parts of the soil. When the soil was completely soaked, electricity was turned on. At 20 V, five mA electric current was again produced. Before reconnecting the electricity, the dimensions of the contamination were 19 cm at its widest and 12 cm at its highest (ca 3 cm up, 9 cm downwards). Over the next two days, there was no significant change in these dimensions. As in the previous experiment, water was accumulated on the cathode side, this time in volume of only about 5 ml. The extent of the contamination at the end of the experiment is shown in Figure 2.6.

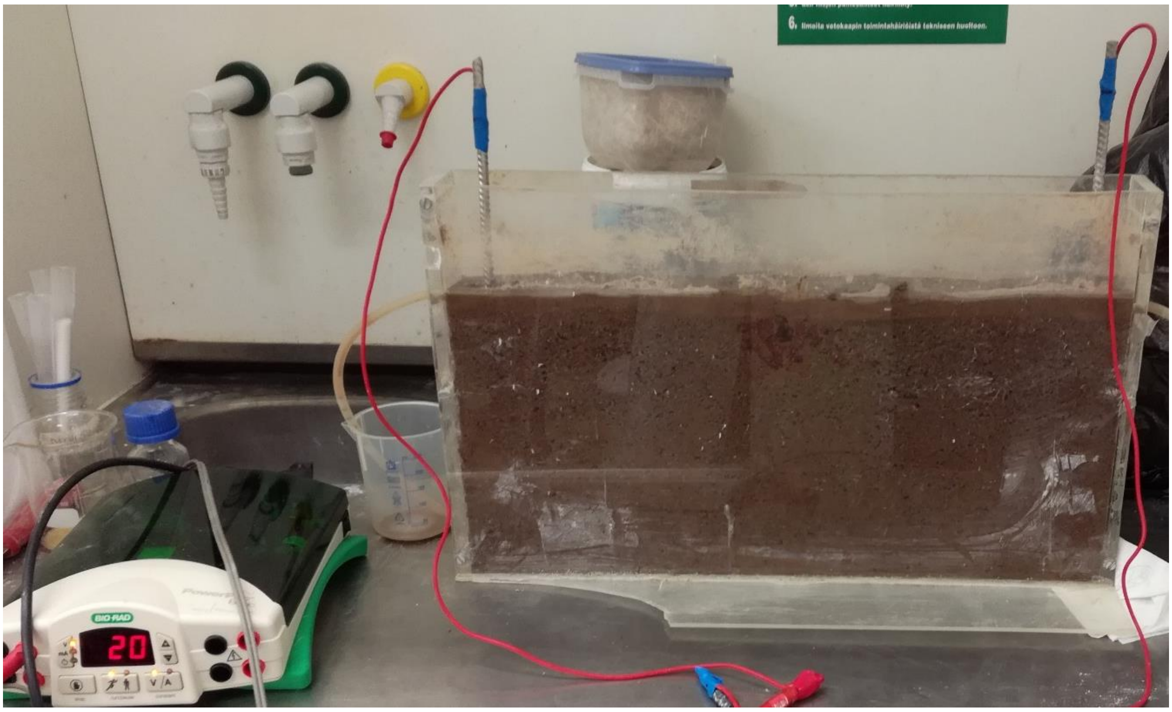

Figure 2.2. An experimental setup of laboratory modeling. On the left is the anode side and on the right is the cathode side.

Figure 2.3. Situation before switching on the electric current - the greenish water-soluble color had started to spread, whereas the oil color had mainly remained in place. The injection spot is marked with the red circle.

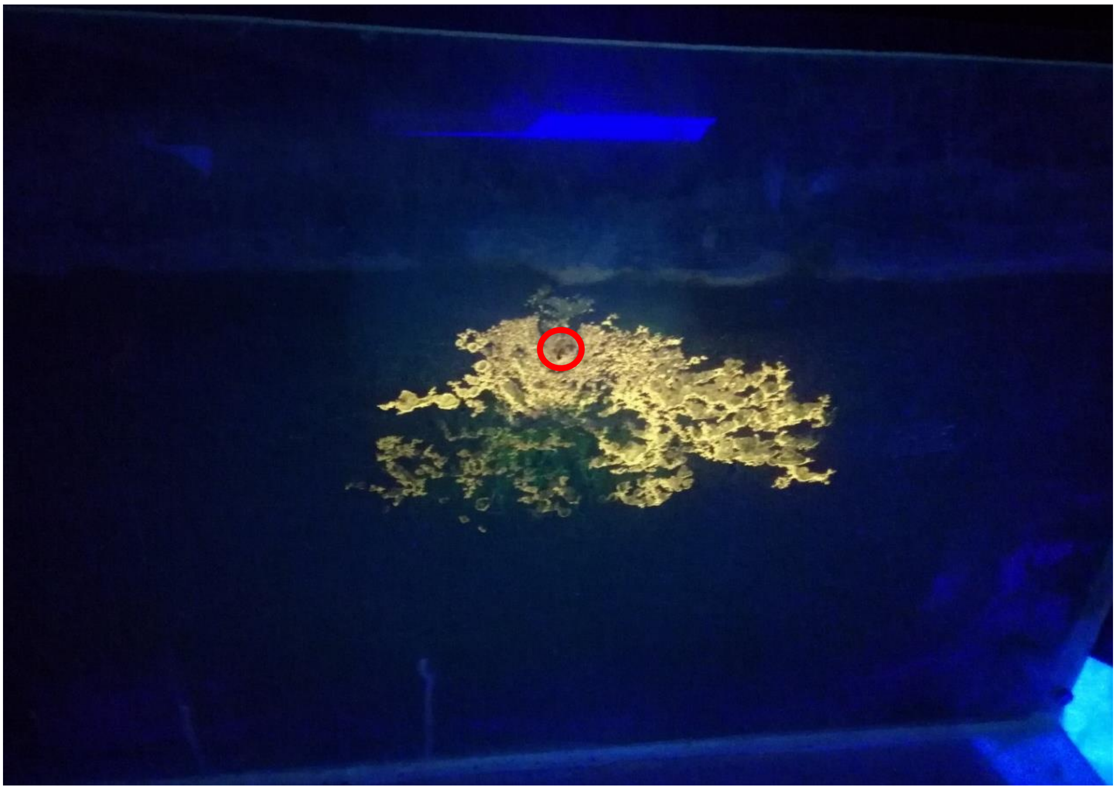

Figure 2.4. A day after the connection of electricity, the artificial pollution was found to have spread in both directions; about 7 cm towards the anode and about 10 cm towards the cathode. The injection spot is marked with the red circle. Small amounts of dyed oil can be seen on top of the soil.

Figure 2.5. During the experiment, more water was accumulated on the cathode side (on the right) and the color of it was more fluorescent than the color of water accumulated on the anode side (left).

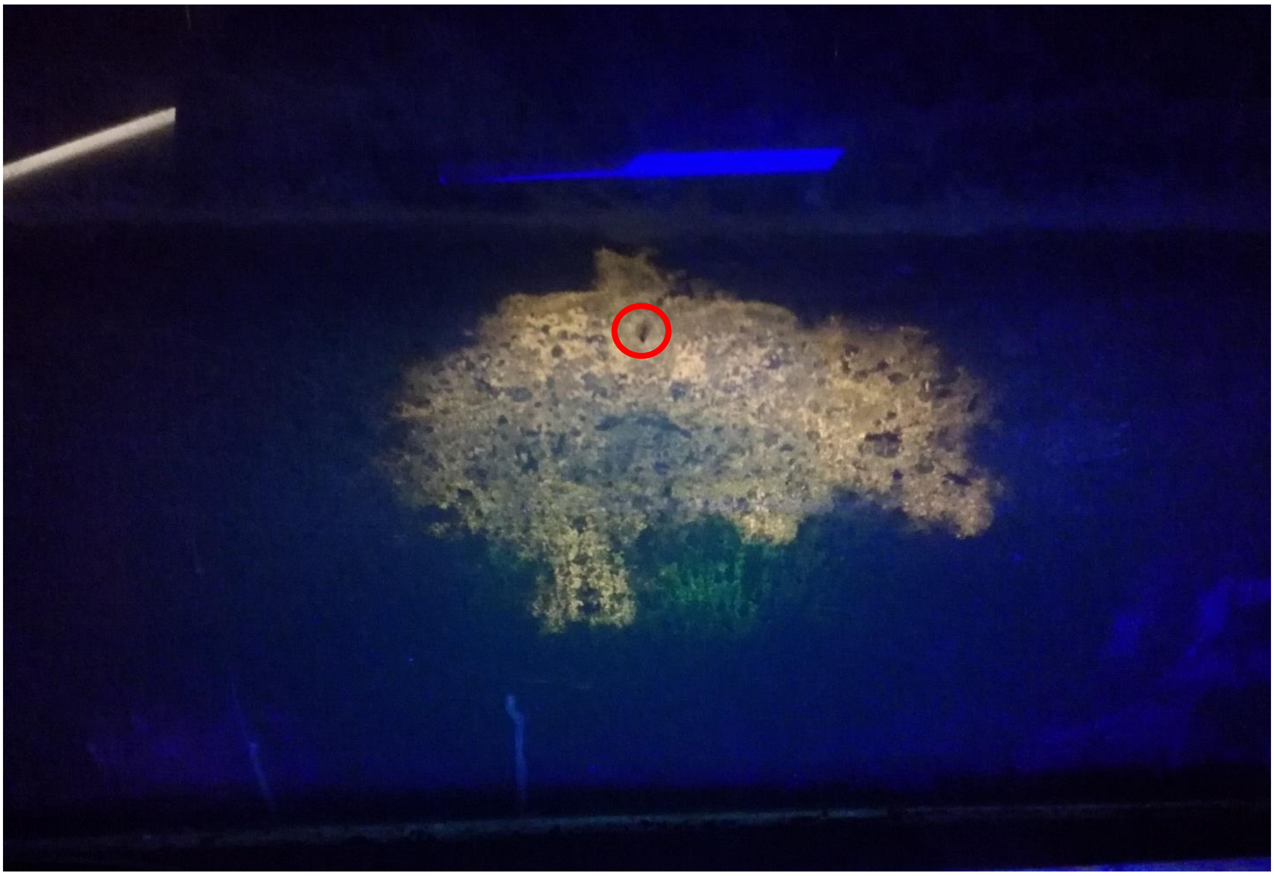

Figure 2.6. The situation after the end of experiment. The maximum width of the contaminated zone was 19 cm and the height was 12 cm. The injection spot is marked with the red circle.

2.3. Tests utilizing artificial soil

The experiment was performed in a smaller vessel (length 18 cm, height 19 cm, width 0.7 cm). A mixture of superfine clay type quartz sand and natural sand, in 50:50 ratio, was used as the soil. Water was added to the vessel with a pipette so that the soil was wet throughout. In the center of the vessel, over 5 cm below the surface, dyed sawdust was added. The same dyes were used as in the previous experiment.

Copper wires were placed at the ends of the vessel as electrodes. The system was then switched on and 8 mA electric current was generated at 50 V. In the following morning, the voltage was increased to 100 volts, producing 5 mA current. The experiment was ended 24 hours after the start of the experiment. Fluorescein was found to have moved towards the cathode while the oil color remained mainly in place.

The problem with the experiment was that the water passing through vessel towards the cathode could not be discharged from the vessel, which in turn might have affected also the migration of the oil. Possibly with some filtering material at both ends of the vessel, water could have absorbed into it, thus enabling better movement of oil.

Figure 2.7. The situation before the start of experiment.

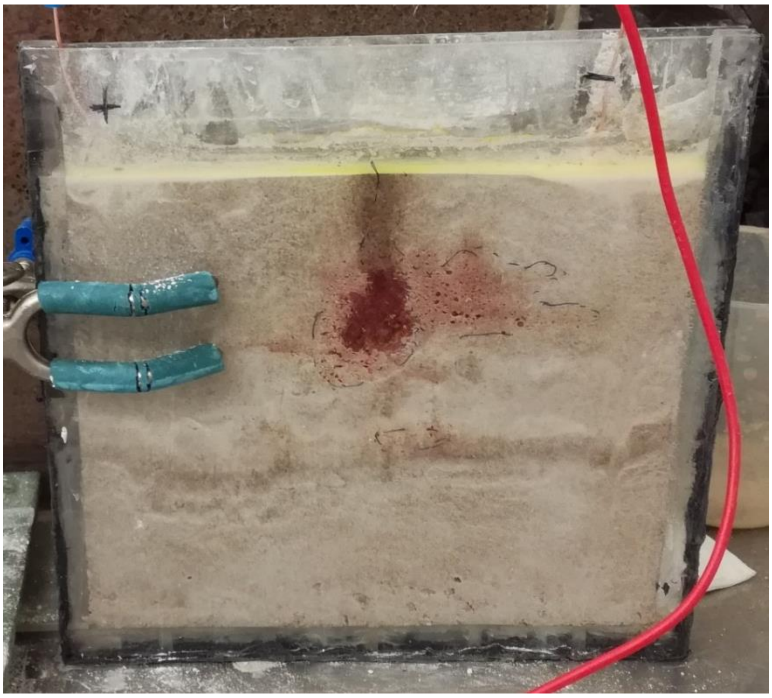

Figure 2.8. The situation immediately after switching on the electricity. The water-soluble fluorescein (yellow color) had migrated towards the surface. The spreading before electricity has been marked with a black dashed line.

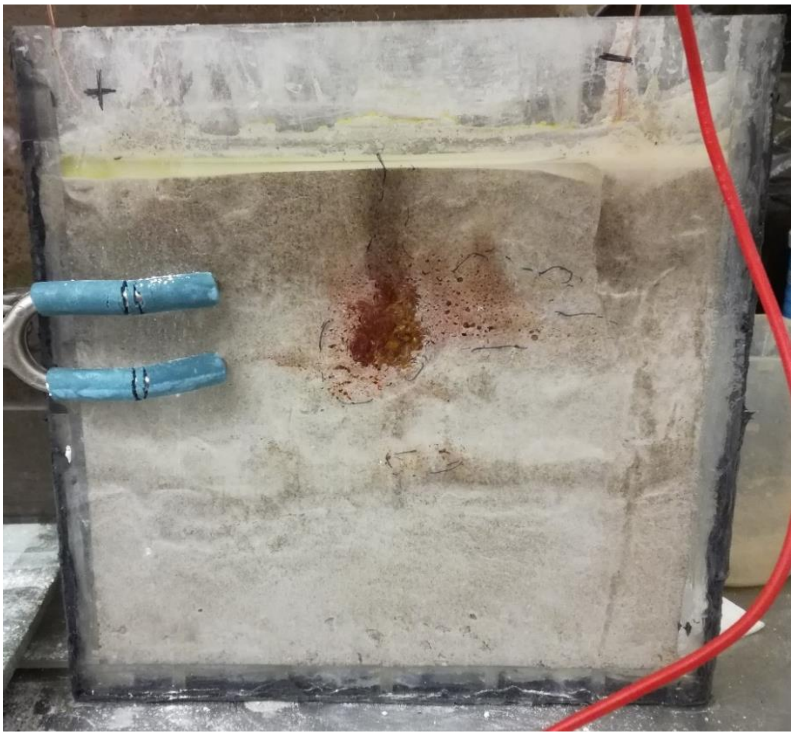

Figure 2.9. The situation about an hour after switching on the electricity. Fluorescein had moved towards the cathode, while the oil (red) had remained mainly in place, except for the right (anode) end, where the red color is slightly reduced.

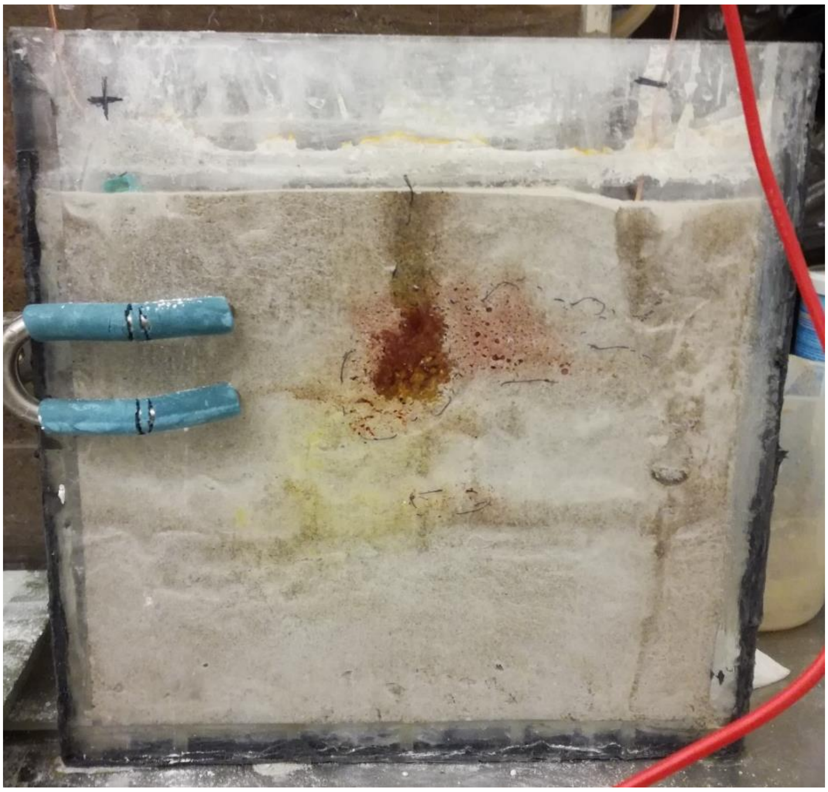

Figure 2.10. Situation after about 24 hours. Fluorescein has clearly moved towards the cathode, while the oil contamination has still remained in place.

3. CHEMICAL OXIDATION

3.1. Lab-scale tests

In remediation hydrogen peroxide (H_2O_2) can be utilized as a chemical oxidant that degrades organic compounds through the so-called Fenton’s reaction or rather, string of reactions. In this reaction the breakdown of hydrogen peroxide is catalyzed by iron salt or mineral iron in the soil, and reactive radicals are formed. For the radical producing reaction to happen in sufficient efficiency, iron needs to be dissolved in the aqueous phase, and this condition is only met in acidic pH. The pH range in which the catalytic iron in soluble in water can however be expanded by adding chelating agents such as citrate into the soil.

Regardless of the reaction route, breakdown of H_2O_2 in water or soil may increase volatilization of volatile contaminants, which should mean that H_2O_2 could be utilized as a physical form of remediation for these particular compounds. Whether the primary reaction mechanism is chemical or physical may play a minor role in cases when vapors are able to exit the non-saturated soil, and when only volatile compounds are present. On the other hand, if also non-volatile fractions are present, which is often the case, treatment through the physical mechanism cannot be seen as the optimal solution.

In several laboratory and lysimeter scale studies, it was determined whether chemico-physical H_2O_2 treatment would be a sufficient method for removal of VOCs from the groundwater, and how non-volatile fractions of diesel would react in similar circumstances. In addition, the effect of chelating citrate on chemical oxidation of aged diesel contaminated soil was studied in the lysimeter scale.

3.1.1. Laboratory scale tests with natural waters received from Nastola and Motala.

A water sample from Nastola from an area contaminated with gasoline and a sample from Motala from underneath a chemical cleaning facility, with high concentration of tri-chloro ethylene, were used for testing the applicability of the H_2O_2 method on VOCs in the aqueous media trapped in the pore space of soil.

Dry quartz sand was weighed into decanter glasses with 20 M of Fe(III)sulfate added as the catalyst and the water was then added. The ratio between water and solid phases was the same in both tests, whereas the volumes themselves differed (2 l / 10 l in the gasoline test 1.2 l to 6 l in the TCE test). The effect of a 2 M dose of H_2O_2 on contaminant removal was compared to that in a control treatment with only the water added. With the gasoline contaminated water, also H_2O_2 concentrations of 0.5 M and 1 M were tested, and the water also when appearing as a free water phase. In each case samples were withdrawn after 20+ hours since the H_2O_2 addition, when the reaction had waned and no gas was being produced.

All samples were analysed at Eurofins according to the standard methods mod. ISO 11423-1 and mod. EN ISO 10301 utilizing HS/GC/MS.

3.1.2. Results

Results indicated a successful removal of the contaminant for all gasoline components already with a 0.4 M dose of H_2O_2 (Table 3.1). Due to the higher contamination level in the Motala water, end concentrations for trichloroethylene were still above LOQ-level with the full 2 M dose of peroxide. In general, it was found that the method was applicable for a wide range of VOCs, regardless of their molecular weight. According to these results, similar method would in principle be applicable for both sites in question.

Table 3.1 Results from the tests with natural water samples from Nastola and Motala. Trichloroethylene was the sole component present in the Motala samples, listed last under the category of halogenated compounds.

		original	c(H2O2) seperate water phase				water in pore space	
			0 M	0,4 M	1 M	2 M	0 M	2 M
	compound				c (µg/l)			
Aromatic	benzene	2	4	<0,1	<0,1	<0,1	1	<0,1
	toluene	130	250	<1	<1	<1	69	<1
	Ethylbenzene	79	120	<0,1	<0,1	<0,1	3	<0,1
	m+p-xylene	130	230	<0,1	<0,1	<0,1	170	<0,1
	o-xyleeni	120	200	<0,1	<0,1	<0,1	140	<0,1
	n-propylbenzene	<0,1	0,3	<0,1	<0,1	<0,1	<0,1	<0,1
	isopropylbenzene	0,2	0,2	<0,1	<0,1	<0,1	<0,1	<0,1
	2-ethyltoluene	10	14	<0,1	<0,1	<0,1	10	<0,1
	3-ethyltoluene	10	15	<0,1	<0,1	<0,1	12	<0,1
	4-ethyltoluene	7	11	<0,1	<0,1	<0,1	7	<0,1
	1,2,3-trimethylbenzene	8	12	<0,1	<0,1	<0,1	10	<0,1
	1,3,5-trimethylbenzene	1	13	<0,1	<0,1	<0,1	8	<0,1
	1,2,3,5-tetramethylbenzene	2	3	<0,1	<0,1	<0,1	2	<0,1
	1,2,4,5-tetramethylbenzene	1	2	<0,1	<0,1	<0,1	1	<0,1
	naphtalene	2	3	<0,5	<0,5	<0,5	5	<0,5
Ethers								
	MTBE	2	3	<0,1	<0,1	<0,1	3	<0,1
	TAME	1	1	<0,1	<0,1	<0,1	0,6	<0,1
Aliphatic								
	2-methylpentane	4	4	<1	<1	<1	2	<1
	3-methylpentane	3	3	<1	<1	<1	<1	<1
	methyl-cyklopentane	2	3	<0,5	<0,5	<0,5	1	<0,5
	cyclohexane	1	2	<0,5	<0,5	<0,5	0,7	<0,5
Halogenated	1,2-dibromoethane	1	1	<0,1	<0,1	<0,1	1	<0,1
		original	c(H2O2) seperate water phase				water in pore space	
							0M	1 M
					c (µg/l)			
	trichloroethylene	3700					310	2

3.2.1. VOC composition test

The validity of the PID-method was tested with methyl tetra butyl ether (MTBE) spiked pore water,. MTBE was chosen as the target compound because of its environmental relevance but also because of its high water solubility and therefore, low amount of the contaminant appearing as non-aqueous phase liquid (NAPL).

To detect whether contaminant removal was primarily happening through volatilization rather than chemical oxidation, concentrations of MTBE, as well as its possible chemical breakdown products, both in the gaseous and the aqueous phases were monitored.

The treatment with 5 M concentration of H_2O_2, both with and without the 20 mM Fe(III)sulfate catalyst was compared with plain water control. Gaseous samples were withdrawn 15 minutes, 60 minutes and 240 minutes after the peroxide injection. Absorbent collector Anasorb 747, SKC 226-81A coupled with a Markes Acti-Voc pump was used for this sampling. A different 20 liter PVP bucket was used for each measurement to limit the transport of vapors. Water samples were withdrawn 20+ hours after the injection, due to gas producing reactions still taking place after 240 minutes.

The absorbent sample and the water were analyzed at the accredited laboratory Eurofinns according to standard methods ISO11423-1 and ISO20595. The absorbent collector was analyzed gas chromatographically at the Finnish Institute of Occupational Health, with the accredited method KEMIA-TY-006.

3.2.2. Results

The results indicated that the balance between reaction mechanisms was altered by addition of catalyst in regards to breakdown products of MTBE, aceton and Tetra butyl formate (TBF). This was likely because of the pH lowering effect of the catalyst addition. With added catalyst, no peak in volatilization was detected, which would suggest that reductions were related to the chemical mineralization occurring. These breakdown products were also detected in higher doses than in the soil mineral catalysed treatment. In the latter case volatilization couldn't be ruled out either, but its role in the total removal of MTBE was by comparison only moderate, as without the added catalyst heightened volatilization was documented and found adding to the removal efficiency during the initial stages (Table 3.2).

Table 3.2. Concentrations of MTBE and its breakdown products in the gaseous and aqueous phases in the tested treatments. The percentage corresponding with MTBE concentration in headspace relates to the mass added in the beginning.

		ambient headspace				water	
		C9-C11					
	time	**cyclical**	**MTBE**	**TBF**	**Acetone**	**MTBE**	**Acetone**
		mg/m3	mg/m3	mg/m3		(µg/l)	(mg/l)
5 M H_2O_2+	15 min	<0.3	120 (5%)	10	<1		
20 mM Fe(III)SO_4	60 min	<0.3	94 (4%)	14	<1		
	240 min	<0.3	1,8 (0,1%)	1.9	<1		
	>20 h					<0.5	1.0
5 M H_2O_2	15 min	<0.3	430 (18%)	<0.6	<1		
	60 min	<0.3	320 (13%)	<0.6	<1		
	240 min	<0.3	160 (7%)	1.6	<1		
	>20 h	<0.3	7,6 (0,3%)	2.8	1,9	8.8	1.8
Control	15 min	0	160 (7%)	<0.6	<1		
	60 min	0	240 (10%)	<0.6	<1		
	240 min	2.9	290 (12%)	<0.6	<1		
	>20 h					7700	<0.05

These results indicate that in the previous test, chemical mineralization had been the primary reduction mechanism. The situation would therefore be somewhat different on field, where additional catalysts would not be added and the soil pH would in most cases be closer to neutral. With positive results also from the test without added catalyst, natural soil pH treatment would still allow for considerable reductions of volatile contaminants, and in these cases the total effect would be achieved by combination of both the chemical and physical removal mechanisms.

3.3.1 MTBE spiked water lysimeter test

Pilot-scale tests for MTBE contaminated water was performed in $2m^2$ metal lysimeters at SOILIA field research station. Water spiked with MTBE (750 mg/l) was treated as a separate water phase and also as pore water withheld in a $1m^3$ column of soil (Figure 3.1.). In the free water phase test water was poured into the lysimeters, after which the MTBE, and then the H_2O_2 and was added in 1 M H_2O_2 concentration. In the control study, the volume of peroxide was compensated by a corresponding volume of water. The total volume of the aqueous phase was 400 l. Fe(III) in concentration 2 mM to total volume was used as the catalyst.

Samples were taken by bucket every 24 hours until peroxide concentration was measured to have fell below 0.0%. PID values and temperatures were recorded at the time of each sampling. During the first hours after the addition, the on-going reaction prevented samples from being analyzed.

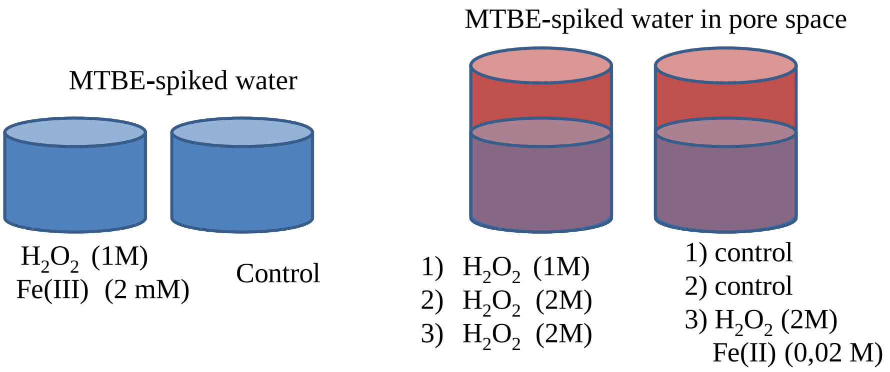

Figure 3.1. The test setup for the MTBE spiked water treatment in free water and pore water phases.

In the soil experiment MTBE spiked water was poured into the soil columns, with or without peroxide. Water samples were withdrawn from the bottom valves of the lysimeters and PID values and soil temperature were measured from 0.5-1 m deep holes in the soil column. As with the water experiment, samples with viable gas forming were not analyzed.

The experiment consisted of three steps (Figure 3.1). During the first step H_2O_2 was added in concentration 1 M per total aqueous phase volume, of which 50 % was in the soil originally, the concentration thus corresponding with that in the free water phase experiment. During the next two steps peroxide concentration was doubled to 2 M to total volume. The total aqueous phase volume increased after each step by 40 liters of further peroxide and corresponding H_2O_2 additions and also new MTBE was therefore added. After two steps the addition of H_2O_2 in concentration of 2 M to total volume was repeated, while the control treatment was replaced with a test with similar peroxide addition but with an additional iron(II) catalyst added in dose 20 mM . At the closure of these experiments, after the water phase had been removed, the soil column was sampled in four vertical sub-samples for VOC analysis for verifying that the system was in balance.

3.3.2 Results

Results from both the free water phase experiment and pore water experiment in lysimeter scale indicated successful removal of the contaminant, but also significant differences across the two medias (Figure 3.2 a & b.). Lower efficiency for soil bound contaminant was to be expected according to both literature and technology providers. Also, since additional catalyst was used in the water experiment, pH was adjusted to a level more optimal for chemical mineralization.

In the lysimeter experiment H_2O_2 addition of 2 M led to 31% reduction in MTBE concentration compared with the concentration in the control treatment at same date. Only 50% of the added MTBE could be detected in the aqueous phase of the control lysimeter, which means that large portion of the MTBE was volatized already during injection. Repeated injection with 4 M dose resulted in further 90% reduction in MTBE concentrations, totaling now 98% reduction from the concentrations in the control treatment. Another injection in similar 4 M dose led to further 66 % reduction after a follow up period.

Addition of chelate was found successful in the sense that the resulting 88% drop in MTBE concentrations during the day was the highest recorder decline during the experiment. In this case reaction intensity was still found to have been too high as no peroxide was detected at the bottom of the lysimeter.

Initial drops in concentrations were in all cases followed by rebounds in concentration. Their relative size was found to increase with the concentrations in the aqueous phase decreasing. Similar type of rebounds are associated with air sparging techniques, and are caused by the returning concentration balance between the two medias, air and water. The effect of the rebounds on the total reductions was still relatively low.

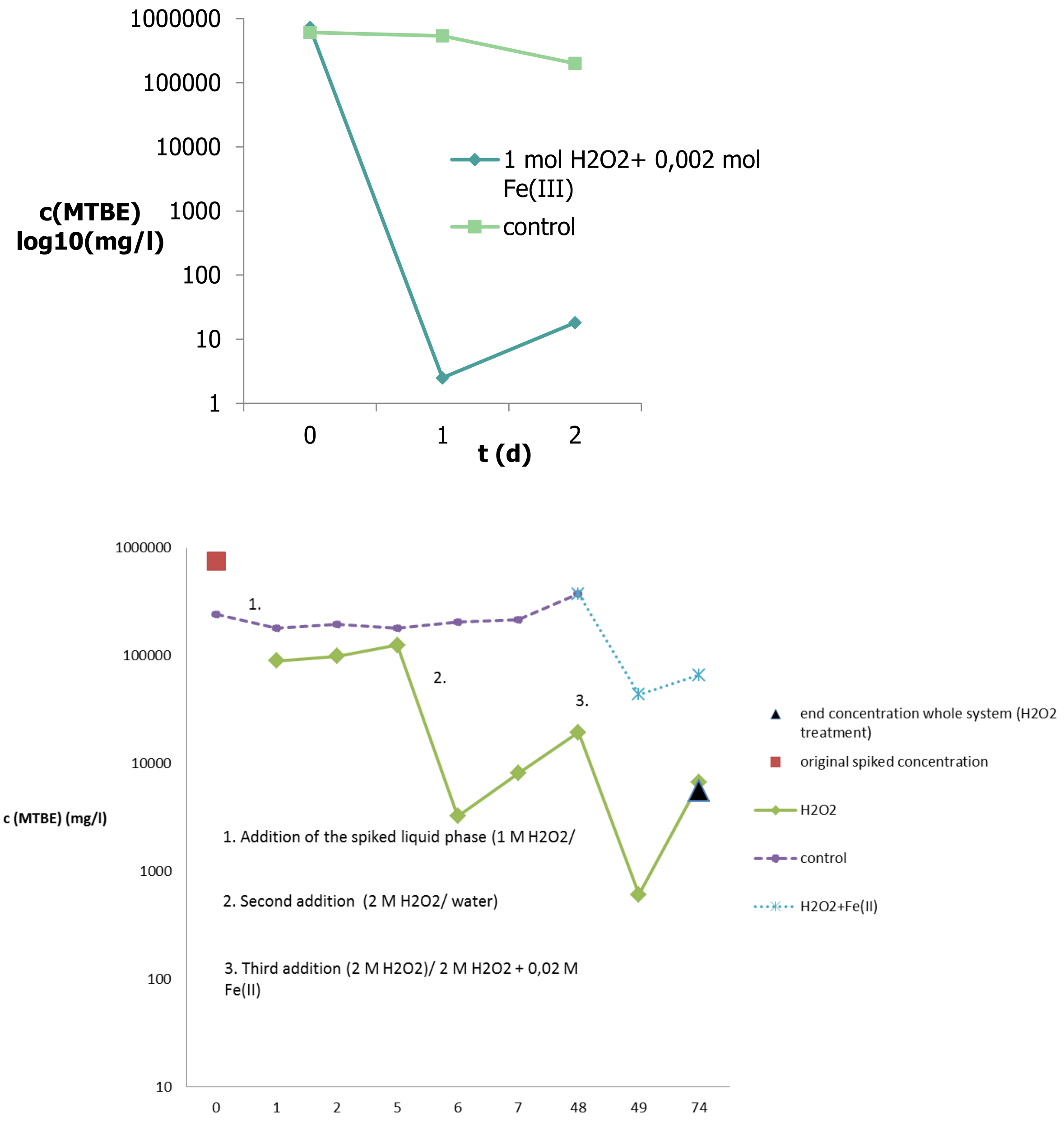

Figure 3.2 a & b. Results from the free water phase experiment (a) and pore water experiment (b). Non-continuous x-axis in figure 3.2 b. LOG10 transformed Y-axis in both cases.

3.4.1. Aged diesel contaminated soil lysimeter test

Chemical oxidation of diesel contaminated soil and the role of additional catalyst and chelate were tested in a pilot test, with aged spiked diesel contaminated soil. The different treatments are pictured in figure 3.3. Approximately 2 t dw of soil with 50 liters of water withheld, was weighed into the lysimeters and sampled for the original concentrations of oil hydrocarbons. The samples were withdrawn vertically, from two depths, 0-50 cm and 50 cm downwards, in three separate drillings.

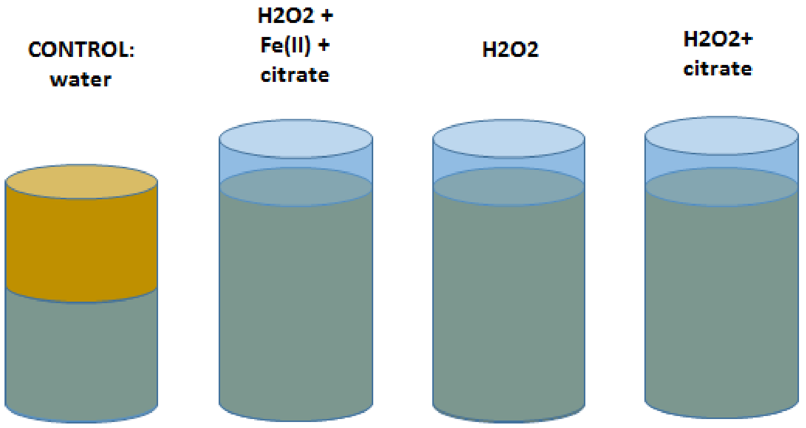

Figure 3.3. Different treatments of the aged diesel contamination lysimeter test. In tests with added H_2O_2 the formation of gases was lifting the aqueous phase above soil surface, whereas in the control treatment it was allowed to descend.

The catalyst $Fe(II)SO_4$ and the chelate tri-sodium citrate were added into the soil columns amended in 50 liters of water. The concentrations for the additives were 3 M H_2O_2, 24 mM $Fe(II)SO_4$ and 61 mM trisodium citrate.

H_2O_2 additions were performed twice with a three week interval, once the peroxide concentrations were under detection limits as measured with peroxide strips (Merck peroxide test). Peroxide was added to the original total 3.1 M concentration, whereas citrate and Fe(II)SO_4 were diluted through this addition to a lower level.

While the H_2O_2 breakdown reaction was still ongoing, the sampling of both soil and water could only be performed from the surface. Temperature was measured during each site visit.

After the experiment was concluded, the soil column was sampled from depths 0-5 cm, 5-50 cm, 50-100 cm and 100-150 cm, with three individual samples from each depth. Oil hydrocarbons in soil were analyzed according to standard ISO 16703:2005 with HP 6890 Gas chromatography device with FI-Detector. Oil in water was analyzed according to standard method SFS-EN ISO 9377-2 by Eurofins.

3.4.2 Results

For aged diesel contaminated soil, reductions in the 10% range were achieved for all treatments with added H_2O_2, with no significant difference between the three test with differing amounts of catalyst of chelate (Figure 3.3). The performance level for diesel appeared hence relatively low, whereas the total mass of the contaminant in the soil far exceeded the amount of MTBE in the corresponding test. This would mean that in terms of H_2O_2: contaminant mass ratios, the differences to the MTBE tests were less critical.

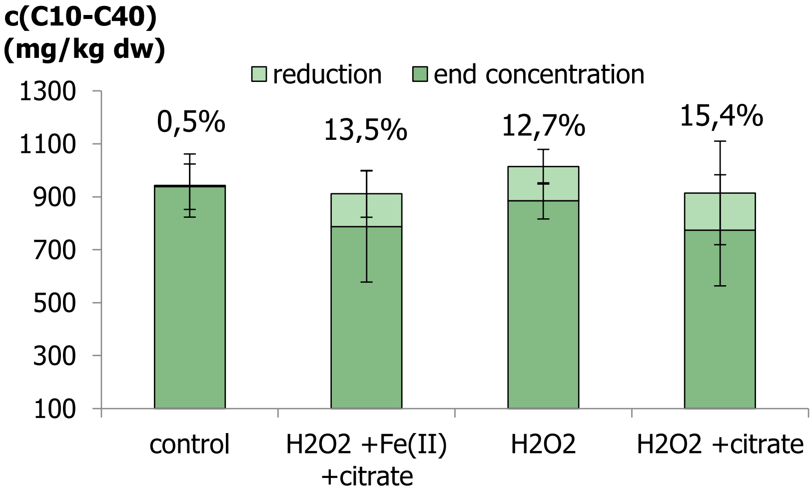

Figure 3.3. Diesel contaminated soil lysimeter scale test results, average reductions ± standard deviation. Reductions per original level are shown in numbers percent.

Both in the lysimeter test and small scale tests modelling the same phenomena, oil was found to accumulate to the soil surface as a result of the sparging effect. This phenomenon is pictured in figure 3.4. Because of this vertical transport, the soil samples withdrawn from the top soil during the treatment were not representative of the total oil concentrations.

Figure 3.4. Addition of H_2O_2 into quartz sand spiked with red-dyed diesel. The reaction is mobilizing the oil towards the soil surface.

The results indicate that chemical treatment of aged diesel contaminated soil would lead to temporal mobilization of the contaminant, whereas with VOCs, this effect could be in principle benefitted from. Due to the high total mass of the contaminant in soil in most cases of diesel contamination, in comparison to water soluble VOCs, the former is more difficult to treat as it would require higher amounts of H_2O_2. When the aforementioned consequences of the physical mechanisms are taken into account, the two contaminants are prone to act differently.

Both the suitability tests for areas contaminated with VOCs and the related field treatment of site Loppi have been reported in a more thorough manner in the Master’s thesis of M.Sc. Niina Lallukka, “VOC-yhdisteiden poistaminen pohjavedestä vetyperoksidin kuplitus –menetelmällä” (In Finnish, with an abstract written in English) reported as a deliverable.

Both the laboratory and the lysimeter scale studies with MTBE contaminated water and aged diesel contaminated soil have been used as a material for the article "Fenton's reaction based chemical oxidation in suboptimal pH conditions can lead to mobilization of oil hydrocarbons but also contribute to the total removal of volatile compounds" submitted to the Journal "Environmental Science and Pollution Research" in June 6th 2019. This article will be made available through open-access once accepted for publication.

4. BIOFLUSHING

4.1. Methyl-β-cyclodextrin laboratory scale test

In some biostimulation treatments, the primary bottleneck for biological degradation is the low bioavailability of the contaminant hydrocarbons. Low bioavailability is the desired state when only environmental risks are being considered, but without removing this bottleneck, biostimulation efforts can be ineffective. In these cases soaps can be introduced to help dissolve the compounds with low bioavailability. Biodegradable soaps are preferred whereas products with high biodegradability tend to inhibit the degradation of the contaminant by acting as more readily available carbon sources than the contaminant itself. Also the total dose of the soap need to regulated, so that the oil hydrocarbons are being released into the aqueous phase in sufficient doses for them to be degraded before being spread into groundwater or outside the contaminated zone.

Methyl-β-cyclodextrin (CD) has been chosen as the optimal surfactant based on results from former studies. Cyclodextrin is proceduced from a raw material containing strach. It is a cyclical sugar that binds the hydrophobic target compound in its hydrophobic inner circumference with Van der Waals interaction and thus dissolves it in water due to the hydrofilic outer circumference of the forming complex. CD itself is biodegradable but not to the extent where is would act as a more readily available source of organic carbon.

The effect of CD on the removal of oil hydrocarbons was tested in a laboratory scale test with soil withdrawn from site Karjaa. At the site the contaminated zone had been treated with bioflushing for several years, the most recent results suggesting that the water soluble fractions had successfully degraded. After the remediation steps already performed, the highest measured C10-C40 concentration detected has been 1500 mg/kg, found to consist almost entirely of aliphatic compounds in the C12-C15 and C16-C21 ranges.

In the laboratory test, soil samples taken from the site were mixed with the treatment solution (200 g of soil, 300 ml of solution). Three different treatments were tested: 5 % and 1 % (v:v) (CD) and water control. During the first step, bottles were shaken in 1-hour cycles, five times altogether. Phases were allowed to separate between each shaking. During the second time, the experiment was repeated in a similar manner but with 5-hour shaking periods. The water phase was sampled after each step. Since the soil was completely water saturated, the results are not reflective of a situation where the solvent is merely filtrated through the soil column. With the tests it was however possible to see to which degree the solubility of a particular fraction range can be increased in an optimal situation. All treatments were performed as three replicas, with one of these per treatment randomly selected for fraction analysis. The two remaining replicas were tested only for fraction sums C10-C40, C10-C21 and C21-C40.

4.2. Results

Based on the results, the amount of CD positively affected the hydrocarbon concentrations in the aqueous phase. The mean concentrations from the different treatments differed at both sampling times for all measured oil hydrocarbon groups (C10-C40, C10-C21 and C21-C40) (Figure 4.1). The added benefits concern specific fractions differently, as the efficiency remained particularly high for the C16-C21 range aromatic compounds (Table 4.1). For C10-C12 aliphatic compounds, the final removal rate (48%) was achieved already during the initial shakings. In addition, it was found that the efficiency was dependent on the CD concentration rather than the total dose as by using 1% CD concentration, final results were achieved within similar period as when 5 % CD concentration was used, whereas the efficiency itself was still weaker. The same phenomenon appeared to concern other fractions as well, but to a lesser extent.

The results suggest that CD could be utilized either as an enhancer of a biological treatment or as a physical remover through soil flushing, and the amount of CD to be added should be chosen according to the application.

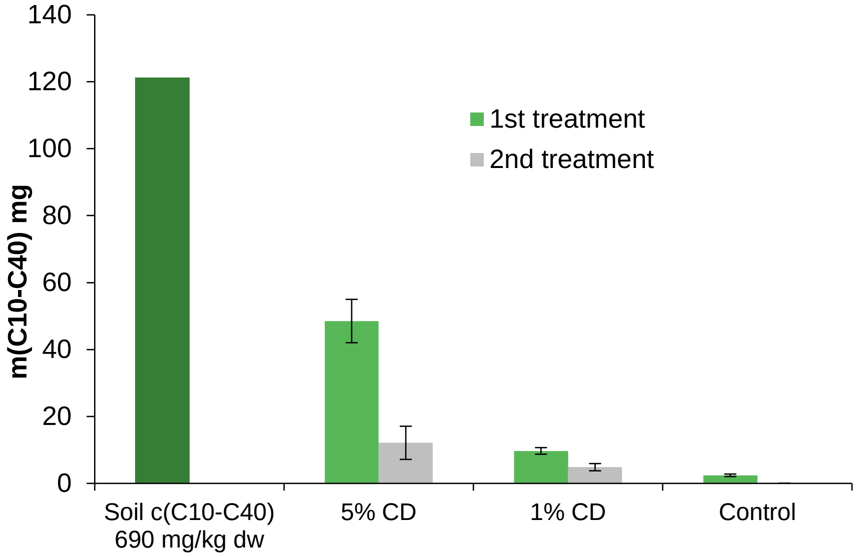

Figure 4.1. Amount of oil (mg) dissolved in water. The original contaminant mass in soil (concentration multiplied by soil dry weight 0.18 kg) is shown on the left: Figure shows average values ±standard deviation.

Table 4.1. The portion of the initial oil mass in soil per fraction range, dissolved into the aqueous phase after each experiment phase. In the results for the second phase, the reduced initial concentration has been taken into account.

	original concentration in soil	**5 % cyclodextrin**			**1% cyclodextrin**			**control**		
	(mg/kg dw)	**1.**	**2.**	**total**	**1.**	**2.**	**total**	**1.**	**2.**	**total**
Arom. C10-C12	< 30									
Arom. C12-C16	44	54 %	15 %	**61 %**	10 %	2 %	**12 %**	1 %	0 %	**1 %**
Arom. C16-C21	30	43 %	85 %	**91 %**	11 %	0 %	**11 %**	0 %	0 %	**1 %**
Arom.C21-C35	<30									
Aliph. C10-C12	84	48 %	-2 %	**47 %**	6 %	0 %	**5 %**	2 %	0 %	**2 %**
Aliph. C12-C16	290	64 %	10 %	**67 %**	12 %	3 %	**15 %**	2 %	0 %	**2 %**
Aliph. C16-C35	490	34 %	16 %	**45 %**	7 %	4 %	**11 %**	1 %	0 %	**1 %**
C10-C21	790	48 %	13 %	**55 %**	9 %	3 %	**12 %**	1 %	0 %	**1 %**
C21-C40	150	34 %	17 %	**45 %**	6 %	3 %	**8 %**	4 %	-1 %	**3 %**
C10-C40	950	45 %	12 %	**52 %**	9 %	3 %	**11 %**	2 %	0 %	**1 %**