INSURE
Innovative Sustainable Remediation

REPORT ABOUT PILOT TESTS

5/2019 UHEL

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1. INTRODUCTION

Currently, the most commonly used treatment for contaminated areas is excavation, where contaminated masses are removed from their environment and transported elsewhere for treatment or final storage. To minimize the transport of both clean and contaminated masses, the related costs and process-bound CO_2 emissions, sustainable *in situ* remediation alternatives have been developed. During the INSURE project, several of these methods were tested at eight pilot sites, five of them located in Finland, two in Latvia and one in Sweden (Figure 1.1).
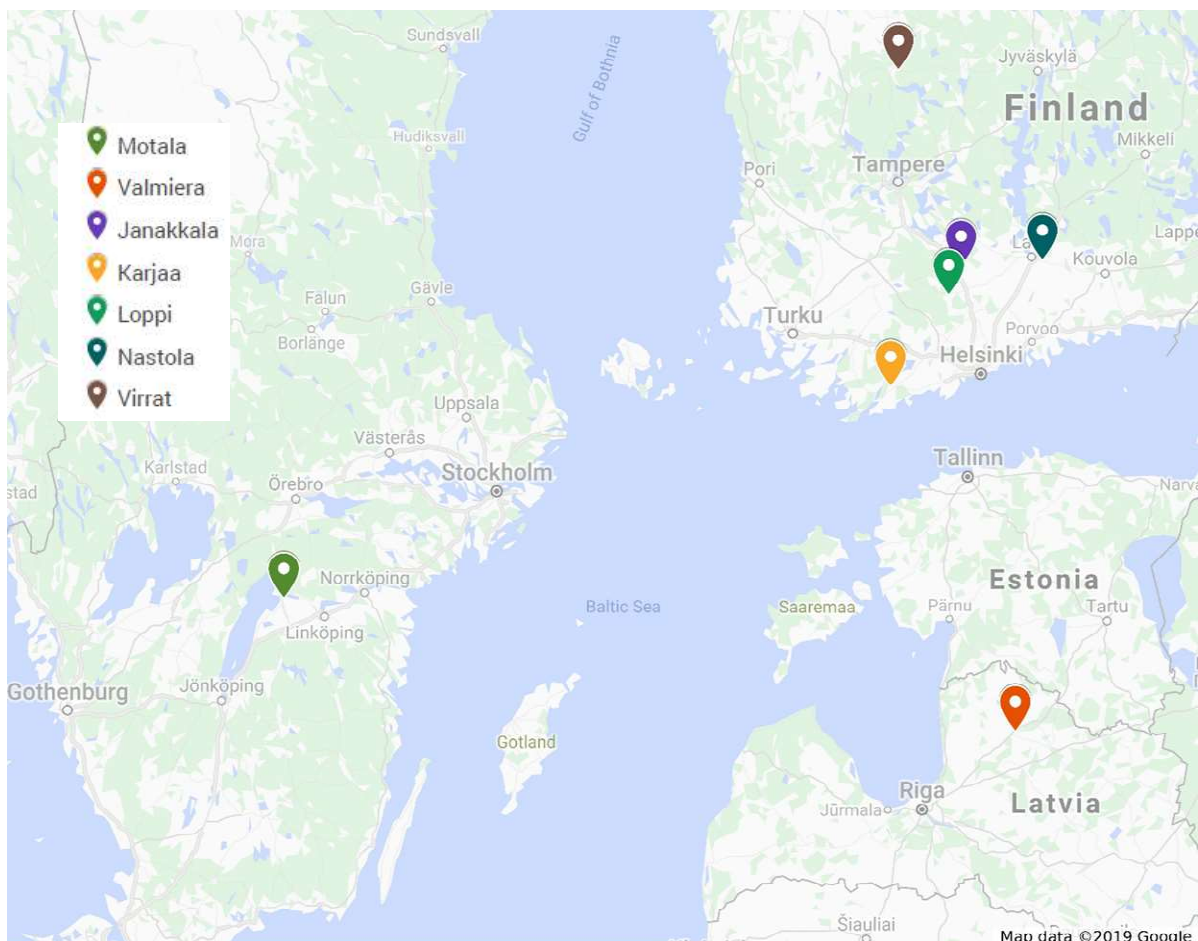

Figure 1.1. The locations of the eight pilot sites. Two different pilot sites are located in Valmiera.

2. ELECTROKINETIC BIOREMEDIATION

2.1. Introduction

In biological remediation of sites contaminated with organic compounds, the naturally occurring biological degradation is accelerated by removing the possible bottlenecks of biological activity. The ones most often targeted are lack of oxygen or another electron acceptor, lack of nutrients, of which nitrogen is the most important in terrestrial systems, and lack of moisture when working in the non-water saturated zone. In these cases nutrient amended water is injected into the contaminated zone via ground water tubes. With horizontal tubes the problem may be that the radius of influence is rather limited, and the nutrients end up in ground or surface water instead of the contaminated zone itself. Electro-osmosis can then be introduced to increase the horizontal vector of the injected water. The principle is explained in Figure 2.1.
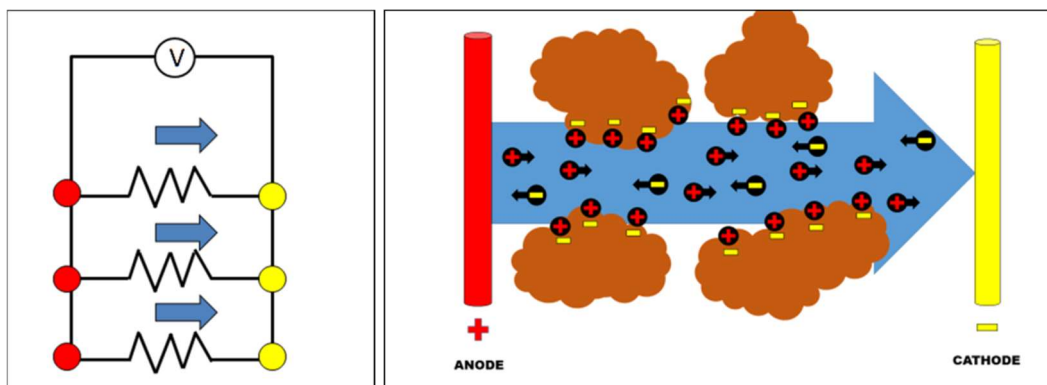
Figure 2.1 a-b. a) The parallel circuit from above, with the movement of the aqueous phase shown in blue arrows. b) cut-view of the mechanism in soil. Soil particles bind ions from the aqueous solution due to their surface charge. The opposite ions remain free in the aqueous media and travel in the electric field according to their charge. Due to its viscosity, water is being dragged along in a horizontal movement and the radius of influence is hence increased.

The method was tested at three sites, Villähde, Motala and Valmiera, all of them distinct in regards to the groundwater level conditions (Figure 2.2). Aim of the research was to develop applications for both non-saturated zone and below groundwater level contamination.

Figure 2.2 a-c. a) Site Villähde, non-saturated zone application b) Site Motala, below ground water level application c) Site Valmiera, non-saturated zone application reaching the ground water level

2.2. Site Villähde/Nastola, Finland

The site was studied in 2013/14 in relation to an experiment by Nordic Envicon Oy and the University of Helsinki in the project TANKKI. The study site is within an industrial furniture factory area. The contamination is due to a tank filling accident in the early 2000s. The site is within a 1-class groundwater area (0453251 Villähde). The treatable part of the site is uncovered and not in use while the contamination is likely to have spread under built structures, some of them still in use. The C10-C40 levels in the suspected contaminated depth, 11-13 m, were 100 mg/kg both before and after the aforementioned remediation studies in autumns 2013 and 2014, respectively. The soil is gravel with high permeability with stratum of lower permeability appearing in depth 6m, above the contaminated zone.

2.2.1. Methods

Biostimulation was suggested as the treatment method, aided with electro-kinetic pumping to enable horizontal movement of the injected solution. This was decided since the concrete floor and the building denied full access from aboveground and because during the TANKKI project, no horizontal movement of water could be ensured by conventional methods.

In June 2016, the site was prepared for the *in situ* treatment. In total six drillings were performed to depth 12 m, to enable the installation of two rows of electrodes in perforated plastic tubes (Figure 2.3). The cathode side was thoroughly sampled: samples from depths at which 2/3 of the samples had a strong diesel odor were analyzed for oil hydrocarbon content, resulting in samples from depths 7 to 11 m being analyzed. The treated zone was 10 m x 3 m x 3.5 m and approximately 100 m^3 in volume and 130 t in mass.

The total nitrogen and phosphorus concentrations were analyzed from three random samples. Nitrogen content was under the detection limit and hence the suspected limiting nutrient. Phosphorus concentrations in the soil exceeded the theoretical required level.

Figure 2.3 a-b. Drilling (a) and installation of perforated tubes (b) at site Nastola in June 2016.
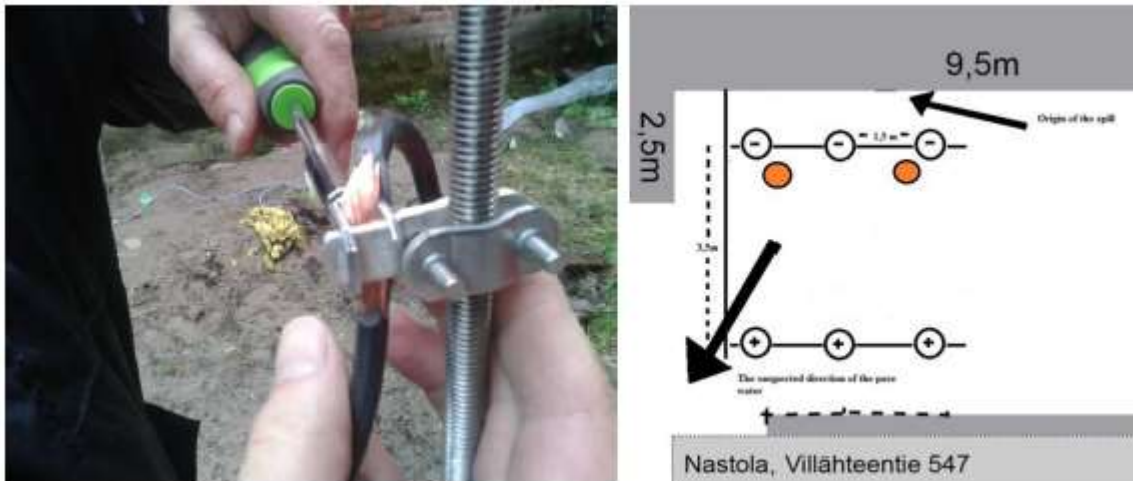
Figure 2.4 a-b. Installation of the electrodes (a). Technical drawing of the area from above (b) Original sampling performed from cathode wells (-), control sampling locations marked by orange spots. The black arrows indicate the origin of the spill (above the cathode row) and the suspected direction of the ground water (to bottom-left)


Figure 2.5. Installation of the water injection system.

The treatment was started in week 25 of 2016 and carried out weekly until week 43 (18 weeks in total), with the weekly injections of 10 Kgs of Suomen salpietari (nitrogen content 27%; 14.5% ammonium nitrogen, 12.5 % nitrate nitrogen) in 2 m^3 of water spread in to the electrode wells within a couple of hours. A 200 V/DC voltage was set between the electrodes and kept on for the duration of the experiment. The effect of watering could be verified with current measurements. Corrosion of the anode electrodes could also be observed as hypothesized. On week 47 two drillings were performed between the three cathodes, near the spots with the highest measured concentrations.

Sampling was done by Nordic Envicon oy or members of UHEL, with the technical assistance of Mitta Oy. All samples were analyzed at Synlab (then Novalab) Finland, according to standard method ISO 16703:2005.

2.2.2. Results

The concentrations in the soil prior to the treatment were mostly under the detection limit even when a strong odor was observed. Two of the 15 samples had concentrations exceeding the threshold value for C10-C40 oil hydrocarbons (300 mg/kg) and the lower guideline value for C10-C21 distillates (300 mg/kg) with an obvious hotspot of 3200 mg/kg dw in 7-8 m depth, near the origin of the spill. After the treatment, three samples with concentrations over the quantification level (LOQ) had average concentration of 100 mg/kg dw and no hot spots with higher overall concentrations were located. The situations before and after 4.5 months of active treatment are shown in Figure 2.6.
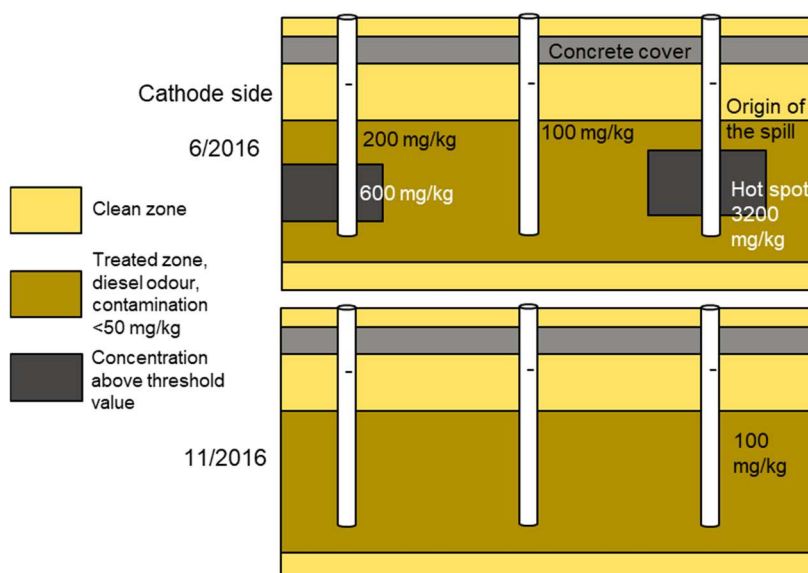
Figure 2.6. A cross-section portrait of the cathode (-) side before and after treatment.

An independent party, consultant Vahanen Oy, performed the final investigations of the area in April 2017. The soil was sampled in three drillings VAH1-VAH3, with VAL 1 within, and the other two southeast from the treatment zone (Figure 2.7). An organoleptic survey of approximately 1 m length soil columns from depths 8-14 m was performed prior to the standard analysis. Groundwater was investigated from two groundwater wells: VAH 1 to the west from the premises and VAH 2 south from the treated zone. No traces of oil hydrocarbons were found on the site at concentrations above or near the threshold value, and it was concluded that no further actions would be required, neither on the study site nor on the larger area suspected to have been impacted by the spill.

Figure 2.7. The site investigations done by consultant Vahanen Oy with the sampling spots marked.

2.3. Site Motala, Sweden

Motala pilot area "Södra stranden" is a complex area near Lake Vättern consisting of several properties. The contamination in the area of around 6000 m^2 come from different sources like finishing industry, oil depots, marina, filling material etc. Some contaminants are in the surface soil, like metals and oil products of the filling material, whereas some contaminants, like trichloroethylene are down to 19 m below ground level. The area has a potential to be developed into a residential area, with active tourist use. Some smaller sub-areas are to be remediated or their use restricted before the projected land use changes can be undergone. One such spot carries former oil depots and has oil contamination in the soil at groundwater level (Figure 2.8).
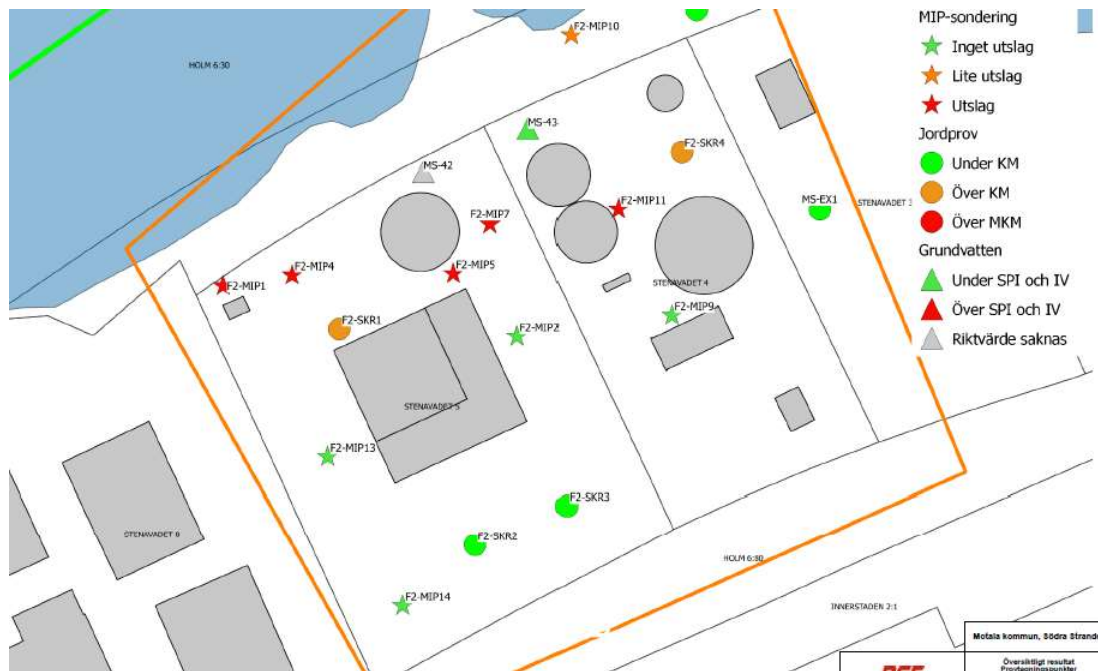
Figure 2.8. The oil hydrocarbon contaminated site, "Södra stranden".

2.3.1 Methods

The installations were performed and the treatment started in July 2017. Groundwater tubes were inserted in two rows in parallel to the lakeshore, 6 m apart from each other. Four groundwater tubes were inserted with 2 m intervals to form a 6 m row of tubes (Figure 2.2 b). The tubes were inserted down to the depth of 5.5 m with perforation starting at 2–2.5 m downwards from the soil surface. When measured, the groundwater level was ca 2.7 m below ground, lower than normal by more than 50 cm. Stainless steel rods, two meters each, with treads were connected with bolts to form 6 m rods that were inserted into the groundwater tubes.

The anode (+) electric cord was attached to the row of electrodes further from the lakeshore, and the cathode (-) cord to the row closer to the lakeshore (Figure 2.9). This arrangement was based on the assumption that the main direction of groundwater flow would be towards the lake. The voltage was turned to the smallest 100V position. The current was measured separately for each of the electrodes.

For the biostimulation a steep V shape ditch was dug along the anode row, with the center ca 1 m from the row. When water started flowing into the ditch (depth almost 3 m), bone meal (ca 300 kg, representing ca 20 kg N) and calcium peroxide (ca 200 kg, 17% of which is released as oxygen within ca 5 months) were spread in the ditch, after which the ditch was filled up.

In September 2017, currents were measured from both anodes and cathodes before and after the voltage was switched from 100 V to 150 V. Anode electrodes were found to have corroded as suspected, and new pieces were added to reach the original electrode height. A similar follow-up visit was done in December and voltage was switched to 200 V.

Data obtained in early 2018 indicated that oxygen was limiting biodegradation. To increase the degradation, 25 kg package of calcium nitrate in 1000 liters of water was distributed over the test area in the end of April 2018. Nitrate (NO_3^-) was utilized to function as an alternative electron acceptor. This addition was repeated every other week for twelve weeks, six times in total. The site treatment was finished in September 2018.
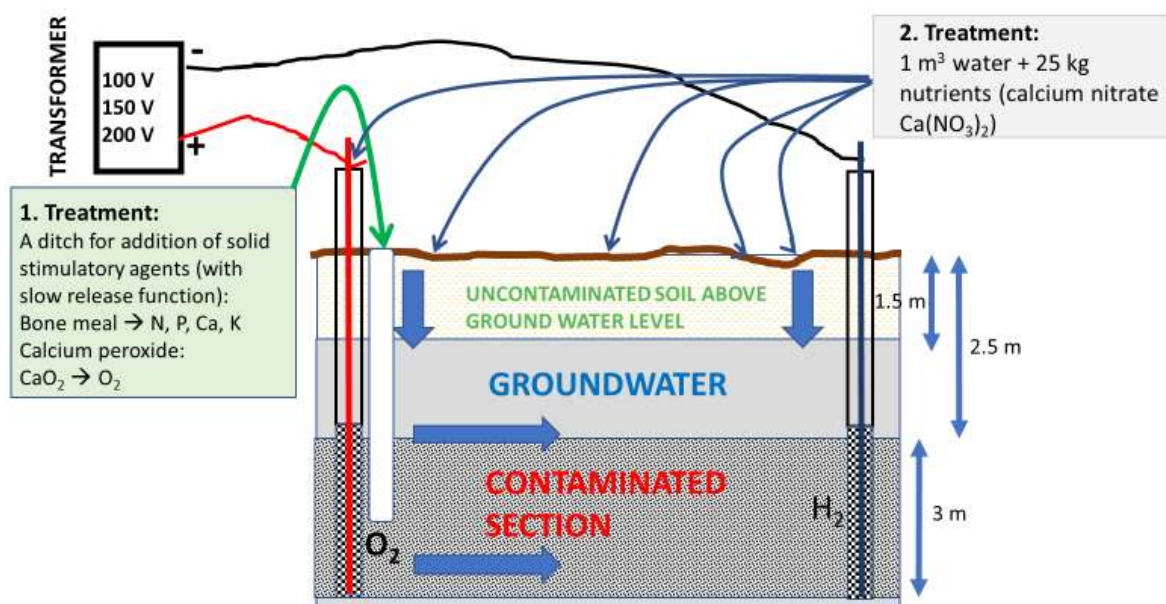
Figure 2.9. A schematic representation of the situation and treatments at Stenavadet. Later obtained data indicated that the water level was fluctuating during the treatment period.

Monitoring of the treatment was done from groundwater samples taken from three of the groundwater tube holes, and from three additional holes within the treatment area, one of which was a previously identified hot spot. Two reference holes were drilled outside the treatment area, ca. 30 m from it, but with a record of also containing oil contamination. Samples were collected from 2.5 m downwards with 50 cm intervals, giving six samples from each sampled hole.

Temperature and oxygen levels were measured from the anode side as well as from a control spot outside the treated zone in September 2017. Soil and water samples were withdrawn before and after, and twice within the experiment. The sampling process, analyses of oil concentrations, pH, etc. were performed by Sweco. Additional soil and water samples were delivered to UHEL Lahti Alma Lab, mainly for nitrogen analysis.

2.3.2 Results

By the time of the sampling in December 2017, the concentrations of aliphatic compounds had not decreased (Figure 2.10). Instead, a possible trend was observed of the oil being mobilized by the slightly elevated temperature and electro-osmotically enhanced groundwater movement. This was supported by the fact that the oil hydrocarbon levels had risen in the top samples and also into the direction of the shore. Mobilized oil would float up to the surface of the groundwater and form a non-aqueous phase liquid (NAPL). This NAPL would then be slowly transported towards the cathodes.

In addition to the data in the figure, the temperature and the oxygen concentrations in the groundwater were measured. The temperature in the field was slightly elevated (ca 11 °C) compared to the controls (ca 8 °C). The water in the anode tubes was oversaturated with oxygen (> 30 mg/L). In the middle of the field it was 2 mg/L indicating active oxygen consumption. In the control tube, the concentration was on average 9 mg/L, which is close to the saturation level of 11 mg/L. As the high concentrations of oxygen had been detected only in the anode pores, and since nitrogen had already been detected in sufficient doses also outside the source (Figure 2.11), it was suspected that oxygen was the primary limiting factor. It was found that the nitrogen concentration in the water phase showed correspondence with the biostimulation effort, whereas concentrations in the soil samples were below LOQ-levels making the soil samples unfit for surveying the situation.

Changes in pH were also monitored. It was found that during the remediation pH in groundwater was very low at the anode site (ca 2), whereas in the middle of the area it was only slightly acidic or near neutral (5.8-6.7) (Figure 2.11). At the cathode site, pH was highly alkaline (near 13). However, pH in soil samples was near neutral and did not vary clearly, indicating a high buffering capacity of the soil.

At the end of experiment, the concentration of aliphatic hydrocarbons had decreased in comparison to the highest concentrations detected in December, ca 40-70 %. However, the concentrations were still relatively high in two spots (S9 and S7, Figure 2.10), indicating that the method was not as efficient as expected. Probably with prolonged treatment time, the concentrations would have decreased still.

At the end of the experiment nitrogen species were analyzed in the form of ammonium (NH_4^+) and nitrate (NO_3^-). Nitrogen species were dispersed as suspected - negative nitrate anions were detected at anode site and positive ammonium cations were detected in much higher concentrations at the cathode site (Figure 2.11). High concentrations of nitrate and ammonium in groundwater may restrict its use as drinking water. For example, in Finland guideline values for nitrate and ammonium in drinking water are 50 and 0.50 mg/l, respectively. Compared with the guideline values, the concentrations detected were manifold. It can be concluded that the amount of added nitrogen should have been much lower. The remaining nitrogen will, however, apparently be used up by the soil microbes while continuing to stimulate the degradation of oil at the site also after the treatment.
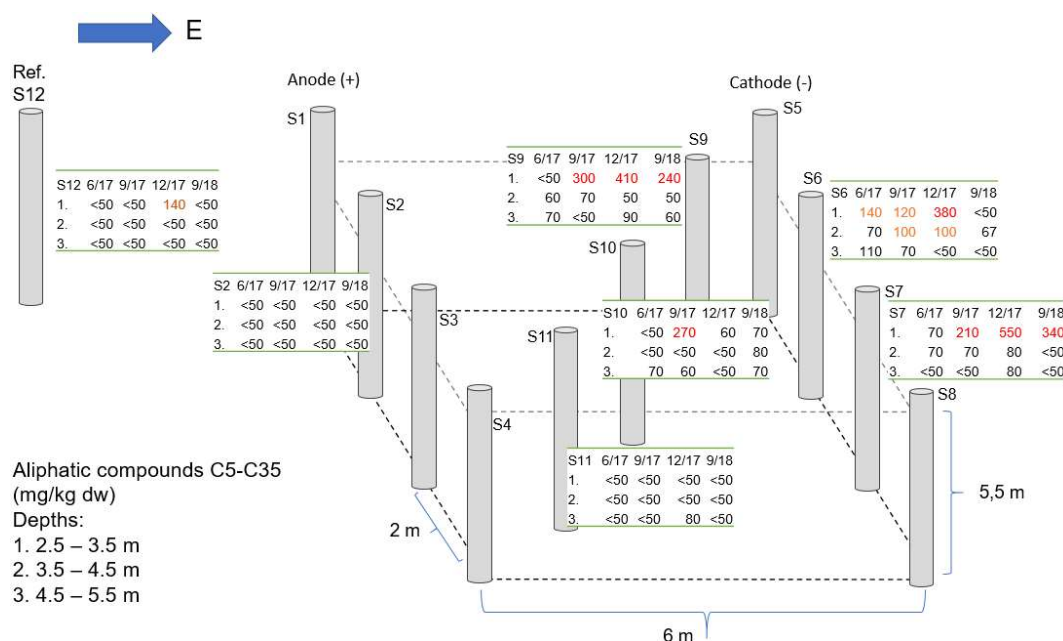
Figure 2.10. Concentration of aliphatic hydrocarbons (C5-C35) in the soil at different depths and sampling dates. Concentrations above 100 mg/kg shown in red.
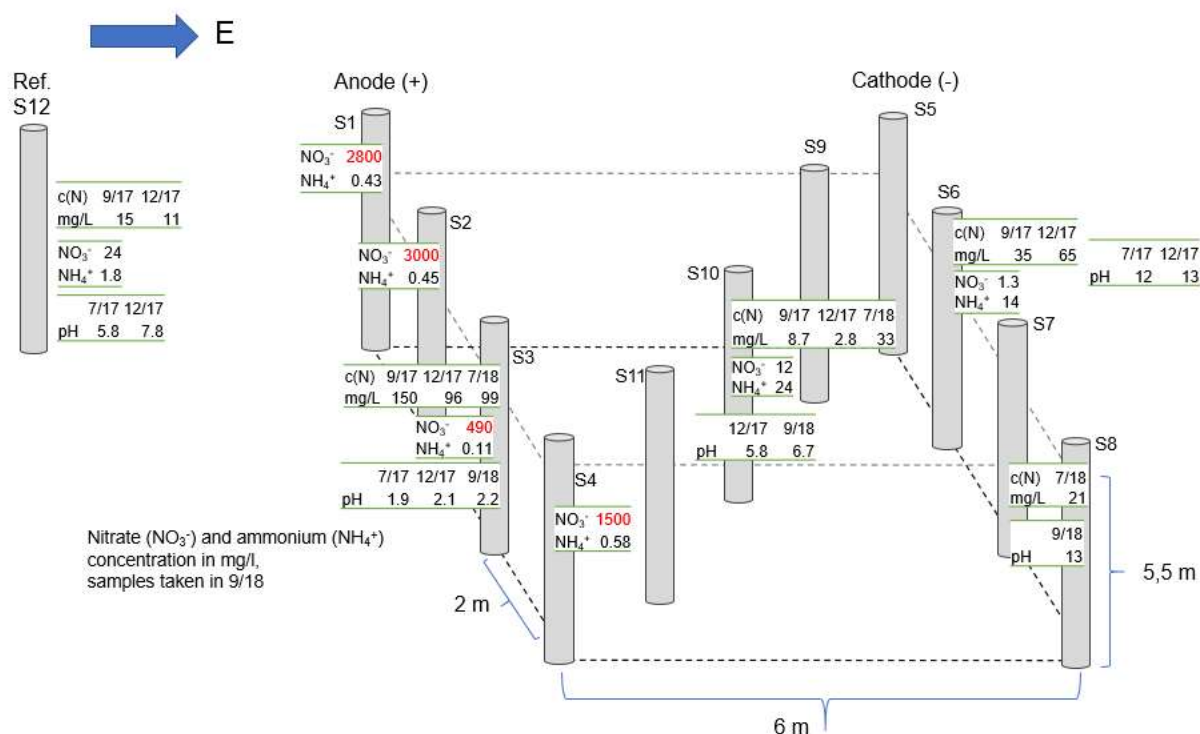
Figure 2.11. Concentrations of total nitrogen (N), nitrate (NO_3^-) and ammonium (NH_4^+) and the groundwater pH.

2.4. Site Dzelzcela iela, Valmiera, Latvia

Site Dzelzcela iela 9 is a former fuel facility of the heat producer Valmieras siltums Ltd, located to the south of the city of Valmiera, in the industrial area. The area of approx. 1.2–1.5 ha has been formerly used for the storage and transshipment of oil products. Nowadays the area is abandoned with partially demolished buildings, fuel tanks and reservoirs (Figure 2.12).

Before the research work was carried out, the area was investigated together with representatives from Municipality of Valmiera and Latvian Environment, Geology and Meteorology Centre. The total area with major oil pollution in the soil is estimated to be around 600 – 750 m^2. The average depth of the contamination is three meters from the soil surface. There are no residential houses in the direct vicinity of the research area and therefore direct threat to human or animal life posed by the presence of the potential contamination is minimal.

On the surface of the soil, there are asphalt, concrete and stone chippings. Under the surface is a layer of mixed loam or earth-filled gravel with construction waste. At the depth of 0.6 - 1.8 m, the soil consists of fine sand or sandy loam. At the depth of 3.5 - 4.0 m is hard sandy loam with intermediate layers of gravel and sand, found to continue to the depth of approximately 16 m within the researched area. The overall filtration properties are poor and not favorable for the migration of the potential groundwater contamination.

During the drilling works, the groundwater was detected at the depth of 1.2-4.0 m but after the installation of monitoring wells and settlement of the levels, the groundwater table stabilized at the depth of 1.70-2.72 m from the soil surface. The estimated groundwater flow is directed westwards or towards the railway embankment and the adjacent ditch.


Figure 2.12. The old oil cisterns at the pilot site.

2.4.1 Methods

Pilot tests in Valmiera were initiated in September 2018 together with the contractor Vides Konsultāciju Birojs Ltd. The 6 x 6 m study square was set to include the groundwater well from where the highest concentration of oil hydrocarbons had been measured and to where it was possible to access with the heavy drilling machinery. The direction of the forming electrical circuit was chosen to direct the injected fluids towards the area suggested to be the most contaminated, that is, the site around the underground tanks, which was originally planned for the *in situ* tests (Figure 2.13).

A spiral drilling method was used for drilling 13 holes (8 electrode wells, 2 control spots outside the treated area, 3 additional spots within the area) up to the depth of 4 meters. At the boreholes, which are marked with "A" (anode) and "K" (cathode), 63 mm polyvinylchloride pipes with perforated filter winding with a 0.5 mm sieve, were inserted. The filter length was 4.0 meters. The ends of the wells were left at 0.3-0.5 meters above the soil surface.
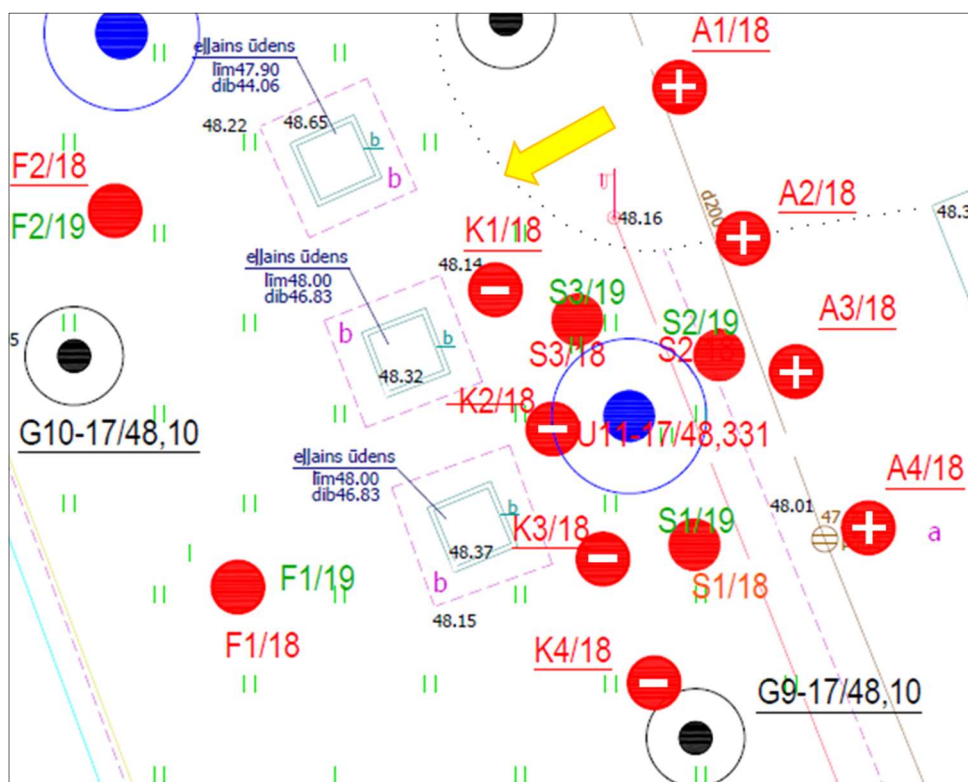
Figure 2.13. The treatment site, showing the anode row marked with (+) and the cathode row with (-). The yellow arrow marks the suspected movement of fluids. The two control drillings outside the treatment area are marked as F1 and F2. The number after the slash character indicates the sampling year. The sampling points inside the treatment area are marked as S1-S3.

Electricity was to be connected directly after the drillings. Due to confusion on the requirements caused by multiple versions of the working protocol, the requirements for the actual transportable unit (inlet: three-phase current, AC 380V, 35A) were not met. Nevertheless, a three-phase current input was installed the following week. The stainless steel rods were connected to serve as electrodes and the cables were connected to the rods and the transformer.

Bioremediation was executed by adding 50 Kgs of ammonium nitrate (+phosphorus) fertilizer and 10 liters of cyclodextrin per month dissolved into water. Cyclodextrin is a biodegradable soap of cyclic sugars that can enhance the solubility of otherwise insoluble oil hydrocarbons (section 4). Injections were suggested to be performed every two weeks by adding 2-4 m^3 of liquid, preferably full 4 m^3. The treatment was finished in April 2019, after ca. six months of active remediation.

Figure 2.14. Finished site installations. The anode side on the left, the cathode side on the upper right near the fence. Tubes in between mark monitoring sampling spots.

Drilling works for the collection of soil samples and for the drawing up of geological cross-section were performed on 20-21st of September 2018. Soil samples were taken from each borehole (altogether 13) in accordance with the ISO 10381-5 standard. They were predominantly taken at four different intervals; from 0.0 m to 1.0 m, 1.0-2.0 m, 2.0-3.0 m and 3.0-4.0 m. Each sample weighed around 100-200 grams. The soil taken out during the drilling process was used for laboratory testing (30%) and the remaining 70 % of soil was used to fill up boreholes. Collected samples were divided in two identical parts, from which one was delivered for further testing in Latvia and the other was given to representatives from the University of Helsinki in case the heavier oil hydrocarbons (C40-C80) are to be analyzed. The testing of samples was done by an accredited laboratory Vides Konsultāciju Birojs Ltd. Biological samples were not withdrawn because they had been required only by Populus Group oy, who was no longer involved in the project.

Groundwater samples were collected in accordance with LVS ISO 5667-11:2011 standard on September 21, 2018 by using polytetrafluoroethylene cylinder. Before the collection of samples, the wells were purified from small gravel particles. Physical and chemical parameters of groundwater were tested (pH, electrical conductivity, and others) using a calibrated device. Before the collection of samples, water was drawn off (equal to the volume of three times of drawing off the water) in order to achieve precise and representative groundwater results from the horizon. Before water was drawn off and samples taken, the detection of the floating layer of oil products was performed and the thickness of layer (if present) measured. At the well No. 11, where the floating layer of oil products was detected, its thickness was measured. In total, three groundwater samples were taken, which were packed and transported fur further testing.

2.4.2. Results

All samples taken before the treatment had a distinct odor, with the samples from, or near, the cathode row and the control sample some meters behind the treatment area appearing to have the highest concentrations. In the area between the electrode rows concentration of C10-C40 fractions were not found to have decreased in a considerable fashion (Figure 2.15.). An approximately 10% decrease in average concentrations was documented, whereas with both positive and negative changes recorded, reductions in this scale could not be considered significant or strictly associated with the treatment, but also resulting from heterogeneous distribution of the contaminant in soil. Largest average reduction was observed in reference spot 1, which was however located into the direction towards which the injected water was flowing, separated from the treatment area with a zone containing underground structures, and therefore likely of decreased local permeability.

From water samples withdrawn in January 2019, from the anode side, the nitrate nitrogen concentration 12 g/l exceeded the concentration in the injected solution 2.5 g/l which would suggest that rather than being distributed sufficiently, the injected fertilizer was accumulating in the ground water tubes. Because of this, fertilizers were no longer added after these results had been received.

It can be concluded that with a site of such a low permeability, the treatment time of six months was not long enough for visible trends to overcome the differences in contamination level caused by soil heterogeneity alone. What could be verified was that the electro-osmotic application of the particular biostimulation protocol was not a financially sound way to treat the site in question as excessive amount of energy was spent with little remediation effect. One probable cause for this was the fact, that the electrodes were reaching the ground water level and large portion of the electricity would be spent in generating heat in the groundwater without significant horizontal movement of pore water achieved in the non-saturated zone.
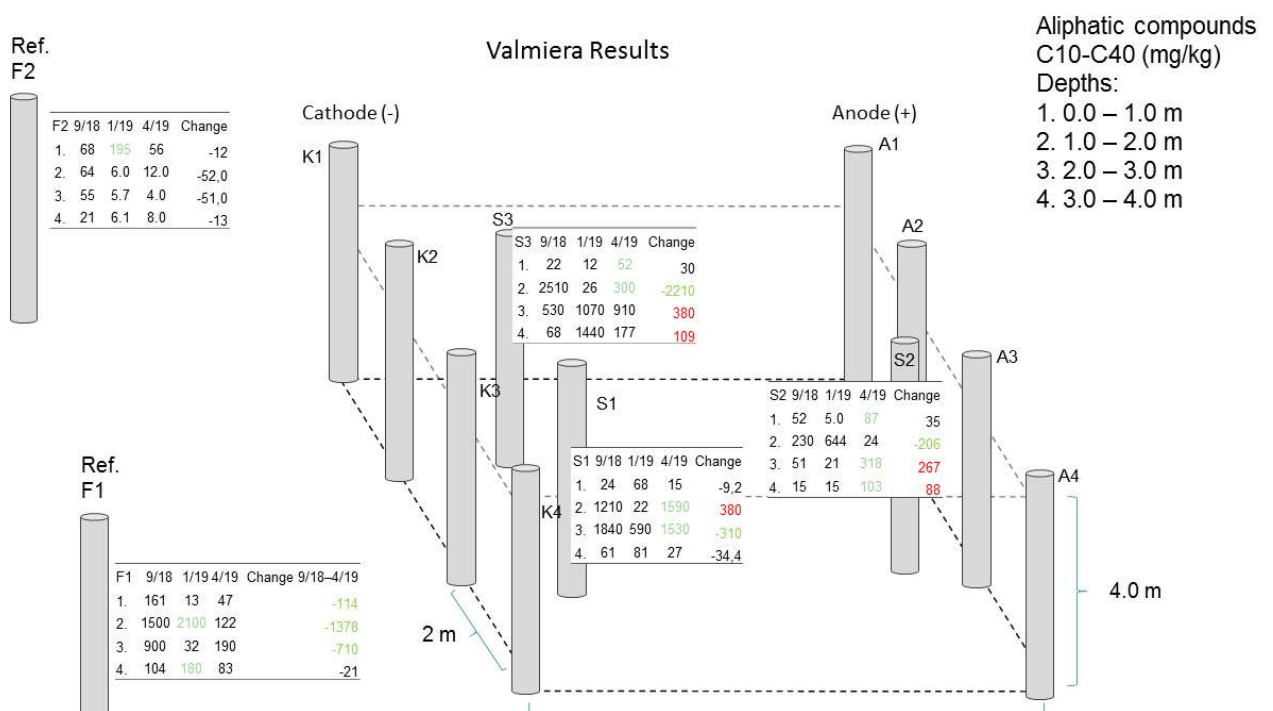
Figure 2.15. Oil hydrocarbon results from soil, from investigations in 9/18, 1/19 and 4/19.

3. HYDROGEN PEROXIDE IN CHEMICAL OXIDATION/SPARGING

In situ chemical oxidation is a method where oxidants are added into groundwater or soil to degrade the organic contaminant through a chemical reaction or string of reactions. The most commonly used oxidant is hydrogen peroxide. Its effectiveness is based on the Fenton's reaction, where the breakdown of hydrogen peroxide is catalyzed by added iron salt or iron minerals already in the soil, producing reactive radicals that are able to degrade organic compounds.

The difficulty in *in situ* remediation is, that the desired reaction will only take place in acidic conditions, and due to the high buffering capacity of soils, majority of the introduced H_2O_2 is expected to react through non-radical producing pathways. The solubility of catalytic iron can be increased through chelating agents that widen the pH range in which significant radical production can be expected.

The attraction of chemical oxidation is that it can be in principle utilized as a multipurpose remediation method for mixed contamination, to a higher degree than bioremediation to which for example both many gasoline additives and heavy oil fractions react poorly. Chemical oxidation can also be relatively fast method, from hours to days, whereas monitoring of rebound concentrations may lengthen the time requirements for *in situ* applications.

Regardless of the breakdown pathway, addition of H_2O_2 into soil will lead to an intensive reaction with gas formation, which could be suggested to work in a similar manner to air sparging, a commonly used method for sites contaminated with volatile organic compounds (VOCs). This would mean that the question of soil pH could be sidestepped when treating VOCs. However the fact that in these cases the reduction mechanism would be physical rather than chemical would have some consequences, especially when working with mixed contamination of both volatile and non-volatile compounds. Still, a sparging effect achieved by injecting liquids rather than gas could increase the potential radius of influence achieved with the same basic installations.

At site Loppi, the sparging effect of H_2O_2 on volatile compounds in the saturated zone was tested near neutral pH. At site Janakkala, chemical oxidation with a chelating agent was performed as the initial step of a multi method treatment for soil contaminated with light heating oil.

3.1. Site Loppi, Finland

The site is an old gas station and car repair shop at Loppi in southern Finland with existing data of both VOC and C10-C40 contamination over a large area. From 1950 to 2002 gasoline, diesel and fuel oil were stored and distributed by both the current and the former site owners. All fuels were stored in underground tanks that have been emptied but are otherwise still left intact. The area was investigated in 2014 and 2016 by consultant Finnish Consulting Group and contractor Nordic Envicon, respectively.

Most of the yard is under an asphalt cover. First meter under the cover is gravel, under which there are up to five meters of silty clay with narrow sand stratums. The site belongs to a classified groundwater area with groundwater level starting at the depth of 3-4 m. The well situated on the site is not in use, and other wells near the immediate area of impact have not been located. The suspected direction of the groundwater is towards North-West or West, that is, towards River Isojoki (Figure 3.1.).
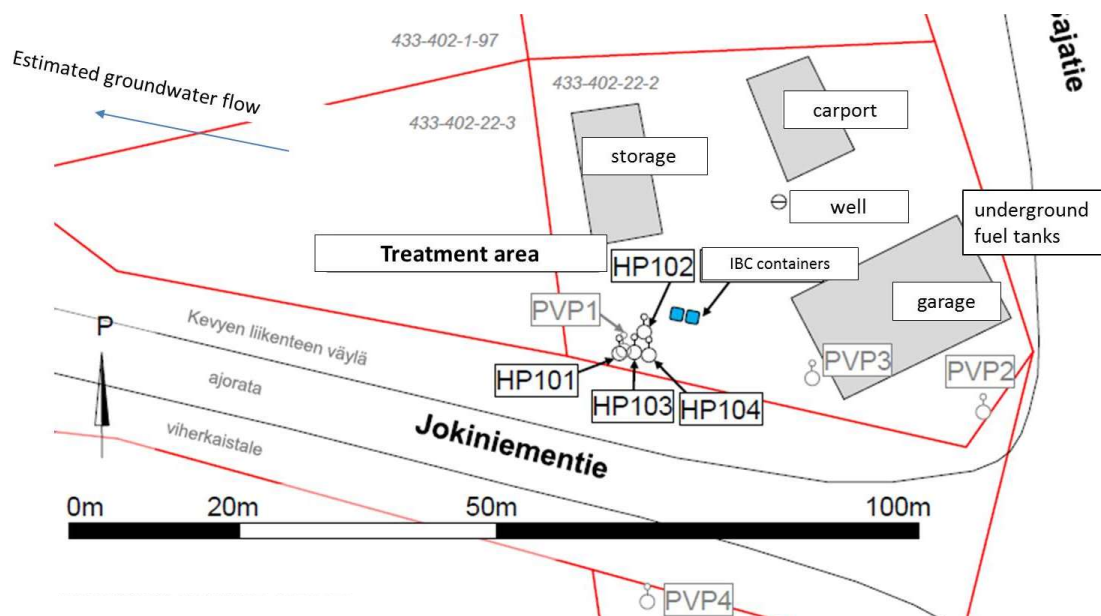
Figure 3.1. A technical drawing of the site Loppi (Jokiniementie 240) with groundwater tubes PVP1-4 and installed monitoring tubes HP101-HP104 marked.

Several VOCs have been found in various groundwater samples from various points around the area: in 2014, the samples from the well had increased concentrations of benzene, oxygenates (MTBE and TAME) and 1,2-dichloroethane. The well is located approximately 20 m from the former fuel distribution spot, to the suspected direction of the groundwater flow. Because further mobilization was considered possible, Finnish Consulting Group assessed that groundwater needs to be treated. In the 2016 surveys, oxygenates were detected from groundwater pipe PVP1 as the only contaminants above detection limits. In the closer vicinity of the tanks, in pipes PVP2 and PVP3, oils and BTEX-compounds were detected, but not oxygenates. In addition, in soil, several compounds have been found to exceed the higher guideline values.

The highest measured concentrations of MTBE were found in the well, groundwater well PVP1 and in the storage tank, whereas the immediate area surrounding the tank has been found clean. The area around PVP1 was chosen for the initial tests. This study area was contaminated only by the water-soluble oxygenates (MTBE and TAME), suggesting a close connectivity to the smaller-scale MTBE-pilots. The area was also uncovered and not in use, enabling faster installations, and a more thorough monitoring through the larger number of wells.

3.1.1. Methods

For the experimental set up, four vertical groundwater pipes were installed to a depth of 5.5 m, with perforation starting at a depth of 0.5 m and hence set to cover only the saturated zone. Protective covers were installed to cover the first meter of the pipes from the top down (Figures 3.2 and 3.3). H_2O_2 injections were started two weeks after the installation. Groundwater was sampled prior to this and air-VOC measurements (using a photoionization detector, PID) were recorded from all groundwater wells in the area.
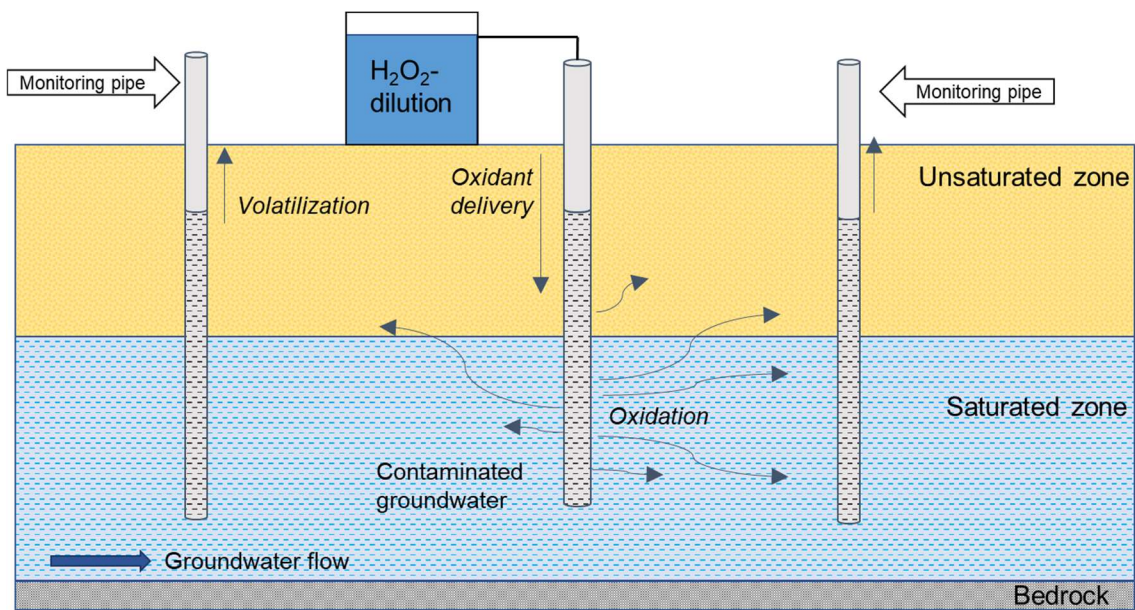
Figure 3.2. Principle of peroxide sparging in the saturated zone
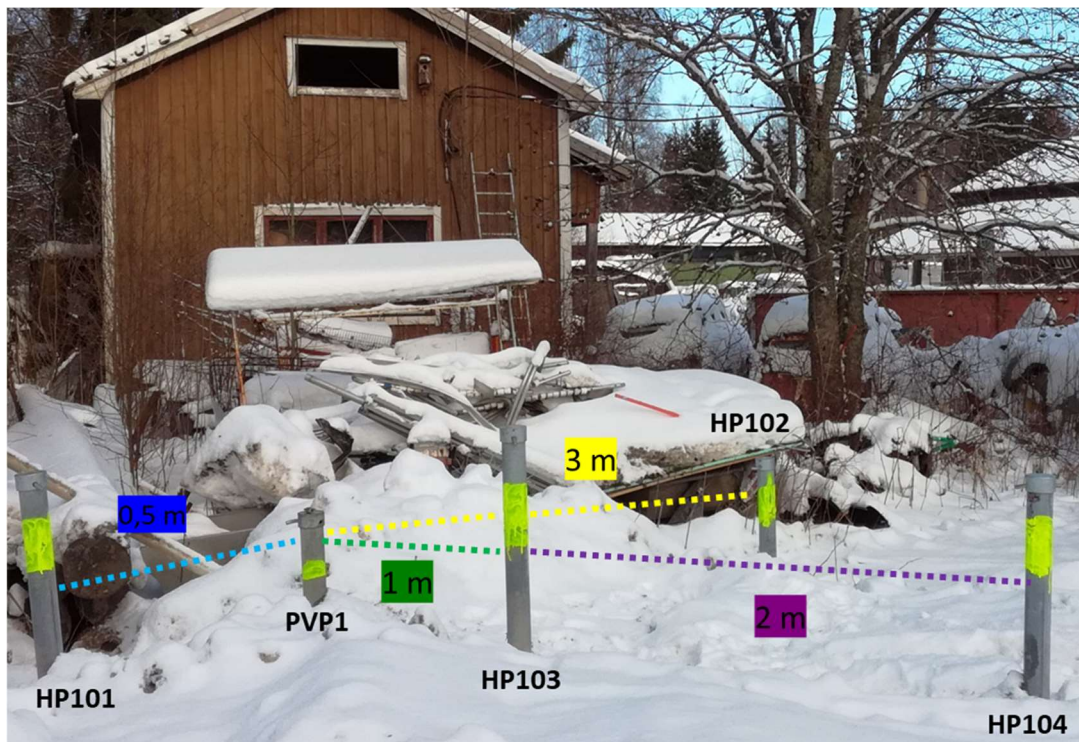
Figure 3.3. The original treatment area showing the distances between each groundwater pipes.

The initial protocol was to inject 1 m³ of diluted peroxide into the selected spot during a single 8-hour session. However, during the first injection in February 2018 with 0±1 °C ambient temperature, only 100 litres could be added because of an insufficient pump. The 50 % peroxide was diluted on site with well and tap water in a 1 m³ container and injected to the tubes in the concentration of 17 %. The dose was approximated with coarse estimates for the radius of effect so that 1 m³ of introduced 17 m-% peroxide would further dilute to level 2 M, a dose used also in the pilot. However, both the introduced volume and the probable immediate radius of effect were lower than the values used for approximation, meaning that the local concentrations were possibly higher.

The injection was continued five days later. With ambient temperatures then in range -18, -13 °C, the growing viscosity of the solvent hampered the pumping. Still, further 200 liters were added. The proposed protocol was completed three weeks later, with 900 liters of 17% peroxide added in all.

The protocol was then repeated two months later in May with unfrozen soil. Now the additions were done in concentration 25 % and to all the groundwater tubes simultaneously. Due to the low levels of contaminants in the original area, the experiment was continued closer to the fuel tank area, in PVP3, because of the detectable concentrations of C5-C10 hydrocarbons and BTEX compounds and a considerable odor of heavier oil hydrocarbons. A less favorable setting for injections was provided as the site was under concrete cover and accessibility was generally lower due to the limited amount of injection tubes.

Figure 3.4 a-b. PVP1 area (a) and PVP3 area (b) during the second period of the experiment.

Only 60 litres of diluted H$_2$O$_2$ could be introduced into PVP3 in a single step. Because of this, a slower injection rate was necessary and peroxide was from then on trickled into the tube in single drops in three separate weekly sessions. The injections were paused in the aforementioned manner, because water samples could not be collected while the reaction was still ongoing. During the last injection, a single 100-litre dose was added into tube PVP2 for a further reference and to enable lifting the peroxide container manually to a height where peroxide would keep flowing to PVP3 undisturbed.

All sites were monitored for PID-values, temperature and oxygen and peroxide concentrations with higher frequency within the first days, but also continued for several weeks for either further dispersal of the peroxide or for possible rebound effects. The experiment was finished in June 2018, 150 days after the initial peroxide injection. Last water samples were withdrawn nine months later. The complete experiment protocol is listed in Table 3.1.

Table 3.1. The protocol for the field experiment. On marked days without injections or sampling, oxygen saturation, peroxide concentrations, water temperature and groundwater level were monitored.

Date	Injection	Water samples	Time from injection (approx.)	Injected volume (L)
14.2.18	PVP1	x	0	100
19.2.18	PVP1	…	0	200
20.2.18	…	…	1 d	
26.2.18	…	…	1 w	
5.3.18	…	x	2 w	
12.3.18	PVP1	x	3 w	900
13.3.18	…	…	1 d	
20.3.18	…	…	1 w	
3.4.18	…	x	3 w	
14.5.18	HP101–4, PVP1	x	2 m	250
15.5.18	…	…	1 d	
18.5.18	…	…	4 d	
28.5.18	PVP3	x	2 w	60
29.5.18	PVP3	…	1 d	20
4.6.18	PVP3	…	1 w	
6.6.18	PVP3	…	…	100 (in 2 days)
12.6.18	PVP3	…	…	150 (in 1 week)
26.6.18	…	x	2 w	
29.6.18	PVP3	…	2,5 w	
6.7.18	PVP2–3	…	…	100 (in 1 week) PVP2: 100
13.7.18	…	…	…	200 (in 1 week)
14.8.18	…	x	1 mo	

The VOC levels in water samples were analysed at the accredited laboratory Synlab (then Novalab Oy) using method Novalab 040 for general C5-C10 levels and ISO 20595:2008 for individual compounds in the same range. The absorbent collector, coupled with pump SKC 222-3 was analysed with gas chromatography at the Finnish Institute of Occupational Health, with the accredited method KEMIA-TY-006. An UltraRAE 3000 handheld PID monitor was used for general PID levels. The diesel concentrations in water were analysed according to standard method SPFS-EN ISO 9377-2 with HP 6890 GC-FID.

3.1.2. Results

Prior to the start of the field experiment, water samples from groundwater wells showed that the initial treatment area was almost clean. Only the concentration of MTBE was above the limit of quantification (LOQ) in four tubes (Table 3.2). Any other VOCs were not detected. Based on the active air sample taken from the tube HP101, the TVOC concentration was also low, 4.7 mg/m^3. During the remediation, VOC concentrations were monitored from tubes HP101 and HP104. The concentrations did not decrease immediately; but first rather saw a slight increase over time. In addition, another oxygenate (TAME) and gasoline fractions (C5-C10) were detected along with MTBE in the tube HP104 (Figure 3.5). However, two months after the end of experiment, before the second stage of the experiment, all concentrations were below the LOQ.

One month after the second stage of remediation, it was found that the concentrations of MTBE in these tubes had increased compared to the initial concentrations. In addition, TAME was detected in small concentrations in both tubes. The concentrations of VOCs analyzed from tube HP102 were still below the LOQ. The remaining two tubes were not sampled due to the previously clean samples. The site was revisited in May 2019 to see whether the concentrations had rebounded. None of the targeted VOCs were detected from samples taken from the pipes HP104 and PVP1, indicating that the original treatment area was still clean.

Table 3.2. The concentration of MTBE (µg/l) in the original treatment area before the first and second stages of the experiment and 1 and 10 months after the second stage.

Date	HP101	HP102	HP103	HP104	PVP1
14.2.2018	6	<1	1	3	3
14.5.2018	<0,5	<0,5	<0,5	<0,5	<0,5
14.8.2018	12	<0,5	NA*	23	NA*
6.5.2019	NA	NA	NA	<0,5	<0,5

*NA = not analyzed
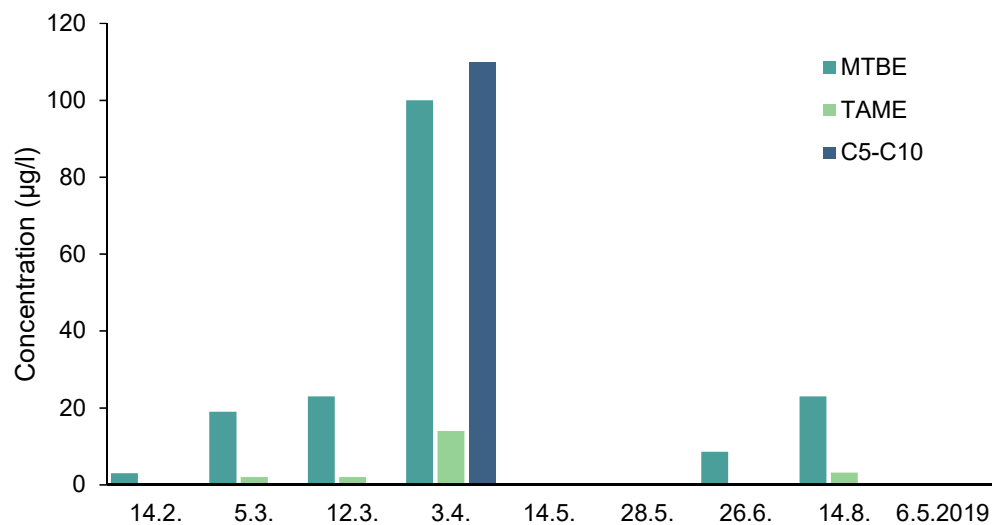
Figure 3.5. The concentrations of MTBE, TAME and C5-C10 (µg/l) in monitoring pipe HP104.

As the concentration of VOCs in the original treatment area had already decreased below LOQ, the treatment was continued in the groundwater pipe PVP3. In 2016, BTEX compounds and gasoline fractions were found in this pipe at levels exceeding water quality standards or the maximum irrigation water concentrations. In a couple of years, concentrations have naturally declined; the decrease has been 73-85%, depending on the compound (Figures 3.6 and 3.7). At the beginning of the treatment, BTEX and gasoline concentrations increased slightly, but in less than a month a decrease was documented. One month after the end of the experiment, slight rebound in concentrations was observed. However, the end concentrations were 88-97% lower than at the beginning of the second stage.

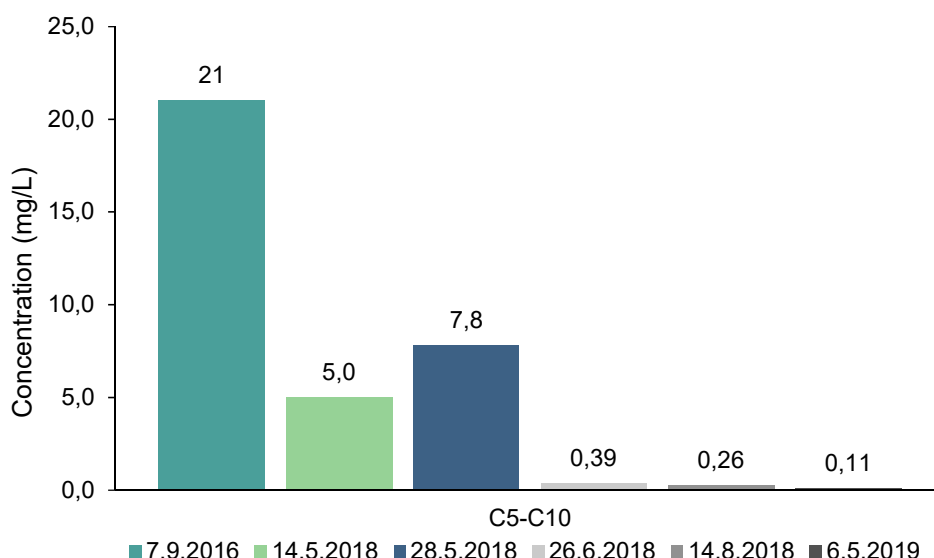The treatment was also found to increase the temperature and oxygen content in groundwater. This may also have a secondary effect, as elevated temperature and oxygen level may enhance the aerobic biodegradation of the contaminants. The spreading of H_2O_2 in groundwater was monitored using peroxide test strips (Quantofix®). Peroxide was found to spread unevenly throughout the test area. Removal occurred in the area where H_2O_2 had spread the most and where the concentration was supposed to be sufficient for producing an effect.

In May 2019, approximately ten months after the last injection, the site was revisited. C5-C10 compounds, including BTEX, were found at the site but only the concentration of benzene had clearly rebounded, from 15 to 28 µg/l in pipe PVP3 (Figure 3.6). However, the concentration was still lower than at the beginning of the treatment in May 2018. The highest concentrations were detected from pipe PVP2, which had not been treated in a similar manner to the other area, as only 100 L of H_2O_2 solution had been injected into the pipe. This spot was also closer to the fuel tanks that were possibly acting as further contamination sources still.

	Benzene	Toluene	Ethylbenzene	Xylenes
■ 7.9.2016	0,86	4,0	1,0	4,1
■ 14.5.2018	0,17	0,75	0,15	1,1
■ 28.5.2018	0,24	1,2	0,72	1,6
■ 26.6.2018	0,006	0,061	0,031	0,14
■ 14.8.2018	0,015	0,087	0,0043	0,15
■ 6.5.2019	0,028	0,01	0,005	0,0057
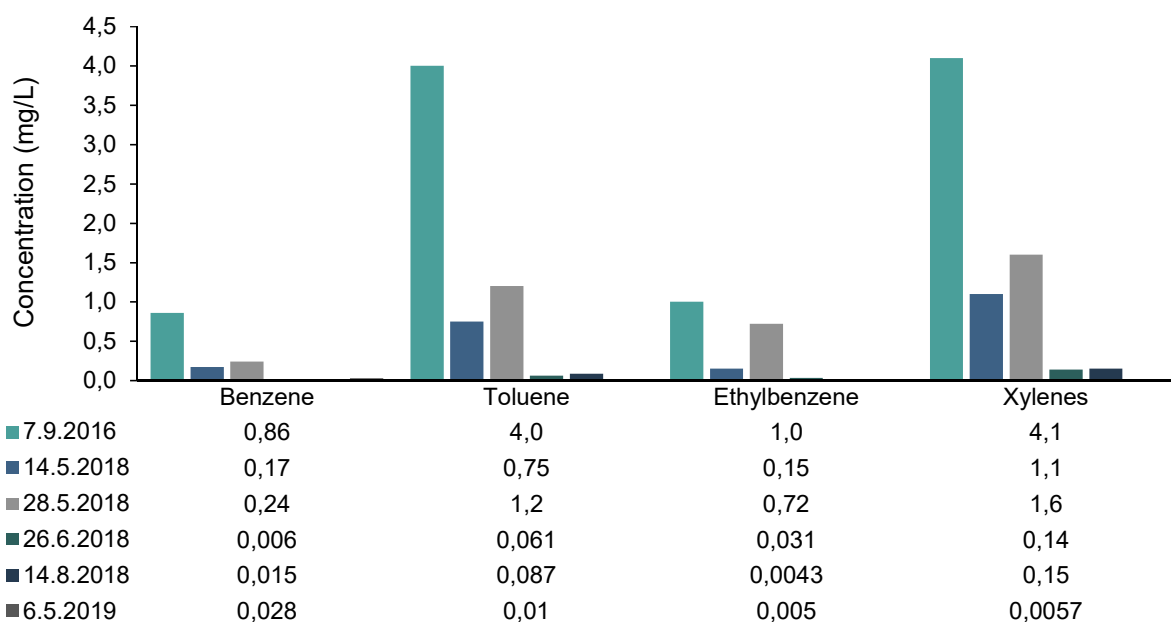
Figure 3.6. BTEX concentrations in groundwater before (2016) and after H_2O_2 injections.

Figure 3.7. Gasoline concentrations in groundwater before (2016) and after H_2O_2 injections.

The elevated MTBE concentrations in this field experiment can generally be explained by the fact that the fuel tanks, which are the most probable source of MTBE, are still located underground. Although the tanks have already been emptied, them being filled with water and then leaking seems to cause a constant source of contamination. Therefore, in order to complete the remediation of the site, it would be essential to empty and preferably remove the underground tanks and any other structures related to them. On the other hand, MTBE was not detected approx. 10 months after the latest injection.

The elevated concentrations of VOCs during the treatment may be also explained by the fact that the addition of H_2O_2 solution has been increasing the groundwater level, thus transporting adsorbed contaminants from soil to water. However, as the experiment continued, the concentrations of VOCs mainly decreased, which can be interpreted as the success of the treatment. For example, the BTEX compounds detected in the groundwater pipe PVP3 were not detected in the original test area, so it can also be assumed that the treatment has actually reduced the levels of the contaminants and not only mobilized VOCs. In case of MTBE, higher end concentrations may be explained by natural seasonal changes in the temperature and groundwater level or flow, in addition to the previously mentioned source of contaminants.

3.2. Site Janakkala, Finland

Preliminary studies and activities on the site were performed during project Tankki in 2013-2014 by superintendent Ramboll Finland Oy, and the contractor responsible for treatments, Nordic Envicon Oy. The study site is located in a residential area on the premises of a single household (Figure 3.8.), not within any major groundwater area. The contamination is due to a hole or holes in a private heating oil tank in the ground, located approximately 1 m from the north corner of the house, left intact, and suggested to remain so by the landowner. The removal was ruled out because of the vulnerable location near the house. Soil samples taken in 2013 showed that the contamination (C10-C40 hydrocarbons) in the area is heterogeneously distributed with concentrations appearing in depth 2.5-3 meters, near the depth of the bottom of the tank, varying between <50 mg - 3300 mg/kg. The soil is clayey and highly impermeable.

3.2.1. Methods

Since it was suspected that the soil under the tank was coarser and had higher oil concentrations, the sampling and water injections were to be performed through small holes in the tank itself. For this, five holes (4 cm ø) were drilled (Figure 3.8.). All samples were sent to Synnlab Oy for oil hydrocarbon analysis. Most remediation activities in project INSURE were found to cause soil mobilization, which resulted in large amounts of soil being pushed into the tank via the injection holes. This soil was found to be relocated from the sides of tank leaving a gap between the tank jacket and the soil, making two of the sampling spots unfit for sampling at certain points of the experiment. Because of this, even when these samples could be withdrawn, average values were calculated from the three spots at the bottom for the treatment follow up. Oil concentrations at the bottom were approximately hundred times higher than in the soil higher up the tank ceilings. Light fuel oil concentrations of 25 000 mg/kg in average were measured from the samples withdrawn from the first 30 cm under the tank prior to the treatment.
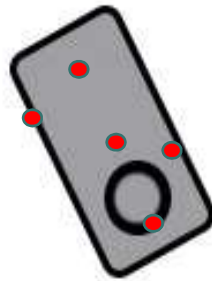
Figure 3.8 a-b. The site after the chemical oxidation treatment (a) and a drawing of the tank with the sampling spots in red (b). Only the results from the three spots on the bottom axis have been used for the surveys, because the other two are higher up the ceiling from where samples could not be withdrawn during all stages of the treatment and also since these concentrations were found to be negligible by comparison.

In 2016, the soil was treated with chemical oxidation based on Fenton's reagent (Table 3.3.). A dose of 1.5 cubes of 15 m-% H_2O_2 was introduced into the soil. The injection was repeated after two weeks and soil samples were withdrawn after each peroxide addition. The volume of the introduced liquid and the peroxide concentration were to result in H_2O_2 concentration of 2 mol/l when diluted to the approximated volume of water near the perimeters of the tank, and not intolerably high even without proper dilution. Tri-sodium citrate was added as a chelate to increase the solubility of catalytic iron in near neutral pH, in dose 25 kg, due to positive examples found in literature.

Oil residues were from then on to be treated biologically. Since both the H_2O_2 and the released oxygen are known to be toxic in higher concentrations, actions were taken to restore the original microbial activity. For living bacterial cells a 20 kg soil inoculum from a successful biostimulation experiment was planted into the tank. Oxygen was introduced as a slow-release calcium peroxide and nitrogen as an agricultural nitrate-ammonium mixture fertilizer, Suomen salpietari (Table 3.3.). During all biostimulation steps, all additives were placed into the tank, and slowly distributed into the treatable zone with a fort monthly dose of water added by the landowner. This frequency allowed for sufficient periods of aerobic conditions in soil in between the additions.

The soil was sampled after 2.5, 4 and 10 months. After 10 months, it was concluded that biostimulation should be continued in a modified form, with slow release fertilizers allowing a low-maintenance treatment and also having a lesser effect on the soil pH. From that point onwards, freshly patented meat industry waste product, bone meal, was used as a slow release source for not only nitrogen, but also for phosphorus, potassium and calcium (Table 3.3.).

Since positive response had mostly been observed in the upper layer of the soil (0-10 cm), degradation was optimized by adding surface activity enhancing product, biodegradable methyl-β-cyclodextrin (CD, Section 4 of the report), in dose 1% to the added water volume (Table 3.3.). In addition, hydrogen peroxide was added in low concentrations (0.5-1 %) to increase the oxygen level, whereas it was likely that also some of the introduced CaO_2 grains were still left in the tank. At this point the area was found water saturated, which meant that further doses of diluted H_2O_2 could not be added, and CaO_2 was from then on utilized as the sole oxygen source. CD was added in the original dose, non-diluted.

After 12 months of the last treatment, the soil was sampled from the monitoring holes only in single 20-30 cm soil columns, since water and sludge in the tank prevented non-disturbed sampling with higher depth sensitivity. An independent party, consultant Vahanen Oy, performed the final investigations on the area in May 2019, with samples withdrawn from a wider area around the tank. A risk assessment was also done based on these results.

3.2.2. Results

The results from the chemical treatment showed a clear decrease in average contamination level but with some hot spots remaining. After the two injections a 64% decrease in average concentrations had been achieved. Some part of this effect was gained through soil mobilization and mixing rather than chemical mineralization. This could be verified by the fact that results from the second treatment showed a 28% increase in oil hydrocarbon concentrations in comparison to the situation after the first dose.

From the samples from the three monitoring spots, it was concluded that 98% total reductions were achieved with the combined protocol, approximately 2/3 with the initial chemical treatment, and the remainder with the different variations of the biostimulation procedure (Table 3.3.). The secondary physical effect of the chemical oxidation treatment was likely also promoting biological degradation through heightened bioavailability of the contaminant and enhanced conditions in the tank in comparison to the pristine soil.

Table 3.3. Oil hydrocarbon levels at different stages of the *in situ* actions. Red color in the total reduction column indicate rebound concentrations from the previous sampling.

PHASE	C(C10-C40) (mg/kg)	TOTAL REDUCTION
ORIGINAL LEVEL	**25 000**	
1ST CHEMICAL TREATMENT H_2O_2 + **Tri-sodium citrate**	**6 700**	**74 %**
2ND CHEMICAL TREATMENT H_2O_2	**9 100**	**64 %**
BIOSTIMULATION 2,5 MONTHS Soil inoculum w/ bacteria **Ammonium nitrate + CaO_2**	**6 200**	**75 %**
BIOSTIMULATION 4 MONTHS Ammonium nitrate+ CaO_2	**2 400**	**90 %**
BIOSTIMULATION 10 MONTHS Ammonium nitrate+ CaO_2	**1 600**	**94 %**
BIOSTIMULATION 16 MONTHS Bonemeal + CaO_2/H_2O_2	**2 000**	**92 %**
BIOSTIMULATION 28 MONTHS Methyl-β-cyclodextrin Bonemeal+ CaO_2/H_2O_2	**430**	**98 %**

According to the inspections performed by Vahanen, the average oil concentrations appeared low on a larger area, but a single hotspot was still located in the soil, suggesting that the concentrations may still locally surpass different guideline values. Mobilization can't be ruled out as a contributor to these occurrences, whereas generally the situation on a larger area appears unaffected from what was concluded from the results of investigations performed in 2013-2014. The risk assessment by Vahanen oy as well a report on the treatment activities by UHEL will be passed unto the local environmental authority, the Centre for Economic Development, Transport and the Environment, who will then decide further need for activities on the site.

4. BIOSOAP METHYL-B-CYCLODEXTRIN

In bioflushing, oxygen or the alternative electron acceptor, and the required nutrients are added into the contaminated zone, often dissolved into water. One potential bottleneck for biological degradation is the low bioavailability of certain hydrophobic oil hydrocarbons. In these cases the efficiency can be enhanced by adding surface active compounds into the water, in such quantities that biological degradation is taking place in high enough efficiency so that the contaminant is not flushed into groundwater or otherwise mobilized beyond the treated zone before being degraded.

One such compound is Methyl-β-cyclodextrin that appears an optimal surfactant for *in situ* applications, based on results from former studies. Cyclodextrin is produced from a raw material containing starch. 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 hydrophilic outer circumference of the forming complex. CD itself is biodegradable but not the extent where is would act as a more readily available source of organic carbon than the contaminant thus inhibiting its biodegradation.

CD was tested in a bioflushing treatment at site Karjaa, but also used at various stages of treatments of site Valmiera and site Janakkala.

4.1. Site Karjaa, Finland

The site under and in close vicinity of a residential building has been contaminated with heating oil (Figure 4.1.). Nordic Envicon oy has been responsible for treating the contamination from January 21st 2015 onwards, according to terms of the verdict from the Uudenmaa Centre for Economic Development, Transport and the Environment. Prior to activities in project INSURE The site has been treated with *in situ* biostimulation, with injections of water amended with nutrients in mass elemental Corg:N:P ratio of 100:10:1 and with oxygen as the breakdown product of 0.5% hydrogen peroxide.

The additives have been injected into the filtration water in the pumping unit situated in the courtyard. The circulation volume is adjusted to the water surface level in the pumping unit. Relatively high concentrations of the non-water-soluble oil hydrocarbon fractions have been detected from the soil samples withdrawn from under the boiler room, and it has therefore been considered unlikely that the bioflushing protocol would lead to further reductions, due to the low solubility. The contaminated zone begins at 50-70 cm below basement floor level and its total volume is not known. The increase the efficiency of the bioflushing treatment, the solubility of the non-water soluble fractions was to be enhanced by adding bio-surfactants into the circulated water. The possible benefits were studied in a laboratory scale test in the summer of 2018.
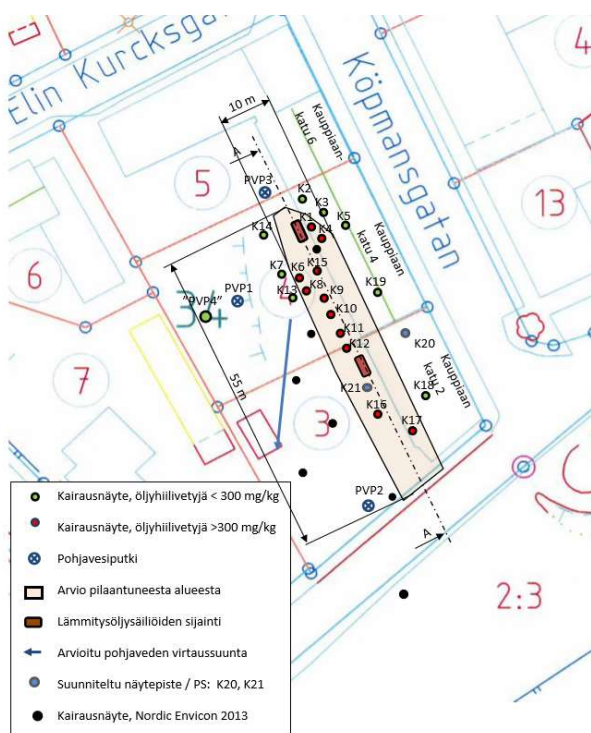
Figure 4.1. Karjaa site map

Prior to the treatment, the highest measured C5-C40 concentration in soil has been 5000 mg/kg, consisting almost solely of midrange (C10-C21) fractions. In 2013, in a single sample (13MN1039) C5-C10 concentration 70 mg/kg was detected, consisting of xylene and ethyl benzene. After the remediation steps already performed, the highest measured C10-C40 concentration has been 1500 mg/kg. The contamination was then found to consist almost entirely of aliphatic compounds in the C12-C15 and C16-C21 ranges.

4.1.1 Methods

Site Karjaa, was introduced into the project due to withdrawal of Populus Group oy in the summer of 2018. All activities on site were postponed till April 2019 due to the slow pace of the authorization process. The initial experiment protocol was presented to the Uudenmaa Centre for Economic Development, Transport and the Environment in October 2018. A risk assessment was required in March 2019 for the plan to be accepted and this was provided in April 2019. The risk assessment was done by UHEL with contractor Nordic Envicon oy utilizing the Soilirisk program. From the UHEL modelling data it was calculated to which degree the addition of 5% CD increases the concentrations of different oil fractions in water in relation to the control treatment. From these coefficients an approximation was then calculated for concentrations in water in a situation where the biostimulation treatment would be enhanced with CD, using the existing results and the aforementioned approximations for the fragment ratios. The risks associated with the ongoing bioflushing treatment were compared with the concentrations measured at the site, and then to the risks from the 5% CD treatment assessed as explained here.

At the site 100 litres of 5% CD were poured into the excavation site with a two week interval between injections (Figure 4.2.). This was the maximum volume of water that could be added in a single dose due to the low permeability. Soil was sampled before and after the experiment period for fragment analysis. The water quality was monitored from samples withdrawn from ground water wells during each site visit.

Figure 4.2. Excavation site used for CD injections at site Karjaa

4.1.2 Results

The excavation site that was used for injections was found clean already after two additions of 5% CD (Table 4.1). During the treatment no oil hydrocarbons have been detected from monitoring sites in concentrations above level of quantification. With project INSURE coming to an end, it is being discussed with the contractor whether the treatment will be continued, which would require monitoring of soil at spots currently unavailable for sampling. Regardless of what is being decided, mobilisation of the contaminant will be followed up at least until late June. Activities and monitoring results will then be reported to the Uudenmaa Centre for Economic Development, Transport and the Environment.

Table 4.1. The targeted oil hydrocarbon compounds in soil before and after two injections of cyclodextrin.

PHASE	C (aliph C12-C15) (mg/kg)	C (aliph C16-C21) (mg/kg)
ORIGINAL LEVEL	110	160
AFTER TREATMENT	<30	<30

5. PHYTOREMEDIATION

5.1. Site Virrat, Finland

The site at Kiertotie 18 is a privately owned industrial site, situated in a lake district in Pirkanmaa. It has been contaminated with oil hydrocarbons and heavy metals. The local environmental authority, Pirkanmaan Ely-keskus (PIRELY), agreed upon the remediation plan in 2016. PIRELY is also taking part in financing the remediation. Phytoremediation was chosen as the most suitable remediation method. The contractor is the Natural Resources Institute Finland, LUKE.

5.1.1 Methods

In 2017, two spots on the site were found to have very high concentrations of hydrocarbons and heavy metals, and they had to be removed by excavation before starting of the planting (Figure 5.1.). The soil at the site was very stony and compacted, and drillings had to be done prior to the planting of hybrid aspen plants in 2017 (Figure 5.2.).

Figure 5.1. Oil and Hb-contaminated hot spots removed by digging before starting the planting.

Figure 5.2 a-b. Drilling holes for planting.

Hybrid aspen and European aspen seedlings were chosen for the phytoremediation. Altogether 1200 aspen seedlings in 17 planting blocks were planted during 2017. First sampling of the site was done in the summer of 2017 according to the experimental design to investigate the soil status at the start of the phytoremediation. The DNA from the samples was isolated and PCR amplified for the identification of bacteria and archaea in the contaminated soil. The DNA samples have been sequenced in late 2017 and the bioinformatic analysis was planned to start in 2018 to detect the microbial communities (bacteria and archaea) present in soil. However, as the Populus Group existed the INSURE project in August 2018, the latter analysis has not been performed.

Figure 5.3 a-b. Hybrid aspen and European aspen seedlings (*Populus tremula* and *tremuloides*).

The site was photographed using DJI Phantom 4 remotely piloted aircraft system (RPAS) in October 2017. The pictures were used for making GIS maps of the phytoremediation. In the end of June 2018 a monitoring of the phytoremediation (the growth of the seedlings) was conducted using the RPAS system. Due to the dry summer, the hybrid aspens had not grown enough for the actual growth to be detected by the RPAS system.

Figure 5.4 a & b. DJI Phantom 4 RPAS equipped with IPad for remote control using specially designed computer program for photographing a preselected area with the mini aircraft

Due to the withdrawal of Populus Group from the project in 31th of August 2018, active follow-up at the site has not been done. The next sampling will be in autumn 2019 with LUKE as the responsible party. The treatment at the site will continue until around 2028.

6. SITE GAIDES IELA, VALMIERA, LATVIA

Gaides iela is located in Valmiera, Latvia. The former pilot site, Krustmali, was investigated but the soil was found to be of insufficiently low contamination levels. The new pilot area is a part of the former Valmiera oil base, an abandoned area with partially demolished buildings.

VentEko has investigated the area to determine the characteristics, volume and extent of groundwater pollution with oil products as well as its migration potential and impacts on environment. It was found out that the major part of territory does not conform to the requirements of the Latvian normative acts legislation. The content of petroleum products in the analyzed samples ranged from 74 mg/kg to 7000 mg/kg. The hydrocarbon content of petroleum products exceeding the precautionary threshold (B - 500 mg/kg) was recorded in nineteen samples, including one also exceeding the critical limit C (5000 mg/kg), which can be considered strong ground pollution with petroleum products. In addition, BTEX compounds were also detected.

It can be concluded that the investigated territory is polluted with oil products. The most substantial pollution has been detected in the area of overpass, as well as in the territory that is located closer to former oil base central part. In addition, petroleum hydrocarbons and PAHs have been found in groundwater samples. The total area of groundwater pollution with total petroleum hydrocarbons in the research area is ~ 650 m2. Groundwater level depth varies from 0.7 m to 2.89 m from the soil surface.

Based on these results, VentEKo stated that the site needs to be remediated. Due to the relatively low filtration properties of the soil (clay loam and loam), *ex situ*, i.e. excavation, or *in situ* solidification/stabilization were suggested as the most effective methods for site remediation.

Figure 6.1. A former gas station and some abandoned buildings at the site Gaides iela.
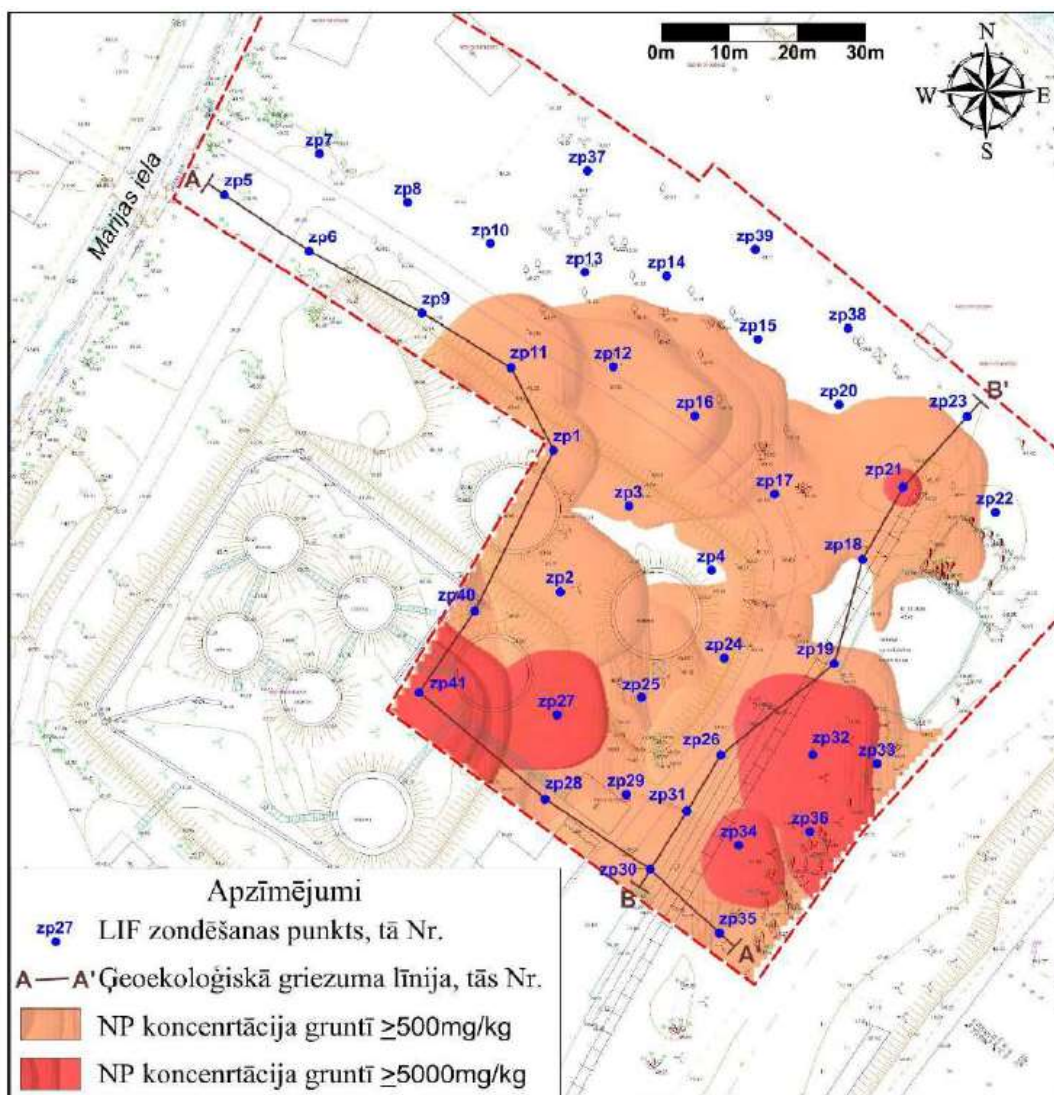
Figure 6.2. A map from the site, showing the most polluted areas. An orange-red color indicate areas with oil hydrocarbon content ≥500 mg/kg and red areas ≥5000 mg/kg.

7. CONCLUSIONS

One of the main reasons why negative or at least skeptical attitudes towards *in situ* remediation prevail is the site specificity, meaning that when positive result are achieved, it is often through trial and error, and there is still a possibility that site conditions may not meet the standards. In project INSURE several methods were tested at different sites and different conditions to see the degree to which they were affected by changes in for example soil type, ground water level and choice of contaminants. Of the six *in situ* treatments envisioned by UHEL, four were at least locally remediated with considerable success (Table 7.1.). Due to the fact that these four were all located in Finland and therefore provided easier access for the researcher parties , it could be concluded that the ability to visit the site with high frequency to re-asses the problem and think for alternative solutions in real time, proved to be vital for a successful outcome.

Table 7.1. The summary of pilot tests.

Pilot site	Country	Contaminants	Method*	Status
Nastola	Finland	Light Heating Oil	Electro-kinetic biostimulation	Finished w/ success
Dzelzcela iela, Valmiera	Latvia	Mazut oil	Electro-kinetic biostimulation, oil bioavailability enhanced with cyclodextrin (CD)	Treatment finished w/ inconclusive results
Södra stranden, Motala	Sweden	Various, mainly light heating oil	Electro-kinetic biostimulation	Treatment finished w/ inconclusive results
Karjaa	Finland	Light heating oil	Bioflushing with CD	Successful local results, on-going
Virrat	Finland	PAHs, metals	Phytoremediation	On-going
Loppi	Finland	VOCs in groundwater	Chemical oxidation / peroxide sparging	Successful local results, treatment on hold
Janakkala	Finland	Light heating oil	Chemical oxidation + bioremediation	Successful local results, treatment on hold
Gaides iela, Valmiera	Latvia	Oil (petroleum, BTEX)	...	Not started

Main results or insights achieved in the project were:

- Electro-osmotic biostimulation proved to be effective with coarse gravel soil, contrary to some findings in literature. When working on sites with clayey silt soil type, the efficiency was too low for the treatment to be considered financially reasonable. In both of these cases (Motala and Valmiera) it is suggested that excessive amounts of electricity was spent on heating the ground water, without significant effect on the distribution of additives in the contaminated zone. This would suggest that ground water level is a major factor concerning the applicability of the electro-osmotic method.

- For chemical oxidation to be considered a multi-contaminant treatment method near neutral pH, its effect on mobilization of non-volatile compounds is to be further investigated *in situ*. On the other hand, on a site contaminated with volatile gasoline residues, treatment with high concentrations of H_2O_2 proved effective, at least during the spring-summer season. In these cases volatilization was likely adding to the treatment efficiency, and this could be likely further heightened by applying soil vapor extraction in the non-saturated zone

- Use of biosoaps such as methyl-β-cyclodextrin can speed up biostimulation, if the soap in question is not biodegradeable to the degree it acts as a more readily available carbon source for the degrades. This increased effect is due to the bioavailability of the contaminant being increased with heightened water solubility. This would mean that the associated risks are also heightened, and the balance between overall sustainability and the environmental risks should be considered by all stakeholders.

- Positive remediation outcomes were achieved at several different sites, in difficult conditions. In most cases this required a "trial and error" type approach and continuous reassessment of the situation. In situations as the ones described here, these outcomes are still hoped to encourage different interest groups into considering the potential advantages of *in situ* applications in remediation of contaminated soil or groundwater.