INSURE

Innovative Sustainable Remediation

SITE PROGRESS REPORT 3 (1/2019) UHEL

EUROPEAN UNION
European Regional Development Fund

Interreg
Central Baltic

1. Site Janakkala, Finland (UHEL)

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 on a residential area on the premises of a single household (Fig 1.1.). The leaking was due to a hole or holes in the private heating oil tank dug in the ground, approximately 1 m from the north corner of the house, left intact, and suggested to remain so by the landowner. The contamination on the area is heterogeneously distributed with concentrations from 2,5-3 meters, near the bottom of the tank, varying between <50 mg - 3300 mg/kg. The soil is clayey and highly impermeable, Because of this, and because it was suspected that the soil under the tank was coarser and had high concentrations, the sampling and water injections were decided to be performed through small holes in the tank itself. For this, five holes (4 cm ø) were drilled (Fig 1.2.). Higher concentrations were indeed found in the preliminary sampling. Because of the soil mobilization, the original sampling holes could be used repeatedly for subsequent samplings.

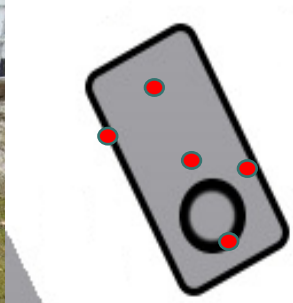

Fig 1.1. The site after the chemical oxidation treatment

Fig 1.2. Drawing of the tank with the sampling spots in red, only the results from the three spots on the bottom axis have been used for the surveys since the other two are higher up the ceiling where the oil hydrocarbon concentrations are negligible by comparison.

In 2016 the soil was treated with chemical oxidation based on Fenton's reagent as described in site progress report 1. The hydrogen peroxide injection was performed twice with a two-week interval, with sampling performed immediately before each reagent injection. Since both hydrogen peroxide and the released oxygen can be toxic in higher concentrations, steps were then taken to restore the original microbial activity. This was attempted by introducing a soil transplant from a successful biostimulation treatment,

carrying bacteria capable of digesting diesel oil hydrocarbons. Oxygen was introduced as calcium peroxide and nitrogen as an agricultural nitrate-ammonium mixture fertilizer, Suomen salpietari. The soil was sampled after 2,5, 4 and 10 months. New nitrogen was added after 2,5 months. According to the last sampling it was concluded that biostimulation was likely effective but should be continued in a modified form. From that point onwards, freshly patented meat industry waste product bone meal was used as a slow release source for nutrients, as explained in site progress report 2. Positive response has so far mostly been observed in the upper layer of the soil (0-10 cm) (table 1.1).

Table 1.1. Oil hydrocarbon levels at different stages of the in situ actions.

	Average c(C10-C40) (mg/kg dw)	Total reduction
Original level	25000	
1st chemical treatment	7000	72 %
2nd chemical treatment	9000	64 %
Biostimulation 2,5 months	6000	76 %
Biostimulation 4 months	2500	90 %
Biostimulation 10 months	1600	94 %
Biostimulation 16 months	2000	92 %

The total reduction after 10 months of biostimulation was 94% from the original level, whereas during the last six months the efficiency was lower than expected (table 1.1.). After 16 months, the removal rate was slightly reduced. Soil has been found to be poorly permeable, which hinders the percolation of injected liquid into soil and makes the sampling difficult.

Degradation has since been enhanced by adding surface activity enhancing product, biodegradable methyl-β-cyclodextrin. Also, hydrogen peroxide has been added in low concentration (0,5-1 %) to increase oxygen level. Cyclodextrin and hydrogen peroxide, mixed with water, and bone meal have been added into the tank about monthly. The next plan is also to add calcium peroxide into the tank as a source of oxygen. Calciumperoxide is a slow release product so a steadier and lengthier oxygen release with a single addition should be provided. Calciumperoxide has been successfully used in underwater biostimulation purposes in a different setting.

2. Site Motala, Sweden (UHEL)

Sampling, drilling and installations for the UHEL's electro-osmotic biostimulation treatment for the oil hydrocarbon contaminated site (Fig 2.1.) were made by Sweco in June 2017, as explained in detail in the site progress report 2 (1/2018).

The first biostimulation treatment was started in June 2017. A steep V shape ditch was dug along the anode row, with the center ca 1 m from the row. When water started to flow 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 into the ditch, after which the ditch was filled up.

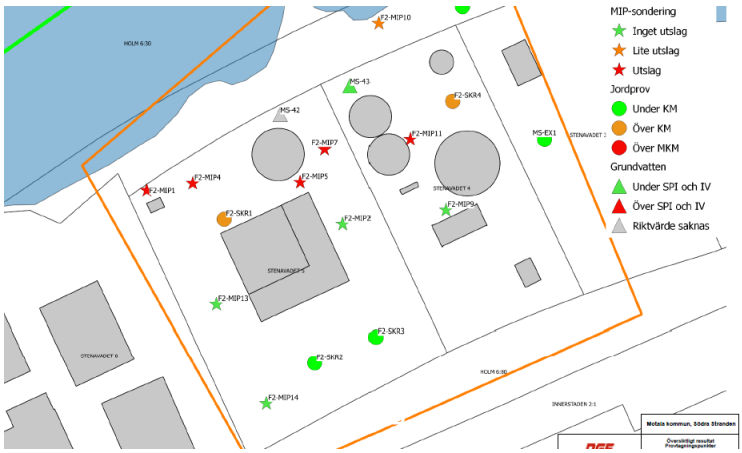

Fig 2.1. The oil hydrocarbon contaminated site Södra stranden.

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. Similar follow-up visit was done in December 2017 and voltage was switched to 200 V.

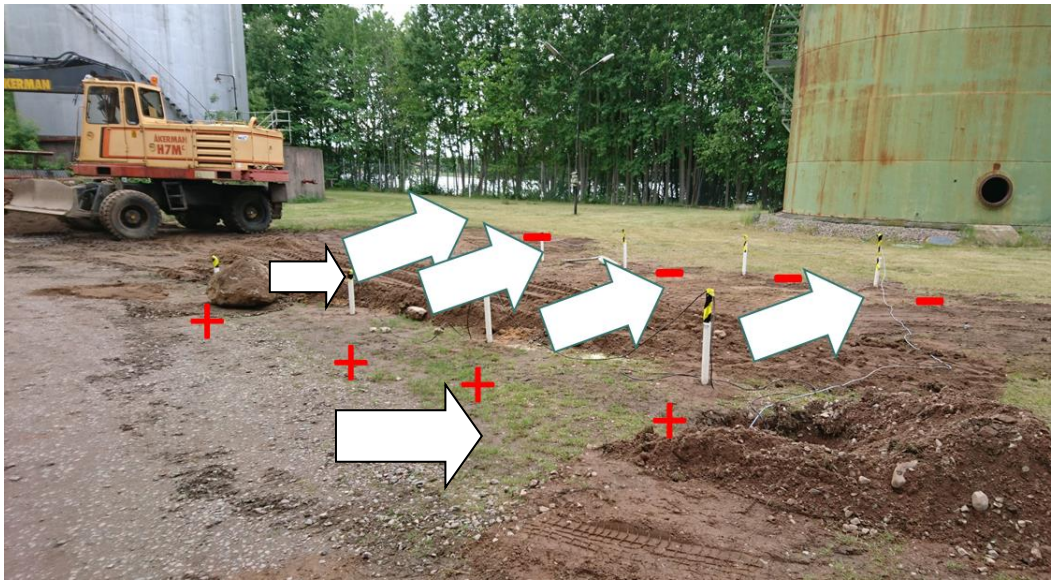

Fig 2.2. The study area with the direction of the electric field: anodes to the left, cathodes to the right. Water flow direction is also from left to right, from anode to cathode.

By the time of the sampling in December 2017 the concentrations of aliphatic compounds had not decreased (fig 2.3) as explained in site report 1/2018. In addition to the data in the figure, the temperature and the oxygen concentrations in the ground water were measured. The temperature in the field was slightly elevated compared to the controls. The oxygen in the anode tubes was oversaturated (> 30 mg/L) while in the middle of the field it was 2 mg/L showing that oxygen was actively consumed. As 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, it was suspected that oxygen was the primary limiting factor. To increase the degradation, 25 kg package of calcium nitrate with 1000 liters of water were mixed in a Cipax tank and the solution was distributed over the test area in the end of April 2018. Nitrate (NO_3^-) was used because it can function as an alternative electron acceptor replacing oxygen. The addition was done every other week for twelve weeks, six times in total. Site treatment was finished in September 2018.

In the end of experiment the concentration of aliphatic hydrocarbons had decreased. Compared to the highest concentrations detected in December 2017, concentrations had decreased ca 40-70 %. However, the concentrations were still relatively high in two spots (S9 and S7, fig 2.3), indicating that the method was not as efficient as expected. Probably with prolonged treatment time the concentrations would have been even lower.

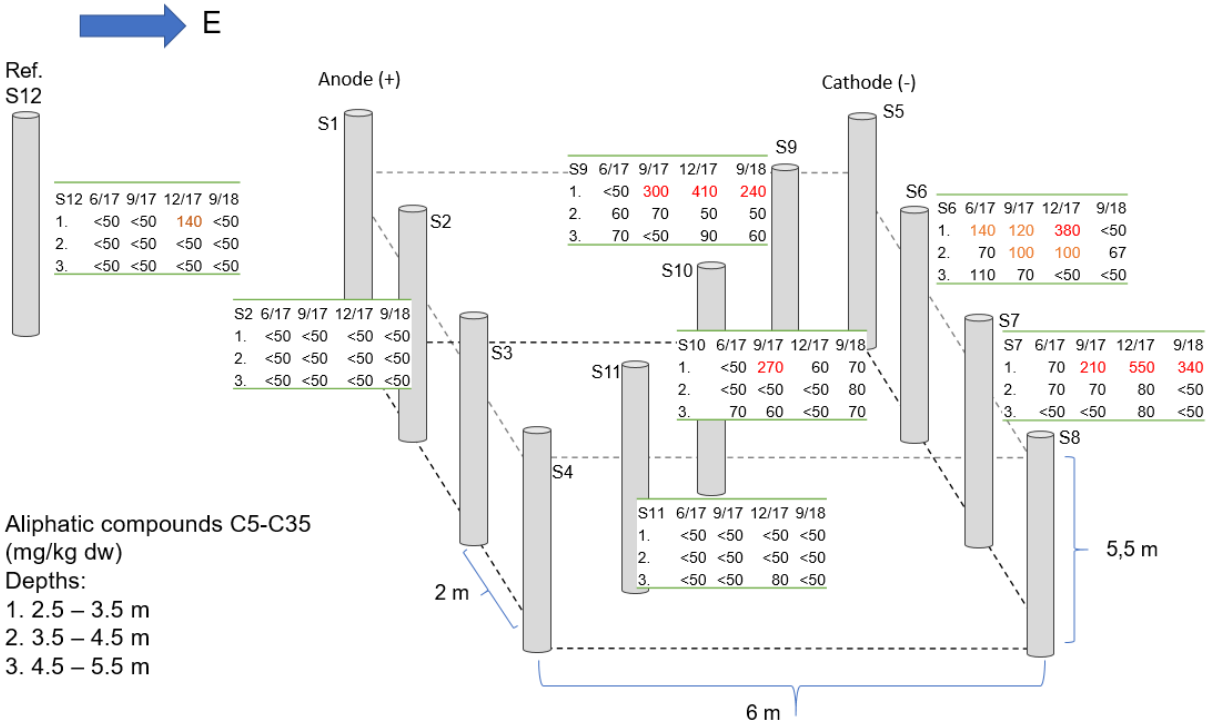

Fig 2.3. Concentration of aliphatic hydrocarbons (C5-C35) in the soil at different depths and sampling dates.

The water samples previously received from Motala were previously treated by POP for DNA isolation. The isolated DNA was PCR amplified in 2017, but due to problems with proof reading PCR enzymes, the preparation for sequencing took a long time. The PCR products were send for sequencing in late 2017. Contrary to earlier plans, bioinformatics analysis has not started. Also, soil samples taken in December 2017, were delivered to Populus Group Oy for biological analysis. Contrary to earlier plans, DNA isolation from the soil samples for identifying the microbial communities during remediation have not yet been executed.

3. Site Valmiera, Latvia (UHEL)

Pilot tests in Valmiera were initiated in September 2018. University of Helsinki was represented by Harri Talvenmäki and Niina Lallukka who arrived at the site approximately on Wednesday the 19th of September 2018. Representatives of the Valmiera city and Peteris Birzgalis of Vides Konsultāciju Birojs and his crew were already present.

On Wednesday, the positions of the electrode rows were determined and marked. The smaller area pinpointed in the original plan was, and had already been, found unsuitable because of underground tanks that would potentially compromise both the drillings and the treatment. The new study square was set to include the ground water well from where the highest oil hydrocarbon contamination levels had been measured, and otherwise the 6 x 6 m^2 square was set in the only possible way for it to be accessible for 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 original targeted site around the underground tanks (fig 3.1).

Fig 3.1. The treatment site: the original target area marked in darker blue with the intended electrode rows marked with (+) and (–) symbols. The new chosen site in lighter blue with the suggested anode row marked with (+) and the cathode row with (-). The arrows mark the suspected resulting movement of fluids. The two control drillings outside the treatment area are marked with spots in light blue.

The soil drillings could be performed relatively fast as the soil (clayey sand/silt) was easy to penetrate. Still, with the high number of drillings, 13 (8 electrode wells, 2 control spots outside the treated area, 3 additional spots within the area) the task was finished

only on Friday morning. The samples were divided into two, the other remained with Vides Konsultāciju Birojs and the other half travelled to Finland in case the heavier oil hydrocarbons (C40-C80) are to be analyzed. Biological samples weren't withdrawn because they had been required only by Populus Group oy, who are no longer involved in the project. All samples 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. The contamination appeared to be in depth 1-3,5 m.

Electricity was to be installed on Thursday. Due to some 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) weren't met. An alternative version of the same sheet suggested lower input (so called two-phase current, AC 230V 25 A). The most probable cause for multiple versions of the same plan is that the requirements for the transformer in question are unnecessarily high for the task at hand and a smaller unit would have been suitable had Valmiera or Vides Konsultāciju Birojs purchased their own. Nevertheless, a three-phase current input was promised for the following week. The stainless steel rods were connected to serve as electrodes, but no cables were connected. All the pieces belonging to the electrical set up, apart from electrode rods, were delivered and left at the site by UHEL to help start the experiment as fast as possible.

Additionally, some remediation chemicals were delivered; methyl-β-cyclodextrin (60 liters) and bone meal. Cyclodextrin is a biodegradable soap of cyclic sugars that can enhance the solubility of otherwise non-soluble oil hydrocarbons. Bone meal, a multi nutrient product used in Motala was found unsuitable for the purposes: The slow releasing compound has usually been dug into the ground rather than dissolved into the injected water volume and in this case the anode side was set on covered area disallowing effortless digging. Also, some versions of the protocol suggested the use of electron acceptors and because of all alternative electron acceptors were thought to be more difficult to locate, ammonium-nitrate mix, also used in Villähde, was chosen. A sufficient product with added phosphorus could be find from the nearby store in large doses and was later picked up by Peteris. He was advised to add 50 kgs. of ammonium nitrate (+phosphorus) and 10 liters of cyclodextrin per month. Injection was suggested to do every two weeks by adding 2-4 m^3 of liquid, preferably full 4 m^3. The treatment should last 5 to 6 months.

All installations were completed by the time of the INSURE partner meeting in early October 2018, during which Martin Romantschuk and Harri Talvenmäki visited the site to see everything was running as planned (Fig 3.2)

Fig. 3.2. Finished site installations. Anode site on the left, cathode site on the upper right near fence. Tubes in between mark alternative sampling spots.

4. Site Gaides iela, Latvia (Vidzeme)

Former project site Krustmaļi was investigated in February-March 2017 and found to be less contaminated than expected. Thus, an alternative site, Gaides iela, has been suggested for pilot tests but a final acceptation from the site owner hasn't yet been provided.

5. Site Villähde/Nastola, Finland (UHEL)

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 contamination was due to a filling accident in 2001. The area was treated in 2016 as described in status report 1/2017. The site was considered clean by an independent consultant, as described in site progress report 1/2018, and no further actions on the site were therefore required.

6. Site Virrat, Finland (POP/UHEL)

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

As explained in site progress report 2, 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 summer 2017 according to the experimental design to get the soil status at the start of the phytoremediation. The DNA from the samples was isolated and PCR amplified for 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 figure out the microbial communities (bacteria and archaea) in soil.

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

Due to the withdrawal of Populus Group from the project, bioinformatic analysis nor active follow-up have not been done. UHEL will take over the future reporting of Virrat pilot site.

7. Site Loppi, Finland (UHEL)

A new pilot site was included into the project because of the withdrawal of Populus. The site is a car repair shop at Loppi in Southern Finland with existing data of both VOC and C_{10}-C_{40} 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. Basic research on the area was done in 2014 by Finnish Consulting Group, and geographical surveys were performed by contractor Nordic Envicon in 2016.

Most of the yard is under concrete 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 depth of 3-4 m. The suspected direction of the ground water is towards North-West or West, that is, towards River Isojoki.

One VOC of concern was MTBE (methyl tert-butyl ether). Highest measured MTBE concentrations were found in groundwater well PVP1, and in the storage tank (fig. 7.1), whereas the immediate area surrounding the tank has been found clean. The area around PVP1 was chosen for the initial tests since in the latter the contaminated water appeared as a free water phase, and thus the treatment would betray the characteristics of an *in situ* field application. The study area was contaminated only by the water soluble oxygenates (MTBE and TAME) and 1,2–dichloride ethane, suggesting a closer connectivity to the pilots made earlier with MTBE spiked water. The area was also uncovered and not in use, enabling faster installations, and a more thorough monitoring through larger number of wells. Also, since the diesel-lysimeter test hinted towards a possible mobilization of heavier oil hydrocarbons, those were by choice excluded from the initial field test.

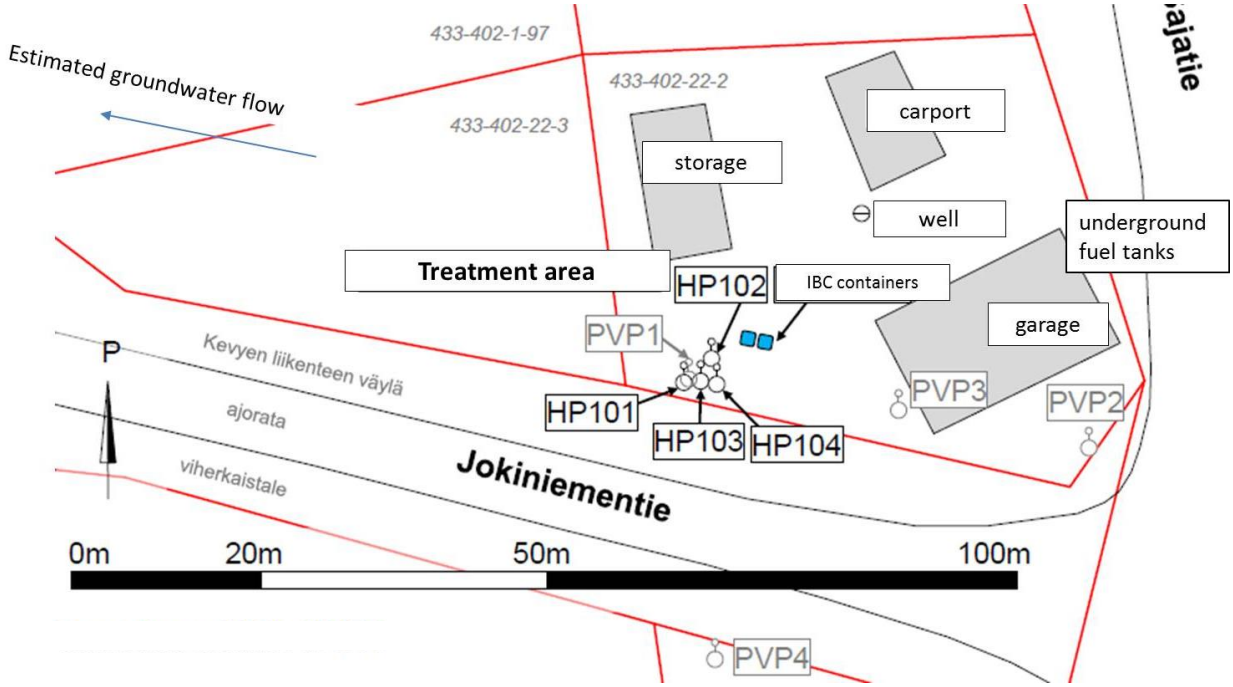

Fig 7.1. Loppi (Jokiniementie 260) technical drawing with groundwater tubes PVP1-4 and installed survey tubes HP101-HP104 marked.

For the experimental set up, four vertical groundwater pipes were installed to depth 5,5 m with perforation starting in depth 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. H_2O_2 injections were started two weeks after the installation. Groundwater was sampled prior to this and air-VOC measurements (using photoionization detector, PID) were recorded from all ground water wells on the area.

Fig 7.2. The site used for both frozen and molten soil tests, surrounding PVP 1.

The initial protocol was to inject 1m^3 of diluted peroxide into the selected spot during a single 8-hour session. In the first installation in February 2018 with 0±1 ˚C ambient temperature only 100 litres could be injected because of an insufficient pump. The 50 % peroxide was diluted on site with tap water in a 1m^3 container and injected to the tubes in the concentration 17 %. The dose was approximated with coarse estimates for the radius of effect; so that an 1m^3 of introduced 17 %-m peroxide would further dilute to level 2 M, a dose used in the pilot. However, both the introduced volume and the probable immediate radius of effect were lesser than the values used for approximation.

The injection was continued five days later but with ambient temperatures then in range -18 to -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 warm soil. Now the additions were done in concentration 25 %, and to all the ground water tubes simultaneously. Due to low levels of the contaminants in the original area, the experiment was continued closer to the fuel tank area in PVP3 because of high concentrations of other VOCs and a considerable odour of heavier oil hydrocarbons. A less favourable 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.

Fig 7.3 a-b. PVP 1 area (a) and PVP 3 area during the 2nd period of the experiment

Only 60 litres of diluted H_2O_2 could be introduced to PVP 3 in a single step. Because of this, 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 since water samples couldn't 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 PVP 3 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 stopped in June 2018, 150 days after the initial peroxide injection.

8. Site Karjaa, Finland (UHEL)

Another new pilot site, Karjaa, was included into the project because of the withdrawal of Populus. At Karjaa in Southern Finland, an oil contaminated area underneath a residential building has earlier been remediated by bioflushing by adding nutrients and 0.5 % hydrogen peroxide (as a source of oxygen) into water. In bioflushing, nutrient- and oxygen-rich water is infiltrated through contaminated soil, during which the water is also cleaned.

Samples taken under the floor of the boiler room indicate that the concentration of water-insoluble components is still high. The continuation of the current bioflushing cannot be expected to result in a better removal, as low solubility of contaminants reduces its efficiency. Pollution begins at a depth of 50-70 cm under the floor, and there is no precise information on its extent.

The treatment has been proposed to be enhanced by using cyclodextrin, which acts as a surfactant. Uusimaa ELY Centre has accepted the follow-up plans but requires an environmental risk assessment, as cyclodextrin may increase the solubility and mobility of contaminants and as the pilot area is in the groundwater area. The risk assessment of using cyclodextrin will be done using Finnish SOILIRISK program.

The effect of cyclodextrin for the removal of oil hydrocarbons has already been tested at laboratory scale. Soil samples taken from the site were mixed with the treatment solution (200 g of soil, 300 ml of solution). Three different treatments were made: 5 % and 1 % (v:v) cyclodextrin (CD) treatments and water control. In the first step, bottles were shaken in 1-hour cycles five times altogether. Phases could separate between each shake. On the second time, the experiment was repeated but with 5-hour shaking periods.

Based on the results, the treatment affects the hydrocarbon concentrations in water and the mean values of the different treatments differ at both times for all measured oil hydrocarbon groups (C10-C40, C10-C21 and C21-C40) (fig 8.1). The removal efficiency remained high, especially with the C16-C21 aromatic compounds. With C10-C12 aliphatic compounds, the final removal rate (48%) was achieved during the first shakings. Also, it was found that the efficiency was dependent on the CD concentration; by using 1% CD final but weaker result was achieved in the same time than by using 5 % CD. The same phenomenon appears to be less pronounced with other fractions, i.e. on the second time, the original efficiency decreased on average by about one third, regardless of the CD concentration. The results suggest that the additive could be used either for more effective biological treatment or for soil flushing. The dose would need to selected on the basis on which of the two methods is more desirable: with higher dose the removal rate is higher, but in biological treatment only small amount of oil hydrocarbons should be mobilized at a time so that they are biodegraded in sufficient timeframe to avoid the overt risk of mobilization.

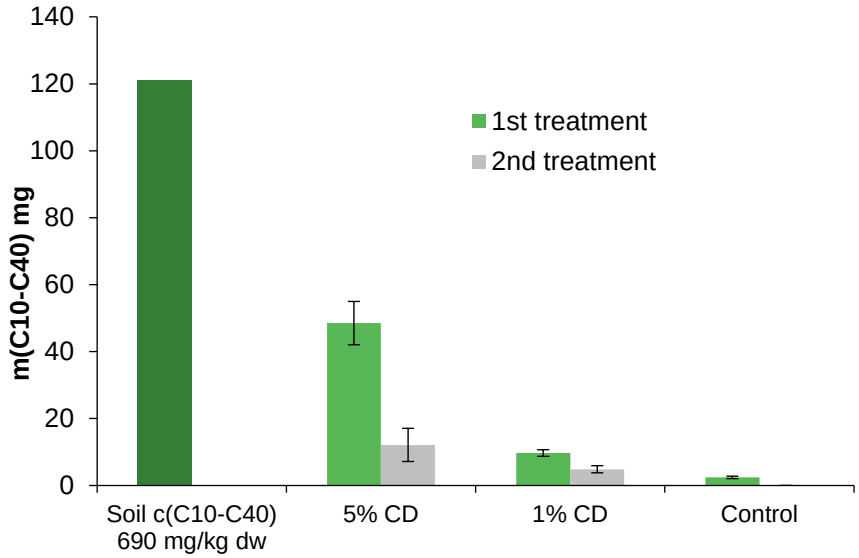

Fig 8.1. Amount of oil (mg) dissolved in water. On the left is shown the amount of oil in homogenized soil (multiplied with soil dry weight 0.18 kg)