INSURE

Innovative Sustainable Remediation

# REPORT ON REMEDIAL ALTERNATIVE SELECTION AND RISK VALUATION – SITE KARJAA

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Interreg
Central Baltic

# 1. Introduction

Site Karjaa, located in southern Finland, is a heating oil contaminated area (figure 1). The contaminated zone is underneath a residential building and 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.

Before remediation, the highest analyzed oil hydrocarbon (C5-C40) content was 5000 mg/kg and consisted almost entirely of middle distillates. In 2013, one sample had a C5-C10 concentration of 70 mg/kg, consisting of xylene and ethylbenzene. After the *in situ* biostimulation treatment, the maximum concentration (C5-C40) dropped to 1500 mg/kg. Based on the fractional analysis, the contamination composed almost completely of aliphatic hydrocarbons in ranges C12-C16 and C16-C21.

The latest 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 the 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 estimated area of contamination is 500 $m^2$. Soil type in the depth of contamination is fine sand / silt.

One option to enhance bioflushing is to add surfactants, in this case cyclodextrin. Cyclodextrin (CD) is a biodegradable soap of cyclic sugars that can enhance the solubility of otherwise insoluble oil hydrocarbons. The possible risks of its use were evaluated in a detailed risk assessment. After that, other possible remedial alternatives were compared with bioflushing systems in a decision matrix to see the whether any of those would have been a more suitable choice.

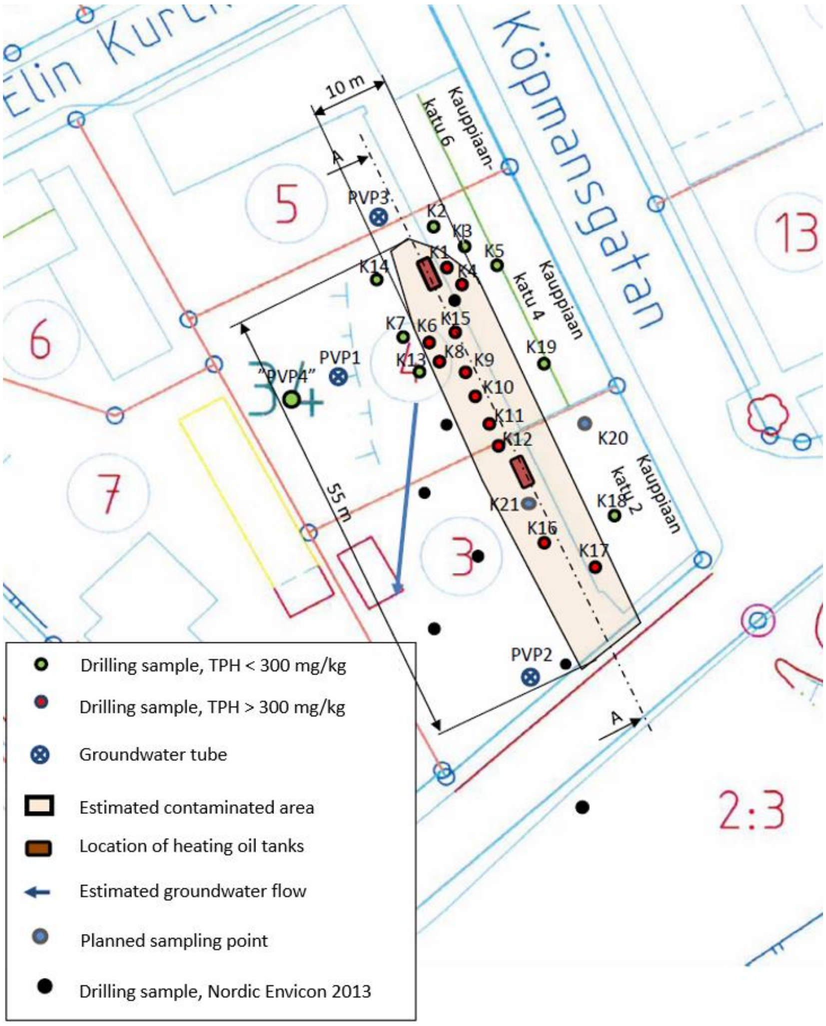


Figure 1. A map of the site.

# 2. Summary of risk assessment

Based on the results of analysis, bioflushing can no longer significantly reduce oil concentrations. On the other hand, due to the silty soil and low mobility of detected contaminants, it can be concluded that residual oil does not migrate to a wider area and is unlikely to cause harm to health or the environment.

The suitability of CD treatment at the site was tested in laboratory-scale modelling studies executed at the University of Helsinki. Cyclodextrin was found to increase the amount of hydrocarbons, especially those with low water solubility, dissolved in water when compared with water treatment alone. Before the implementation of enhanced bioflushing, the authorities required a risk assessment. Possible environmental and health risks related to the use of cyclodextrin are the spread of pollution with groundwater and transport into indoor air through a hole in the basement's floor. The risks to indoor air are mainly related to volatile components that have not been detected at the site after 2013. Possible exposure routes are shown in figure 2.

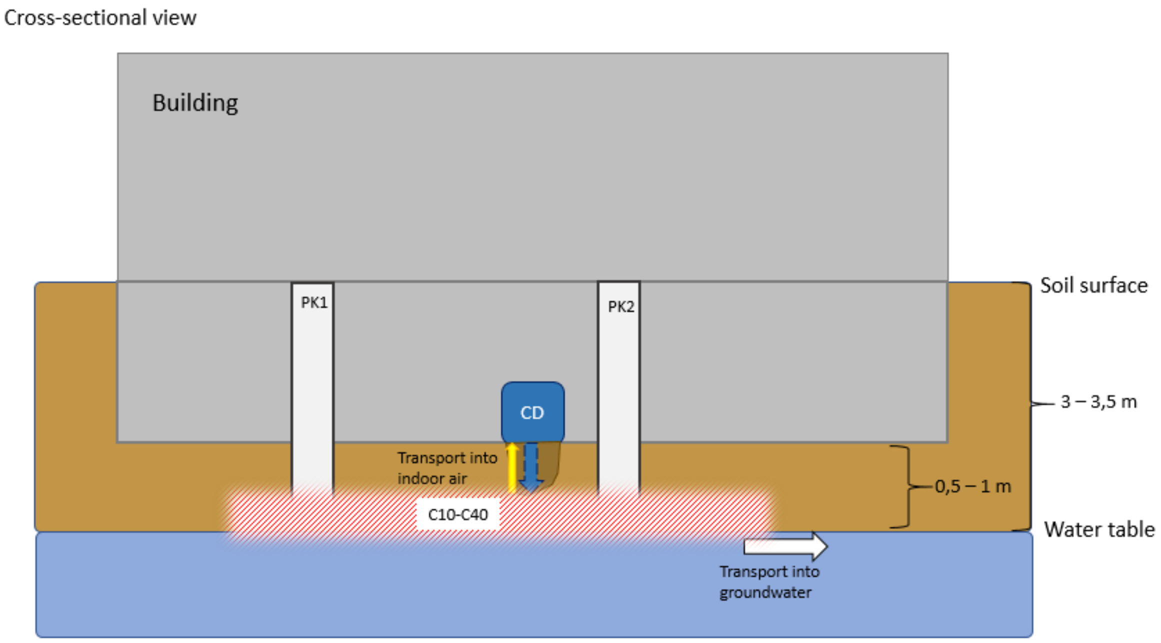


Figure 2. A conceptual model of the site Karjaa. The blue arrow indicates diluted cyclodextrin, which is injected into contaminated area. Cyclodextrin may affect to the transport of contaminants (C10-C40 hydrocarbons) into indoor air or groundwater (yellow and white arrows, respectively).

The risks of current bioflushing and 5 % CD treatment were calculated in detail using a Finnish Soilirisk program. Based on the experiments and risk assessment, enhancing biostimulation by adding CD increases the risk of mobilization of aromatic components in range C12-C16 and C16-C21. This may lead to increased oil content in groundwater. Based on the assessment, however, the proposed remediation activities will not significantly increase the risk of mobilization in the area compared with the current actions. Instead, it will enhance the ongoing remediation by extending the efficiency to those fractions whose low water solubility has earlier been limiting the effectiveness.

# 3. Summary of remediation alternatives

In this remedial alternative selection and risk valuation process, all probably suitable remediation alternatives were evaluated. As the treatable zone is partly located beneath a residential building, *ex situ* methods such as excavation are impractical. Thus, possible alternatives include mainly on site or in situ techniques. As the site is contaminated with heavier oil hydrocarbons (with carbon number C10-C40), suitable techniques in addition to bioflushing and enhanced bioflushing include natural attenuation, solidification/stabilization, electrokinetic remediation, phytoremediation, bioventing and chemical oxidation. In comparison, the possible impacts of 0-alternative (nothing is done) and excavation, which is the most widely used *ex situ* technique in Finland, were also evaluated. Principles of each technique, as well as factors concerning their suitability for the site, are described in Appendix 2.

# 4. The decision process

In the first phase of the decision process, impact categories were chosen. Impacts to be assessed were partly based on indicators listed in a Finnish Ministry of the Environment's guideline *Risk assessment and sustainable risk management of contaminated land*.

The impact categories were divided into four larger groups: environmental, technical, economic and social factors. Selected 16 impact categories are described in table 1.

Table 1. Selected criteria and their description.

| Criteria | | Description |
|---|---|---|
| Environmental factors | Impact on air | Release of emission gases, particulates and odour. Emissions may be due to contaminants, treatment technique, use of heavy trucks, handling of waste material etc. |
| | groundwater | Drinking water quality, eutrophication, generation of wastewaters that may cause harm to groundwater, remedial activities that may pollute groundwater even more |
| | soil | Pollution load |
| | ecology | Biodiversity, ecosystems |
| | landscape | Use of land |
| | Use of natural resources and generation of wastes | Solid and liquid wastes, use of virgin materials (eg. sand) instead of recycled materials, materials needed for remediation, energy consumption |
| Technical factors | Suitability: soil type | Is the soil type suitable for implementation? |
| | Suitability: contaminants | How well the technique works for the contaminants present at the site? |
| | Efficiency | How efficient is the method? |
| | Duration | How long the treatment will take time? Pre-tests and monitoring are taken into account |
| | Reaches goals of remediation | Does the method reach the goals, that is, does the method remove contaminants in a sustainable way? |
| Economic factors | Cost | How much the remediation will cost? Installations, operation and monitoring are taken into account |
| Social factors | Impact on neighbourhood | Infrastructure, accessibility, housing |
| | health and safety | Release of toxic gases, particulates, possible groundwater contamination, contaminant residues in soil, remedial actions (eg. use and storing of risky substances like $H_2O_2$) |
| | Concern from nearby residents | Residents opinion on the method |
| | Attitude and acceptance | How well is the method known, what is authorities' opinion on it? |

In the second phase, each remediation alternative was evaluated using the abovementioned criteria. For that, an Excel sheet was used and possible negative or positive impacts were listed in text form. To help the risk valuation process, information was transferred into numbers.

# 5. The valuation of criteria

The matrix includes a quantitative assessment of the significance of the impacts on the different categories. The impacts are graded according to a five-graded scale between -2 and +2. The evaluation can hence comprise both negative and positive impacts, indicated by plus- or minus signs. The idea is based on the evaluation matrix three developed by Swedish Geotechnical Institute (SGI). Unlike in SGI model, in this evaluation matrix impacts are not divided into short- and long-term impacts. However, long-term negative or positive impacts could be scored using the lowest or highest grades.

# 6. Proposed remediation level

Based on the results, soil flushing and enhanced soil flushing are the most suitable remediation alternatives. They may increase the risk of migration of contaminants and injected nutrients into groundwater but on the other hand, these methods are also capable of removing oil hydrocarbons from saturated zone. As evaluated, the continuation of current bioflushing can no longer significantly reduce oil concentrations. Thus, the most suitable option is to enhance it by adding cyclodextrin, which can enhance the solubility of oil hydrocarbons and make contaminants more bioavailable for microbial degradation. Acceptance towards enhanced bioflushing is poorer than that of bioflushing, because there is not enough knowledge or experience of the method. However, risks to groundwater are minimal if the system is designed properly.

Phytoremediation and bioventing also received high scores, but these remediation alternatives are not very suitable due to site properties. Phytoremediation is limited to soils less than 1 m, and groundwater level less than 3 m from the surface. Contamination at the site is located deeper than 1 m from the surface, so phytoremediation may not be an efficient alternative. In addition, built structures do not allow extensive planting. Bioventing in turn is the most suitable for sites with deep groundwater level. Thus, low groundwater level at the site (3 m) limits the use of this technique, unless the soil is sealed to the prevent volatilization of contaminants. In addition, it is suitable only for unsaturated soils. As oil hydrocarbons have been detected in groundwater at the site, they may not be removed using this technique. In many other cases, lack of information limits the use of *in situ* methods.

# 7. References

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# Appendixes

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**Site Karjaa**

Remedial alternative selection and risk valuation

| | Criteria | 0-alternative | Natural attenuation | Soil flushing | Enhanced soil flushing | Solidification /stabilization | Electro-kinetic | Phyto-remediation | Bioventing | Chemical oxidation | Excavation |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Environmental factors | Impact on air | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -1 | -1 | -1 |
| | groundwater | -2 | -1 | -1 | -1 | -1 | 0 | 1 | -1 | -1 | -1 |
| | soil | -2 | -2 | 0 | 0 | -2 | 1 | 1 | 0 | -1 | -2 |
| | ecology | 0 | 0 | 1 | 1 | -1 | 0 | 1 | 1 | -1 | -2 |
| | landscape | 0 | 0 | 0 | 0 | 0 | -1 | 2 | 0 | 0 | -2 |
| | Use of natural resources and generation of wastes | 0 | 0 | -1 | -1 | -1 | -1 | 2 | 2 | 1 | -2 |
| Technical factors | Suitability: soil type | 0 | 0 | 2 | 2 | 1 | 1 | 1 | 2 | 1 | 2 |
| | Suitability: contaminants | 0 | 0 | 1 | 1 | 1 | 1 | 1 | -1 | 0 | 2 |
| | Suitability: other site properties | 0 | 0 | 0 | 0 | -1 | 1 | -2 | -1 | 0 | -2 |
| | Efficiency | 0 | 0 | 1 | 1 | 2 | 1 | -1 | 2 | 1 | 2 |
| | Duration | 0 | -2 | 1 | 2 | 1 | 0 | -2 | 1 | 2 | 2 |
| | Reaches goals of remediation | -2 | -1 | 1 | 1 | -2 | 1 | -1 | 1 | 1 | -1 |
| Economic factors | Cost | 0 | -1 | 1 | 1 | -2 | 1 | 2 | 1 | 1 | -1 |
| Social factors | Impact on neighbourhood | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | -2 |
| | health and safety | -1 | -1 | 1 | 2 | -1 | -1 | 1 | 0 | -1 | -1 |
| | Concern from nearby residents | -2 | -2 | 0 | 0 | -2 | -1 | 1 | 0 | -1 | 2 |
| | Attitude and acceptance | -2 | -1 | 1 | -1 | -1 | -1 | -1 | 1 | -1 | 2 |
| | ***Mean value of the assessments*** | **-0,6** | **-0,6** | **0,5** | **0,5** | **-0,5** | **0,1** | **0,4** | **0,4** | **0,0** | **-0,3** |

| | | | | | |
|---|---|---|---|---|---|
| Assess the impacts - use the values from 5-graded scale to the right | Large pos. impact | 2 | Duration | 1-6 months | 2 |
| | Positive impact | 1 | | 6-12 months | 1 |
| | No impact | 0 | | 1-2 years | 0 |
| | Negative impact | -1 | | 2-5 years | -1 |
| | Large neg. impact | -2 | | <5 years | -2 |
| Efficiency | >90% | 2 | Suitability | Very good | 2 |
| | 75-90% | 1 | | Good | 1 |
| | No impact | 0 | | In between/No impact | 0 |
| | 50-75% | -1 | | Bad | -1 |
| | <50% | -2 | | Very bad | -2 |

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Appendix 1. Risk valuation matrix.

**Site Karjaa**

| **Summary of site properties** | |
|---|---|
| **Source of contamination** | Heating oil accident |
| **Contaminants** | Mainly midweight oil hydrocarbons (C10-C21), also heavier (C21-C40) |
| **Contaminated zone** | At a depth of 50-70 cm under the floor, estimated contaminated area is 500 m2 |
| **Soil type** | Silt |
| **Groundwater** | Groundwater depth 3-3,5 m |

| **Criteria** | | **0-alternative** | **Natural attenuation** | **Soil flushing** | **Enhanced soil flushing** | **Solidification / stabilization** | **Electrokinetic** | **Phytoremediation** | **Bioventing** | **Chemical oxidation** | **Excavation** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Principle | | Nothing is done. | The site is remediated passively using natural biological, physical and chemical processess. Environmental contaminants are undisturbed while natural attenuation works on them. | Contaminated soils are 'flooded' with a solution that moves the contaminants to an area where they can be removed. May also enhance biodegradation. In this case, nutrients dissolved into water and diluted hydrogen peroxide (H2O2) is used to provide nutrients and oxygen for microbes. | In this case a surfactant such as cyclodextrin (CD) would be used to increase water solubility of contaminants. | Reduces the mobility of contaminants through both physical and chemical means. Stabilization reduces the risk by converting the contaminant into a less soluble, immobile, and less toxic form. Solidification refers to the process that encapsulates contaminants. | Electrodes (anodes and cathodes) are placed into soil and a low level direct current crosses the area between electrodes. This causes hydrogen ions to be generated at the anode and hydroxyl ions at the cathode, so a pH gradient develops between the electrodes. Introduced current leads to the migration of contaminants. In case of oil hydrocarbons, the method is based on the ability of current to desorb contaminants from soil particles, making them more bioavailable for microbes and to distibute biostimulation additives horizontally, thus enhancing biodegradation. | Phytoremediation is based on the ability of plants to take up, accumulate and/or degrade contaminants that are present in soil and water environments. It can be divided into five different techiques: rhizofiltration (contaminants taken up by the roots), phytoextraction (uptake of contaminant from the soil), phytotransformation (degradation of contaminants through metabolism), phytostimulation (stimulation of microbial degradation through the activities of plants in the root zone) and phytostabilization (reduction of the migration of contaminants). | Oxygen or air is injected with low pressure into the contaminated soil. As oxygen concentration increases, biodegradation is enhanced. Generally lower air flow rate is used than for soil vapor extraction (SVE). | Chemical oxidizer is injected or otherwise introduced into the contaminated soil (or groundwater) to destoy contaminants. Most widely used oxidizers include permanganate, hydrogen peroxide, persulfate and ozone. Also known as ISCO (in situ chemical oxidation) | Contaminated soil is removed by excavation and hauled off to landfills or otherwise handled ex situ / on site. |
| Suitability | Soil type | All | All | Sand, gravel, silt, till. | Sand, gravel, silt, till. | All (suitability has to be tested in advance). Homogeneous mixing of the reactive material is made difficult in dense soils. | All, most efficient in clayey soils. | Depends on the growth requirements of the plant used | Sand, silt, organic soil, till, not applicable to sites with high clay content | Sand, silt, organic soil, till, not applicable to sites with high clay content | All |
| | Contaminant | All | Biodegradable organic contaminants | Organic compounds such as VOCs, fuels, pesticides, inorganic compounds i.e. metals | Organic compounds such as VOCs, fuels, pesticides, inorganic compounds i.e. metals | Heavy metals and other inorganic compounds, some organic compounds, depending on stabilizing agent. Including medium to heavy hydrocarbons. | Polar organic compounds, anions, kations | Organic compounds such as BTEX, chlorinated solvents, PAHs, petroleum hydrocarbons, excess nutrients | Aerobically biodegradable contaminants. Most successful on mid-weight petroleum products like diesel since lighter products tend to volatilize quickly and can be treated better with SVE, while the heavier products generally take longer to biodegrade. | Capable of degrading a wide variety of contaminants, treatability depends on the oxidizer used. Degradation of aromatic fractions is faster than that of aliphatic fractions. Suitability for removing diesel needs probably more studies. | Almost all contaminants |
| | Other site properties | Site properties do not limit the use of this method | Site properties do not limit the use of this method | Low solubility of heavier hydrocarbons and relatively unpermeable soil (silt) decreases efficiency. | Site properties do not limit the use of this method | Mid-weight hydrocarbons are considered relatively immobile and silty soil prevents their migration. Thus, using stabilization does not bring any big benefit in this case. Used usually on site, stabilization of contaminated masses *in situ* is much more difficult. | Metallic or insulating material in the soil may affect the soil's conductivity. Low solubility of heavier hydrocarbons decreases efficiency. Residential area use may interfere with the installations. | The treatment is limited to soils less than 1 m from surface and groundwater less than 3 m from the surface. Contamination at the site is located deeper than 1 m from the surface, so phytoremediation may not be efficient. Built structures do not allow extensive planting. | Distribution of air is difficult in heterogenic soils. Not suitable for sites with high groundwater level (3 m, like at the site), unless the soil is sealed to prevent volatilization of contaminants. | Heterogenic soil may cause injected fluid to spread unevenly into the contaminated zone. The gases produced by the breakdown reactions may increase the ground water level locally and flood the basement. | Contaminated zone is located partly underneath a residential building, which make excavation a difficult process. Contamination at the site is at the groundwater level, and excavation is applicable only for contaminants located above groundwater, unless combined with groundwater pumping (to prevent spreading of contaminants). |

Appendix 2. Risk valuation matrix, impacts described in the text.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Environmental factors | Impact on air | Possible due to erosion but unlikely as pavement prevents transport to air | Possible due to erosion but unlikely as pavement prevents transport to air | Treating of VOCs may cause emission to air, in which case monitoring is needed. Volatile hydrocarbons have not been detected at the site so possible impact is low. | Volatile hydrocarbons have not been detected at the site so possible impact is low. Increased water solubility of hydrocarbons can cause them to migrate with i.e. capillary forces through the digging hole located in the basement of the building. | No remarkable effect. | No gas or particle pollution | Volatilization of contaminats to air is possible through the plants. In case of mid-weight hydrocarbons volatilization is limited due to hydrophobic properties of these contaminants, which prevents their intake into plants. | Emissions to air, especially into the basement, are possible and need to be monitored. | Emissions to air, especially into the basement, are possible and need to be monitored. Most volatile compounds have not been detected, but chemical oxidation may produce volatile byproducts. | Particle pollution may be possible from excavated masses. |
| | groundwater | Migration to groundwater is possible. | Migration to groundwater is possible. | Migration of contaminants is possible, as injected nutrient solution and recycled water may spread the contaminants. Also, nutrients, especially nitrate, may migrate to groundwater so monitoring is needed. | Migration to groundwater is possible as solution is used to increase water solubility of contaminants. A need for a more detailed risk assessment. | May pose a risk as contaminants are not removed. | Oil hydrocarbons may be mobilized. If nutrients are added, they may migrate to groundwater. | The uptake of contaminated groundwater can prevent the migration of contaminants. Phytoremediation should not cause additional groundwater contamination. | Bioventing is suitable only for unsaturated soils. Oil hydrocarbons that have been detected in groundwater at the site may not be remediated using this technique. Nutrients that may be needed may leach into groundwater and the amount of added nutrients needs to be calculated carefully. | Oxidation reactions may change the oxidation states of metals and alter their mobility, increasing metal concentration in groundwater. The method can be used for groundwater remediation, also. | Excavation at the site near / at groundwater level may need pump and treat or other technique to prevent mobilization of contaminants into groundwater. |
| | soil | Risks remain. | Risks remain until natural processes have degraded the contaminants | Additives may adsorb to soil and decrease soil permeability. | Cyclodextrin does not form high-viscosity emulsions like many other solvents / surfactants do which minimizes reagent residuals left in situ. CD has low affinity of sorption to the solid phase at a wide range of pH values, and thus has only a minor impact on soil. | Does not remove contaminants | Low pH at anode side and high pH at cathode side is generated. May increase temperature and oxygen level (which in turn may enhance degradation) | Phytoremediation should not cause additional soil contamination. Instead, it may reduce possible negative impacts of contaminants and enhance soil structure. | The technique changes the composition of soil pore gases so there will be more O2 and less CO2. These changes should be monitored. Otherwise large negative impact on soil quality is not expected. | May have a high impact on soil properties, such as permeability, organic carbon content, cation exchange capacity, temperature, pH. | High impact as the original soil is removed. |
| | ecology | Risks remain. | Risks remain until natural processes have degraded the contaminants | Depends on the additives; H2O2 may be toxic to soil organisms but the concentration used is low (0,5%) so negative impacts are minimal. | Cyclodextrin is biodegrable and less toxic for soil microbes than many other organic solvents / surfactants. | The treated material rarely functions as a substrate for the plants. In this case, also pavement prevents the growth. | Mobilization of oil makes it more bioavailable. In this case, possible breakdown intermediates are more degradable than the starting material. Thereby there should not be any risk of accumulation of toxic metabolites. | Contaminants may enter the food chain through animals which eat the plants used in these projects. Due to the low uptake of oil hydrocarbons, they should not, in the light of the research so far, be a risk factor | Oxygen may be toxic to anaerobic microbes. High concentration of contaminants may be toxic to microorganisms, thus limiting biodegradation. | Oxidation reactions may change the oxidation states of metals and alter their toxicity. Oxidants theirselves can be toxic to soil organisms. In studies concerning ISCO, microbial populations have not permanently reduced. Oxidation may transfer the contaminants into even more toxic intermediates. | Natural soil ecosystem is removed. Excavation can damage tree roots, which can lower their viability in the long run. |
| | landscape | None | None | Minimal, existing wells / groundwater tubes can be used | Minimal, existing wells / groundwater tubes can be used | Depends on how the stabilizing material is introduced into soil. | Groundwater tubes for electrodes should be installed | Accomplished with minimal environmental disturbance. | Depends on how many injection wells need to be installed. | Depends on how many injection wells need to be installed. | Large disturbance as contaminated soil needs to be removed. |
| | Use of natural resources and generation of wastes | None | None | Depends on the flushing solution. Recovered groundwater may require treatment to meet the appropriate discharge standards. In this case, nutrient- and oxygen-rich water is infiltrated through contaminated soil, during which the water is also cleaned. | Recovered groundwater may require treatment to meet the appropriate discharge standards. In this case, cyclodextrin-water is infiltrated through contaminated soil, during which the water is also cleaned. | Requires additives that cause CO2 emissions in production. Reduces the need for mass transport. | Electricity is needed. Nutrients may be needed to enhance biodegradation. | Generation of secondary wastes is minimal. If accumulating plants are used, they may require special disposal. Nutrients (N, P), if used additionally. | Materials for injection wells and pumping system. Bioventing does not generate wastes that are to be treated. Off-gases may be possible and in that case off-gas treatment may be needed (eg. active carbon). Nutrients (N, P), if used additionally. | Oxidants and possible chelates, materials for injection wells. Generation of secondary wastes is minimal. | Large amount of clean soil needed, excavated material needs handling (eg. biological or thermal treatment, soil washing) or other disposal. |

Appendix 2. Risk valuation matrix, impacts described in the text (continued)

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Technical factors | Efficiency | None | Degradation of contaminants is not guaranteed | Low solubility of heavier hydrocarbons and relatively unpermeable soil (clay/silt) decreases efficiency. Flushing solution may not be able to move through the impermeable soil, and thus cannot easily make contact with the contaminants. | Should be more efficient than soil flushing using nutrient- and oxygen-rich flushing solution. | Does not remove contaminants, only prevents their mobility/spreading into surrounding environment. Stablization *in situ* may fail in sealing all contaminated masses. | Total removal of contaminants may not be achieved and decradation may be a slow process. | Cold climate and high concentration of contaminants may hinder the growth of plants. | Cannot always reach low cleanup limits. Biodegradation may be a slow process and sometimes it may not start at all. Effective only in unsaturated soils. Sometimes nutrients need to be added to enhance biodegradation. | Site-spesific, complete mineralization may not be achieved. A risk for contaminant rebound. | Very efficient as all contaminated soil can be removed. However, there is a risk that some contaminated spots remain. |
| | Duration | None | Long. Low temperatures prevents natural degradation | Short to medium. | Short to medium. | Short. Stabilization *in situ* can be time consuming if a larger area is to be treated. Some treatment methods require time for the material to become strong and tight. | Medium. | Slow (more than one growing season, years to decades). Cold climate slows down the process. | Medium - long (months to years) | Short, if successfully completed. | Short (Note: not actual remediation) |
| | Reaches goals of remediation | No, as nothing is done | May reach but the process is very slow | May reach | May reach | No, as the contaminants are not removed | May reach | The time required for remediation may be too lengthy and due to site properties the goals of remediation are not necessarily achieved. | May reach | May reach | Contamination is removed, so in a way the goal is achieved. However, contaminted soil needs to be disposed or handled in some other way. This method is not regarded as a sustainable option. |
| Economical factors | Cost | None | Active follow-up may be even more expensive than active remediation | Varies with site-specific conditions, i.e. the size of the treatment area and the number of soil flushing cycles required. The cost of soil flushing also depends on the type and concentration of surfactants used. Nutrients and H2O2 are relatively inexpensive. | Varies with site-specific conditions, i.e. the size of the treatment area and the number of soil flushing cycles required. Cyclodextrin is relatively expensive (depends on purity grade, but at the moment lower grade products are not available). | Long-term monitoring often needed, which increases costs. Regarded as one of the most expensive *in situ* methods. | Depends on for example the price of electricity. Other costs include installations and monitoring. | Cost-effective especially for large contaminated sites. | Costs depend on eg. the number of injection wells and treatment of emission gases. Maintenance and monitoring bring additional costs. A cost-effective alternative. | Costs depend on eg. The oxidant used, the amount of oxidant needed and the number of injection wells. If well planned, the method is a cost-effective option. | Costs depends on the volume of polluted masses and the chosen treatment or deposition method for excavated masses. Groundwater treatment increases the cost of action. |
| Social factors | Impact on neighbourhood | None | None | Minimal | Minimal | Depends on how the stabilizing material is introduced into soil. | Medium | Minimal, phytoremediation is aesthetically pleasing and passive, solar energy driven technology. | Minimal disturbance. | Minimal to medium. | Large, temporarily |
| | health and safety | Medium - silty soil prevents migration of contaminants but does not remove them. Degradation products may be even more harmful than precursors | Medium - silty soil prevents migration of contaminants but doesn't remove them. Degradation products may be even more harmful than precursors | Medium - silty soil prevents migration of contaminants. Soil flushing may increase concentration of contaminants (and nutrients) in groundwater, which can cause a health hazard. Wells used for drinking water purposes are not located close to the area, thus possible health risks are minimal. | Medium - silty soil prevents migration of contaminants. Soil flushing may increase concentration of contaminants in groundwater, which can cause health hazards. Wells used for drinking water purposes are not located close to the area, thus possible health risks are minimal. However, possible risks for air and groundwater need to be further studied. | Medium, does not remove contaminants and if the treatment is failed, risks remain. | No secondary pollution. Electric works need extra caution and have to be executed by a professional. | Possible emissions to air, but as explained above, volatilization of mid-weight oil hydrocarbons is limited. | Emissions to the basement are possible but can be prevented by treating emission gases and careful planning of implementation. Nutrients (nitrogen, phosphorus and potassium fertilizers) that may be fed to the soil are harmless to humans, commonly used in crop production and are biodegradable. | Oxidants need careful handling and personal protection equipment are needed. Storing of oxidants may need extra caution (to prevent eg. children to touch them). Emissions to air/basement are possible and need to be monitored. | Spreading of contaminants into the environment eg. by evaporation, dust or water is possible and must be prevented. During excavation personal protection equipment must be used when needed. |
| | Concern from nearby residents | High | High | Minimal | Minimal to medium. | High | Medium | Minimal | Minimal | Medium to high, depends on the chemical used | Medium |
| | Attitude and acceptance | Bad | Bad | Good | Not used in Finland for remediation purposes, so the authorities may be suspicious, especially as the site is located at classified groundwater area. Risk assessment is needed before remedial actions at the site. | Used in Europe and USA. Often low acceptance (in Finland) as the method does not remove / break down pollutants. | Some use in Finland (eg. Eco Harden), mainly in experimental stage. | The method is at an experimental stage, not (mainly) used in Finland. | Have been used in Finland and accepted by authorities. | Used in Finland. Not enough knowledge/experience, which limits the use of this technique. | Most widely used method in Finland, thus it is easy to get a permission.. |

Appendix 2. Risk valuation matrix, impacts described in the text (continued)

## Site Karjaa

| Summary of site properties | |
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| **Source of contamination** | Heating oil accident |
| **Contaminants** | Mainly midweight oil hydrocarbons (C10-C21), also heavier (C21-C40) |
| **Contaminated zone** | At a depth of 50-70 cm under the floor, estimated contaminated area is 500 m2 |
| **Soil type** | Silt |
| **Groundwater** | Groundwater depth 3-3,5 m |

| Criteria | | 0-alternative | Natural attenuation | Soil flushing | Enhanced soil flushing | Solidification / stabilization | Electrokinetic | Phytoremediation | Bioventing | Chemical oxidation | Excavation |
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| Principle | | Nothing is done. | The site is remediated passively using natural biological, physical and chemical processess. Environmental contaminants are undisturbed while natural attenuation works on them. | Contaminated soils are 'flooded' with a solution that moves the contaminants to an area where they can be removed. May also enhance biodegradation. In this case, nutrients dissolved into water and diluted hydrogen peroxide (H2O2) is used to provide nutrients and oxygen for microbes. | In this case a surfactant such as cyclodextrin (CD) would be used to increase water solubility of contaminants. | Reduces the mobility of contaminants through both physical and chemical means. Stabilization reduces the risk by converting the contaminant into a less soluble, immobile, and less toxic form. Solidification refers to the process that encapsulates contaminants. | Electrodes (anodes and cathodes) are placed into soil and a low level direct current crosses the area between electrodes. This causes hydrogen ions to be generated at the anode and hydroxyl ions at the cathode, so a pH gradient develops between the electrodes. Introduced current leads to the migration of contaminants. In case of oil hydrocarbons, the method is based on the ability of current to desorb contaminants from soil particles, making them more bioavailable for microbes and to distibute biostimulation additives horizontally, thus enhancing biodegradation. | Phytoremediation is based on the ability of plants to take up, accumulate and/or degrade contaminants that are present in soil and water environments. It can be divided into five different techiques: rhizofiltration (contaminants taken up by the roots), phytoextraction (uptake of contaminant from the soil), phytotransformation (degradation of contaminants through metabolism), phytostimulation (stimulation of microbial degradation through the activities of plants in the root zone) and phytostabilization (reduction of the migration of contaminants). | Oxygen or air is injected with low pressure into the contaminated soil. As oxygen concentration increases, biodegradation is enhanced. Generally lower air flow rate is used than for soil vapor extraction (SVE). | Chemical oxidizer is injected or otherwise introduced into the contaminated soil (or groundwater) to destoy contaminants. Most widely used oxidizers include permanganate, hydrogen peroxide, persulfate and ozone. Also known as ISCO (in situ chemical oxidation) | Contaminated soil is removed by excavation and hauled off to landfills or otherwise handled ex situ / on site. |
| Suitability | Soil type | All | All | Sand, gravel, silt, till. | Sand, gravel, silt, till. | All (suitability has to be tested in advance). Homogeneous mixing of the reactive material is made difficult in dense soils. | All, most efficient in clayey soils. | Depends on the growth requirements of the plant used | Sand, silt, organic soil, till, not applicable to sites with high clay content | Sand, silt, organic soil, till, not applicable to sites with high clay content | All |
| | Contaminant | All | Biodegradable organic contaminants | Organic compounds such as VOCs, fuels, pesticides, inorganic compounds i.e. metals | Organic compounds such as VOCs, fuels, pesticides, inorganic compounds i.e. metals | Heavy metals and other inorganic compounds, some organic compounds, depending on stabilizing agent. Including medium to heavy hydrocarbons. | Polar organic compounds, anions, kations | Organic compounds such as BTEX, chlorinated solvents, PAHs, petroleum hydrocarbons, excess nutrients | Aerobically biodegradable contaminants. Most successful on mid-weight petroleum products like diesel since lighter products tend to volatilize quickly and can be treated better with SVE, while the heavier products generally take longer to biodegrade. | Capable of degrading a wide variety of contaminants, treatability depends on the oxidizer used. Degradation of aromatic fractions is faster than that of aliphatic fractions. Suitability for removing diesel needs probably more studies. | Almost all contaminants |
| | Other site properties | Site properties do not limit the use of this method | Site properties do not limit the use of this method | Low solubility of heavier hydrocarbons and relatively unpermeable soil (silt) decreases efficiency. | Site properties do not limit the use of this method | Mid-weight hydrocarbons are considered relatively immobile and silty soil prevents their migration. Thus, using stabilization does not bring any big benefit in this case. Used usually on site, stabilization of contaminated masses *in situ* is much more difficult. | Metallic or insulating material in the soil may affect the soil's conductivity. Low solubility of heavier hydrocarbons decreases efficiency. Residential area use may interfere with the installations. | The treatment is limited to soils less than 1 m from surface and groundwater less than 3 m from the surface. Contamination at the site is located deeper than 1 m from the surface, so phytoremediation may not be efficient. Built structures do not allow extensive planting. | Distribution of air is difficult in heterogenic soils. Not suitable for sites with high groundwater level (3 m, like at the site) , unless the soil is sealed to prevent volatilization of contaminants. | Heterogenic soil may cause injected fluid to spread unevely into the contaminated zone. The gases produced by the breakdown reactions may increase the ground water level locally and flood the basement. | Contaminated zone is located partly underneath a residential building, which make excavation a difficult process. Contamination at the site is at the groundwater level, and excavation is applicable only for contaminants located above groundwater, unless combined with groundwater pumping (to prevent spreading of contaminants). |
| Environmental factors | Impact on air | Possible due to erosion but unlikely as pavement prevents transport to air | Possible due to erosion but unlikely as pavement prevents transport to air | Treating of VOCs may cause emission to air, in which case monitoring is needed. Volatile hydrocarbons have not been detected at the site so possible impact is low. | Volatile hydrocarbons have not been detected at the site so possible impact is low. Increased water solubility of hydrocarbons can cause them to migrate with i.e. capillary forces through the digging hole located in the basement of the building. | No remarkable effect. | No gas or particle pollution | Volatilization of contaminats to air is possible through the plants. In case of mid-weight hydrocarbons volatilization is limited due to hydrophobic properties of these contaminants, which prevents their intake into plants. | Emissions to air, especially into the basement, are possible and need to be monitored. | Emissions to air, especially into the basement, are possible and need to be monitored. Most volatile compounds have not been detected, but chemical oxidation may produce volatile byproducts. | Particle pollution may be possible from excavated masses. |
| | groundwater | Migration to groundwater is possible. | Migration to groundwater is possible. | Migration of contaminants is possible, as injected nutrient solution and recycled water may spread the contaminants. Also, nutrients, especially nitrate, may migrate to groundwater so monitoring is needed. | Migration to groundwater is possible as solution is used to increase water solubility of contaminants. A need for a more detailed risk assessment. | May pose a risk as contaminants are not removed. | Oil hydrocarbons may be mobilized. If nutrients are added, they may migrate to groundwater. | The uptake of contaminated groundwater can prevent the migration of contaminants. Phytoremediation should not cause additional groundwater contamination. | Bioventing is suitable only for unsaturated soils. Oil hydrocarbons that have been detected in groundwater at the site may not be remediated using this technique. Nutrients that may be needed may leach into groundwater and the amount of added nutrients needs to be calculated carefully. | Oxidation reactions may change the oxidation states of metals and alter their mobility, increasing metal concentration in groundwater. The method can be used for groundwater remediation, also. | Excavation at the site near / at groundwater level may need pump and treat or other technique to prevent mobilization of contaminats into groundwater. |
| | soil | Risks remain. | Risks remain until natural processes have degraded the contaminants | Additives may adsorb to soil and decrease soil permeability. | Cyclodextrin does not form high-viscosity emulsions like many other solvents / surfactants do which minimizes reagent residuals left in situ. CD has low affinity of sorption to the solid phase at a wide range of pH values, and thus has only a minor impact on soil. | Does not remove contaminants | Low pH at anode side and high pH at cathode side is generated. May increase temperature and oxygen level (which in turn may enhance degradation) | Phytoremediation should not cause additional soil contamination. Instead, it may reduce possible negative impacts of contaminants and enhance soil structure. | The technique changes the composition of soil pore gases so there will be more O2 and less CO2. These changes should be monitored. Otherwise large negative impact on soil quality is not expected. | May have a high impact on soil properties, such as permeability, organic carbon content, cation exchange capacity, temperature, pH. | High impact as the original soil is removed. |

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| | ecology | Risks remain. | Risks remain until natural processes have degraded the contaminants | Depends on the additives; $H_2O_2$ may be toxic to soil organisms but the concentration used is low (0,5%) so negative impacts are minimal. | Cyclodextrin is biodegrable and less toxic for soil microbes than many other organic solvents / surfactants. | The treated material rarely functions as a substrate for the plants. In this case, also pavement prevents the growth. | Mobilization of oil makes it more bioavailable. In this case, possible breakdown intermediates are more degradable than the starting material. Thereby there should not be any risk of accumulation of toxic metabolites. | Contaminants may enter the food chain through animals which eat the plants used in these projects. Due to the low uptake of oil hydrocarbons, they should not, in the light of the research so far, be a risk factor | Oxygen may be toxic to anaerobic microbes. High concentration of contaminants may be toxic to microorganisms, thus limiting biodegradation. | Oxidation reactions may change the oxidation states of metals and alter their toxicity. Oxidants theirselves can be toxic to soil organisms. In studies concerning ISCO, microbial populations have not permanently reduced. Oxidation may transfer the contaminants into even more toxic intermediates. | Natural soil ecosystem is removed. Excavation can damage tree roots, which can lower their viability in the long run. |
| | landscape | None | None | Minimal, existing wells / groundwater tubes can be used | Minimal, existing wells / groundwater tubes can be used | Depends on how the stabilizing material is introduced into soil. | Groundwater tubes for electrodes should be installed | Accomplished with minimal environmental disturbance. | Depends on how many injection wells need to be installed. | Depends on how many injection wells need to be installed. | Large disturbance as contaminated soil needs to be removed. |
| | Use of natural resources and generation of wastes | None | None | Depends on the flushing solution. Recovered groundwater may require treatment to meet the appropriate discharge standards. In this case, nutrient- and oxygen-rich water is infiltrated through contaminated soil, during which the water is also cleaned. | Recovered groundwater may require treatment to meet the appropriate discharge standards. In this case, cyclodextrin-water is infiltrated through contaminated soil, during which the water is also cleaned. | Requires additives that cause $CO_2$ emissions in production. Reduces the need for mass transport. | Electricity is needed. Nutrients may be needed to enhance biodegradation. | Generation of secondary wastes is minimal. If accumulating plants are used, they may require special disposal. Nutrients (N, P), if used additionally. | Materials for injection wells and pumping system. Bioventing does not generate wastes that are to be treated. Off-gases may be possible and in that case off-gas treatment may be needed (eg. active carbon). Nutrients (N, P), if used additionally. | Oxidants and possible chelates, materials for injection wells. Generation of secondary wastes is minimal. | Large amount of clean soil needed, excavated material needs handling (eg. biological or thermal treatment, soil washing) or other disposal. |
| Technical factors | Efficiency | None | Degradation of contaminants is not guaranteed | Low solubility of heavier hydrocarbons and relatively unpermeable soil (clay/silt) decreases efficiency. Flushing solution may not be able to move through the impermeable soil, and thus cannot easily make contact with the contaminants. | Should be more efficient than soil flushing using nutrient- and oxygen-rich flushing solution. | Does not remove contaminants, only prevents their mobility/spreading into surrounding environment. Stablization *in situ* may fail in sealing all contaminated masses. | Total removal of contaminants may not be achieved and decradation may be a slow process. | Cold climate and high concentration of contaminants may hinder the growth of plants. | Cannot always reach low cleanup limits. Biodegradation may be a slow process and sometimes it may not start at all. Effective only in unsaturated soils. Sometimes nutrients need to be added to enhance biodegradation. | Site-spesific, complete mineralization may not be achieved. A risk for contaminant rebound. | Very efficient as all contaminated soil can be removed. However, there is a risk that some contaminated spots remain. |
| | Duration | None | Long. Low temperatures prevents natural degradation | Short to medium. | Short to medium. | Short. Stabilization *in situ* can be time consuming if a larger area is to be treated. Some treatment methods require time for the material to become strong and tight. | Medium. | Slow (more than one growing season, years to decades). Cold climate slows down the process. | Medium - long (months to years) | Short, if successfully completed. | Short (Note: not actual remediation) |
| | Reaches goals of remediation | No, as nothing is done | May reach but the process is very slow | May reach | May reach | No, as the contaminants are not removed | May reach | The time required for remediation may be too lengthy and due to site properties the goals of remediation are not necessarily achieved. | May reach | May reach | Contamination is removed, so in a way the goal is achieved. However, contaminted soil needs to be disposed or handled in some other way. This method is not regarded as a sustainable option. |
| Economical factors | Cost | None | Active follow-up may be even more expensive than active remediation | Varies with site-specific conditions, i.e. the size of the treatment area and the number of soil flushing cycles required. The cost of soil flushing also depends on the type and concentration of surfactants used. Nutrients and $H_2O_2$ are relatively inexpensive. | Varies with site-specific conditions, i.e. the size of the treatment area and the number of soil flushing cycles required. Cyclodextrin is relatively expensive (depends on purity grade, but at the moment lower grade products are not available). | Long-term monitoring often needed, which increases costs. Regarded as one of the most expensive *in situ* methods. | Depends on for example the price of electricity. Other costs include installations and monitoring. | Cost-effective especially for large contaminated sites. | Costs depend on eg. the number of injection wells and treatment of emission gases. Maintenance and monitoring bring additional costs. A cost-effective alternative. | Costs depend on eg. The oxidant used, the amount of oxidant needed and the number of injection wells. If well planned, the method is a cost-effective option. | Costs depends on the volume of polluted masses and the chosen treatment or deposition method for excavated masses. Groundwater treatment increases the cost of action. |
| Social factors | Impact on neighbourhood | None | None | Minimal | Minimal | Depends on how the stabilizing material is introduced into soil. | Medium | Minimal, phytoremediation is aesthetically pleasing and passive, solar energy driven technology. | Minimal disturbance. | Minimal to medium. | Large, temporarily |
| | health and safety | Medium - silty soil prevents migration of contaminants but does not remove them. Degradation products may be even more harmful than precursors | Medium - silty soil prevents migration of contaminants but doesn't remove them. Degradation products may be even more harmful than precursors | Medium - silty soil prevents migration of contaminants. Soil flushing may increase concentration of contaminants (and nutrients) in groundwater, which can cause a health hazard. Wells used for drinking water purposes are not located close to the area, thus possible health risks are minimal. | Medium - silty soil prevents migration of contaminants. Soil flushing may increase concentration of contaminants in groundwater, which can cause health hazards. Wells used for drinking water purposes are not located close to the area, thus possible health risks are minimal. However, possible risks for air and groundwater need to be further studied. | Medium, does not remove contaminants and if the treatment is failed, risks remain. | No secondary pollution. Electric works need extra caution and have to be executed by a professional. | Possible emissions to air, but as explained above, volatilization of mid-weight oil hydrocarbons is limited. | Emissions to the basement are possible but can be prevented by treating emission gases and careful planning of implementation. Nutrients (nitrogen, phosphorus and potassium fertilizers) that may be fed to the soil are harmless to humans, commonly used in crop production and are biodegradable. | Oxidants need careful handling and personal protection equipment are needed. Storing of oxidants may need extra caution (to prevent eg. children to touch them). Emissions to air/basement are possible and need to be monitored. | Spreading of contaminants into the environment eg. by evaporation, dust or water is possible and must be prevented. During excavation personal protection equipment must be used when needed. |
| | Concern from nearby residents | High | High | Minimal | Minimal to medium. | High | Medium | Minimal | Minimal | Medium to high, depends on the chemical used | Medium |
| | Attitude and acceptance | Bad | Bad | Good | Not used in Finland for remediation purposes, so the authorities may be suspicious, especially as the site is located at classified groundwater area. Risk assessment is needed before remedial actions at the site. | Used in Europe and USA. Often low acceptance (in Finland) as the method does not remove / break down pollutants. | Some use in Finland (eg. Eco Harden), mainly in experimental stage. | The method is at an experimental stage, not (mainly) used in Finland. | Have been used in Finland and accepted by authorities. | Used in Finland. Not enough knowledge/experience, which limits the use of this technique. | Most widely used method in Finland, thus it is easy to get a permission.. |