Highlights of INSURE project WP 1 - Sustainable remediation of contaminated sites

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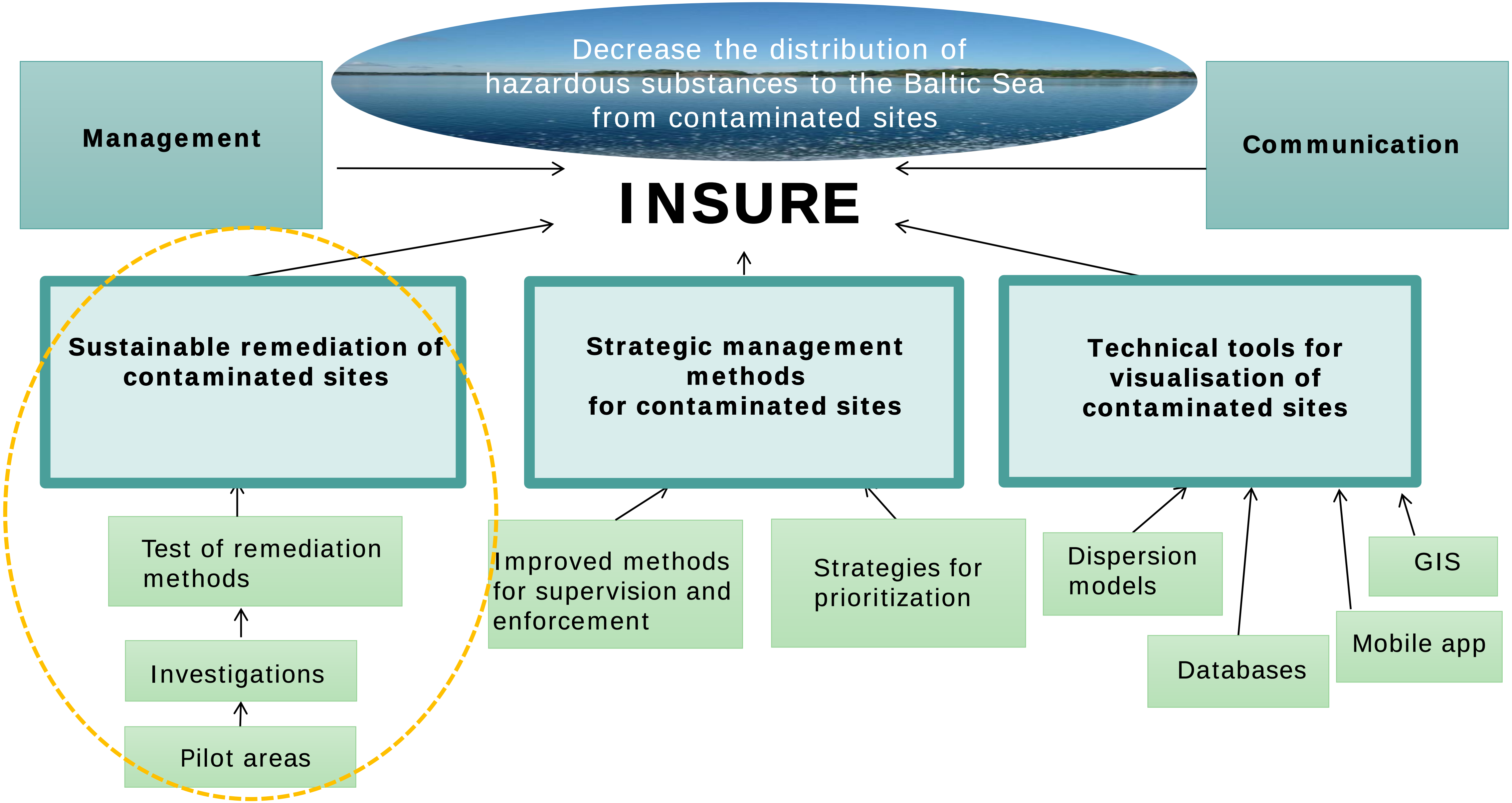
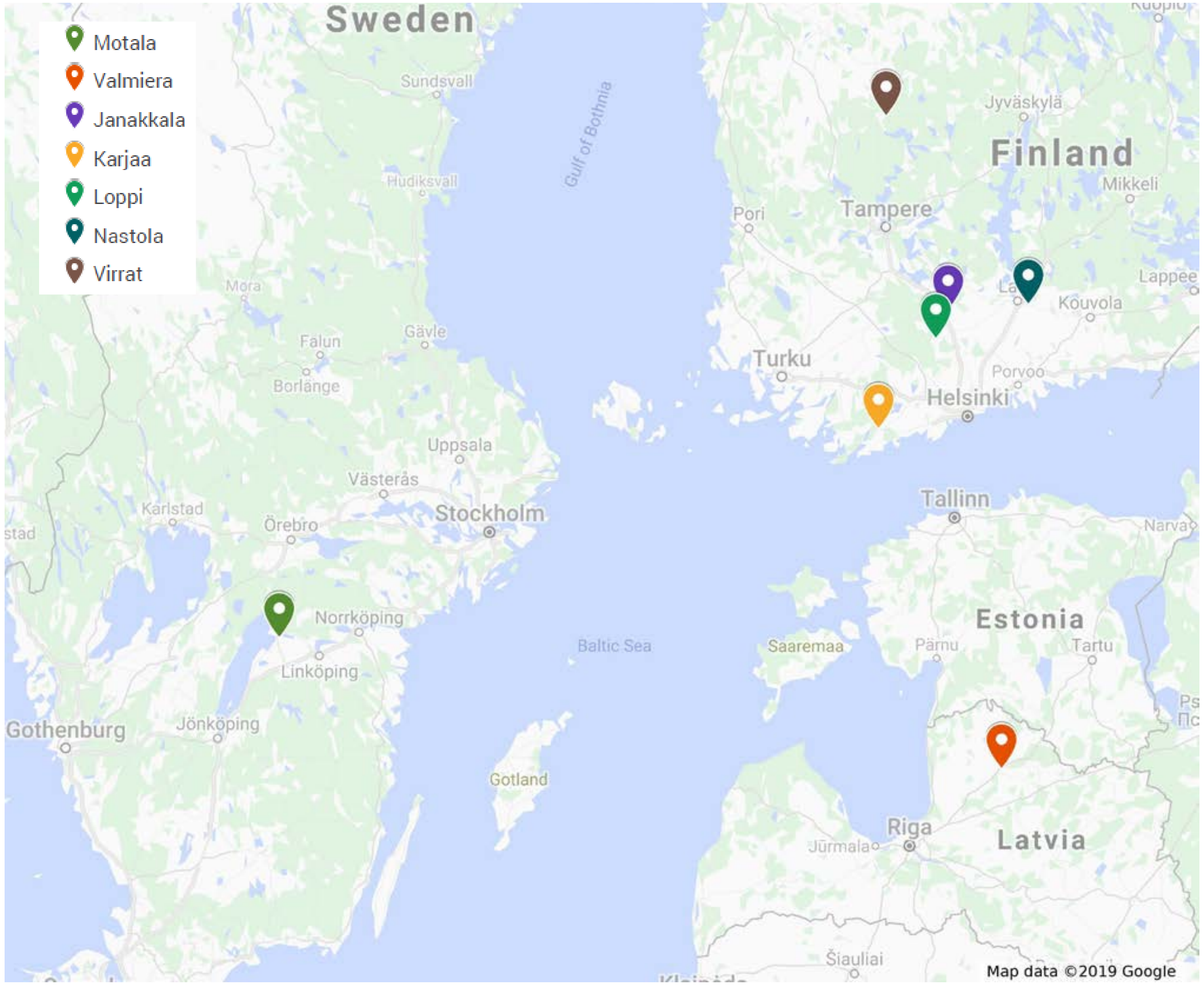

Decrease the distribution of hazardous substances to the Baltic Sea from contaminated sites
Management
Communication
INSURE
Sustainable remediation of contaminated sites
Strategic management methods for contaminated sites
Technical tools for visualisation of contaminated sites
Test of remediation methods
Investigations
Pilot areas
Improved methods for supervision and enforcement
Strategies for prioritization
Dispersion models
Databases
Mobile app
GIS

INSURE pilot sites



Background

- The common way for treatment have been excavation and storage on landfills
- Will to reduce the use of landfills and move from “dig and dump” to alternative remediation methods

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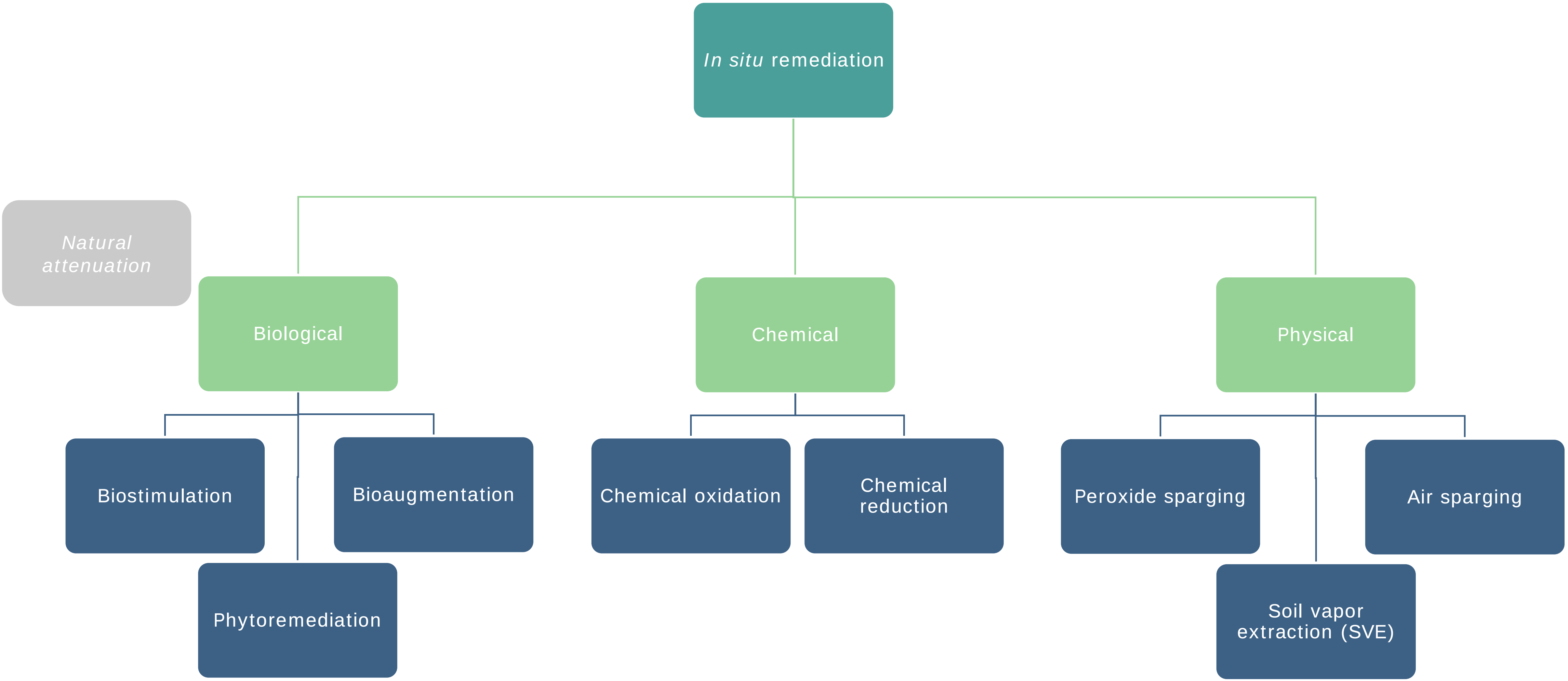


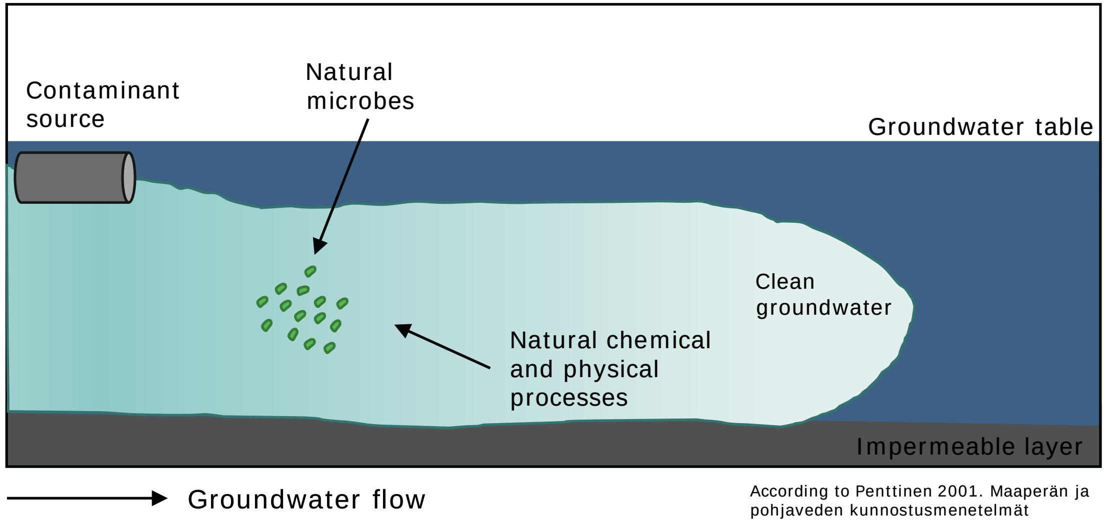
In situ remediation
Natural attenuation
Biological
Chemical
Physical
Biostimulation
Bioaugmentation
Phytoremediation
Chemical oxidation
Chemical reduction
Peroxide sparging
Air sparging
Soil vapor extraction (SVE)

BIOREMEDIATION

Natural attenuation bottlenecks

- Low temperature
- Lack of electron acceptors (O_2, NO_3^-, Fe_3^+, SO_4^-, ...)
- Lack of additional nutrients (N, P)
- Uneven distribution of contaminants and/or microbes
- Low bioavailability of oil (NAPL, adsorption to soil particles)

→ TASK FOR BIOSTIMULATION: TO REMOVE BOTTLENECKS



According to Penttinen 2001. Maaperän ja pohjaveden kunnostusmenetelmät

Kauppi, S., Sinkkonen, A., Romantschuk, M. 2011. International Biodeterioration and Bioremediation 65, 359-368

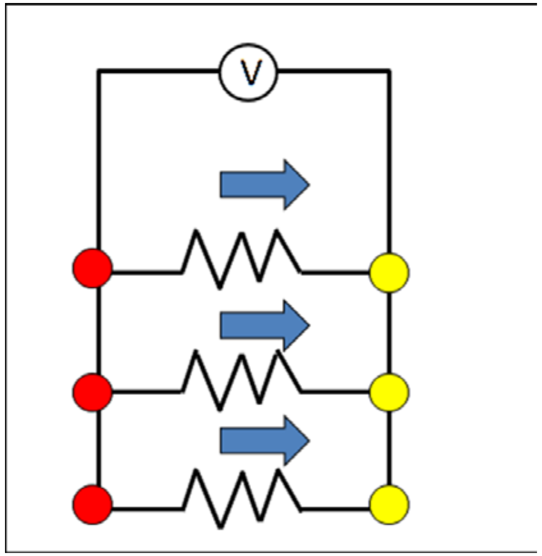
IN SITU REMEDIATION

INSTALLATIONS

a. Drillings across the contaminated zone

b. Installation of perforated plastic tubes (biological: for nutrient amended water)

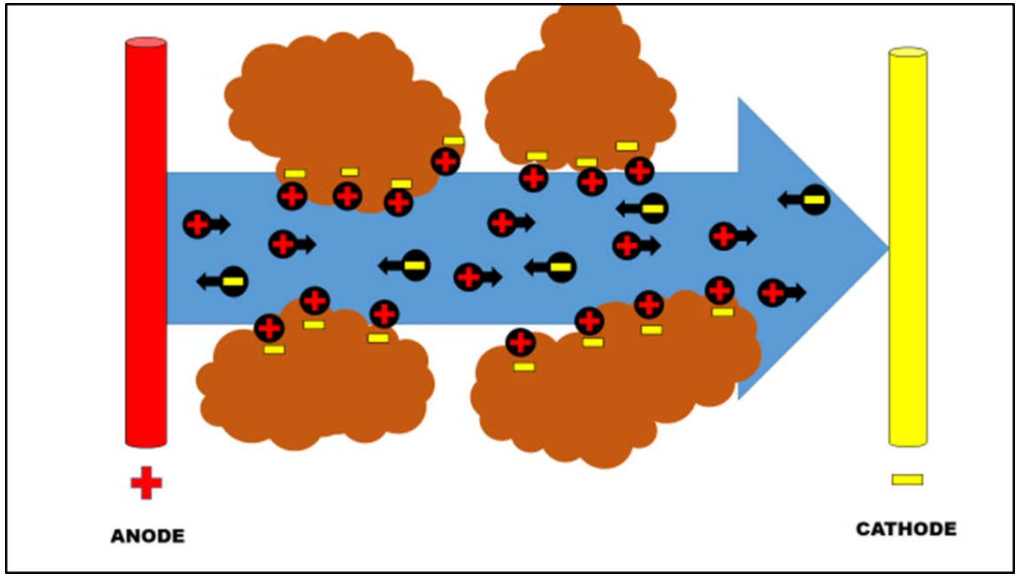
+ ELECTRO OSMOSIS



c. Installation of stainless steel rods

d. Attachment of electrodes to a transformer

e. Parallel circuit (DC) is created into the contaminated zone with two rows of electrodes

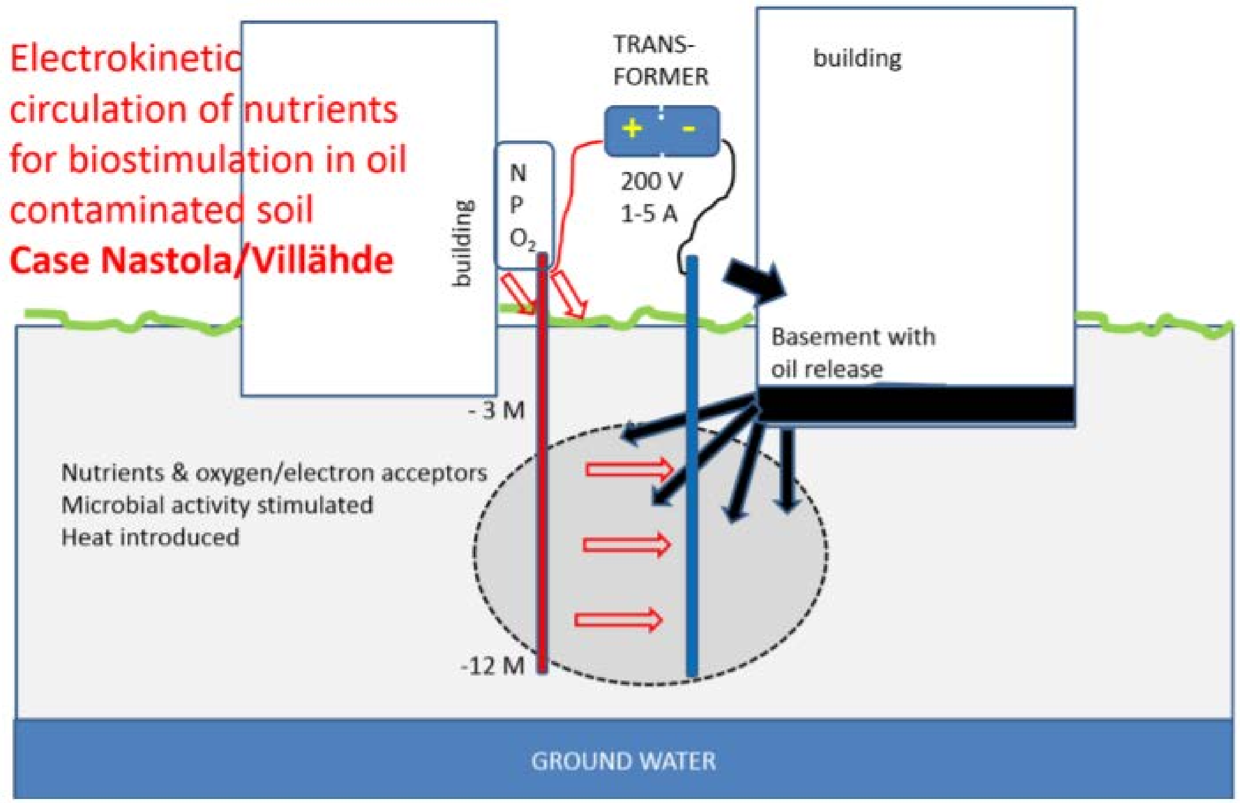


Due to the electric charge of soil particles, ions with opposite charge are bound to the soil and free ions travel towards electrodes according to their charge

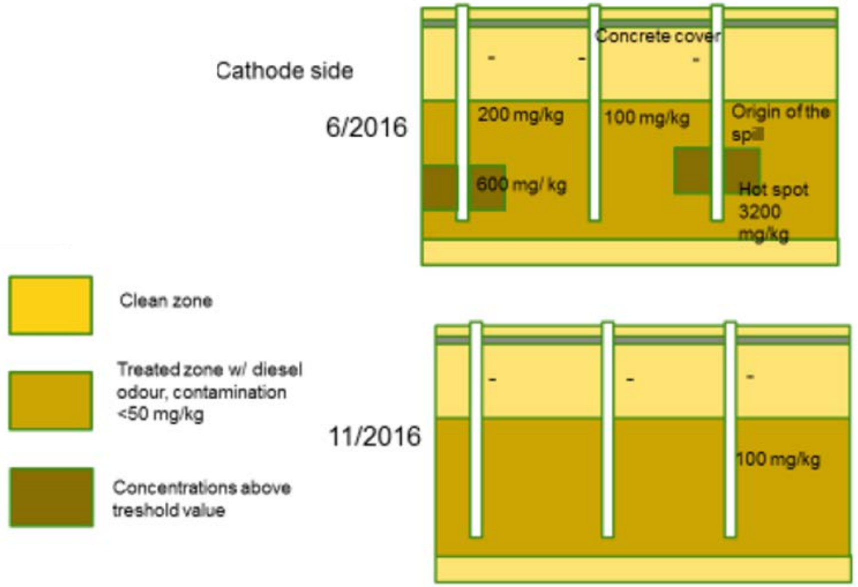
Due to viscosity, water is being dragged from anode to cathode

Heat is generated and nutrients distributed horizontally to stimulate bacterial digestion of organic contaminants

Non-saturated zone application

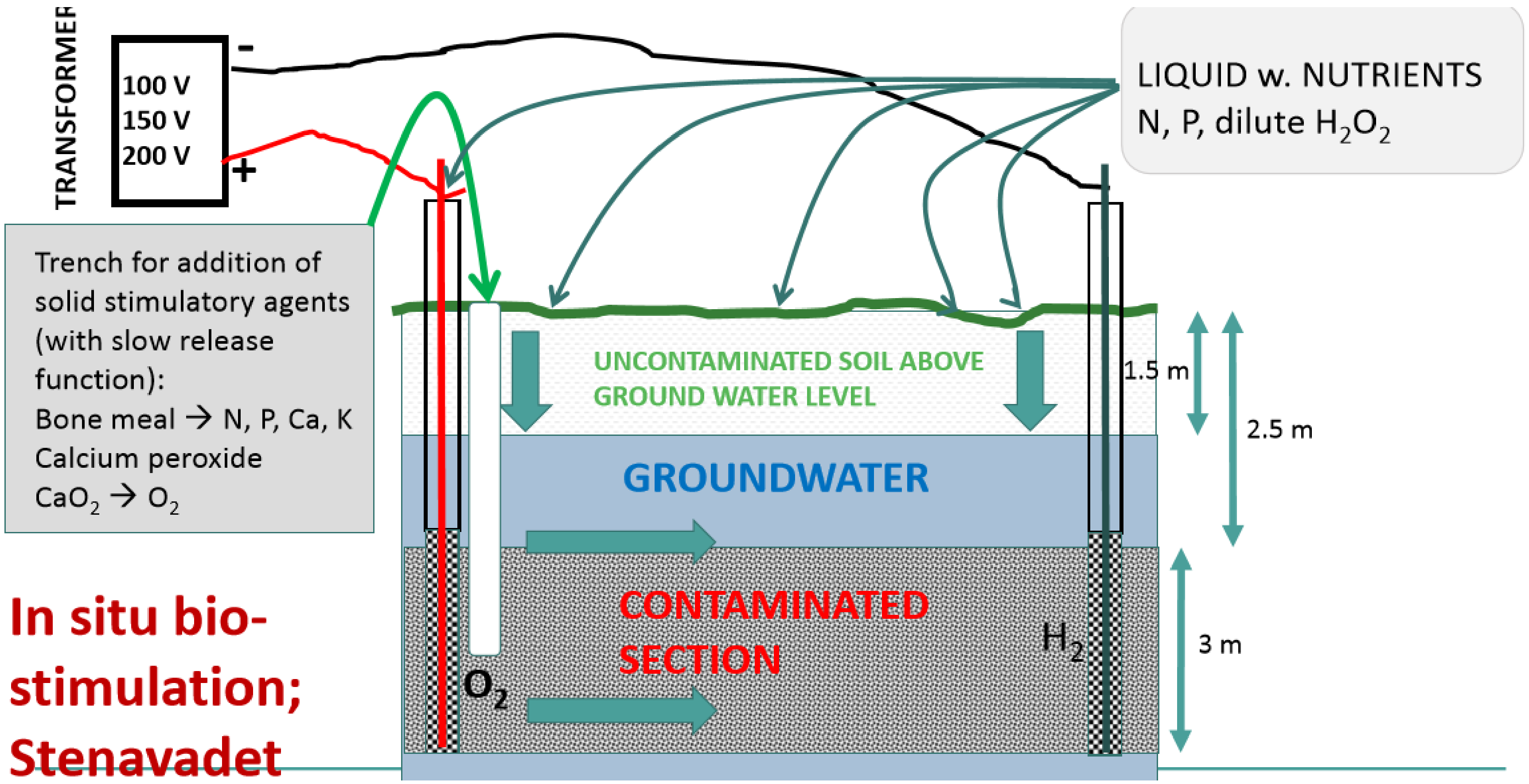


Site Villähde



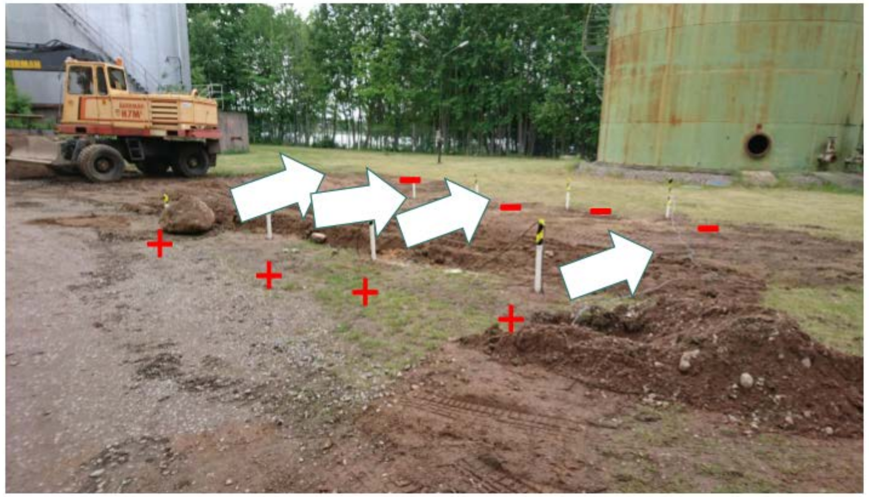
- Two light fuel oil hotspots in 7-10 m depth. Area successfully treated in 4,5 months (2016)
- Injection of nutrient-amended water into the electrode channels

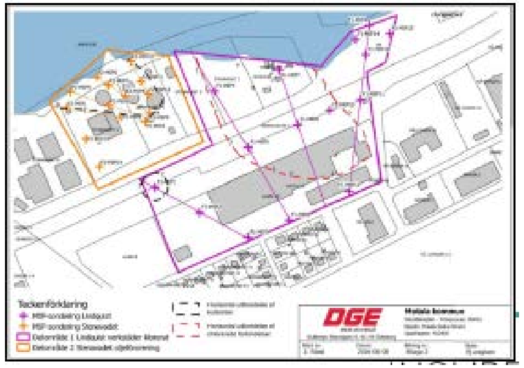
Below ground water level application



In situ bio-stimulation; Stenavadet

Site Motala, Sweden





Site with light fuel oil and volatile compounds below ground water level

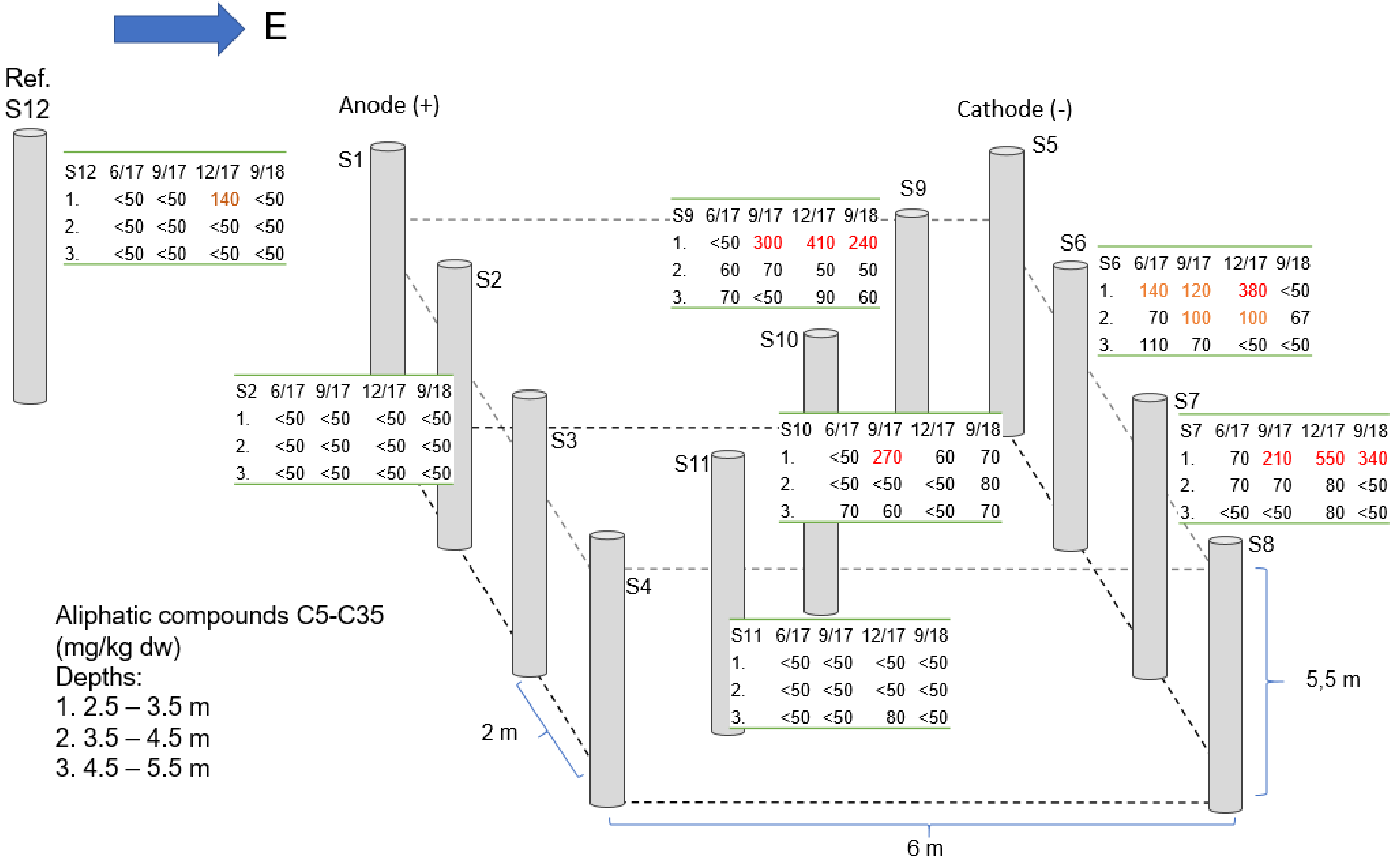
Moving ground water pass a reactive barrier of slow-release compounds bone meal (N, P, K) and calcium peroxide (O)

Partial recovery within the treatment period (2017-2018)

Bone meal

- Soil remediation with meat processing by-product (unhazardous, sterilized)
- REMSOIL® stimulates existing microbes
- Slow release of nutrients (N, P, K, Ca)
  - No leaching
  - Long-lasting stimulation
- Stimulates decomposition of organic contaminants (diesel, PAHs, etc.)
- No effect on soil pH

Motala results



S12	6/17	9/17	12/17	9/18
1.	<50	<50	140	<50
2.	<50	<50	<50	<50
3.	<50	<50	<50	<50

S2	6/17	9/17	12/17	9/18
1.	<50	<50	<50	<50
2.	<50	<50	<50	<50
3.	<50	<50	<50	<50

S9	6/17	9/17	12/17	9/18
1.	<50	300	410	240
2.	60	70	50	50
3.	70	<50	90	60

S6	6/17	9/17	12/17	9/18
1.	140	120	380	<50
2.	70	100	100	67
3.	110	70	<50	<50

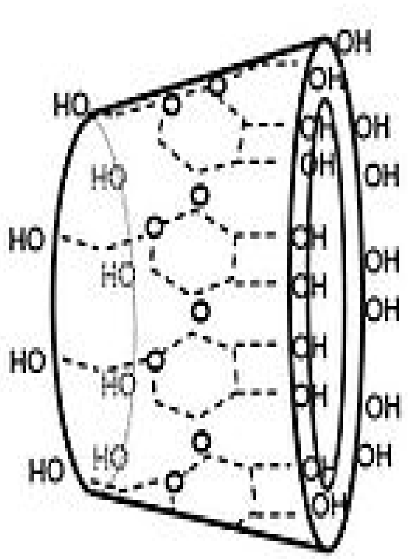
S10	6/17	9/17	12/17	9/18
1.	<50	270	60	70
2.	<50	<50	<50	80
3.	70	60	<50	70

S7	6/17	9/17	12/17	9/18
1.	70	210	550	340
2.	70	70	80	<50
3.	<50	<50	80	<50

S11	6/17	9/17	12/17	9/18
1.	<50	<50	<50	<50
2.	<50	<50	<50	<50
3.	<50	<50	80	<50

Aliphatic compounds C5-C35
(mg/kg dw)
Depths:
1. 2.5 – 3.5 m
2. 3.5 – 4.5 m
3. 4.5 – 5.5 m

Cyclodextrins –site Valmiera, site Janakkala, site Karjaa



Cyclic sugar produced from raw material containing starch,

- hydrophobic center attaching hydrophobic compounds (oils)
- quest-host complex formed through Van der Waals interaction
- hydrophilic exterior makes the complex soluble

-> Non water soluble compounds become soluble and hence more bioavailable

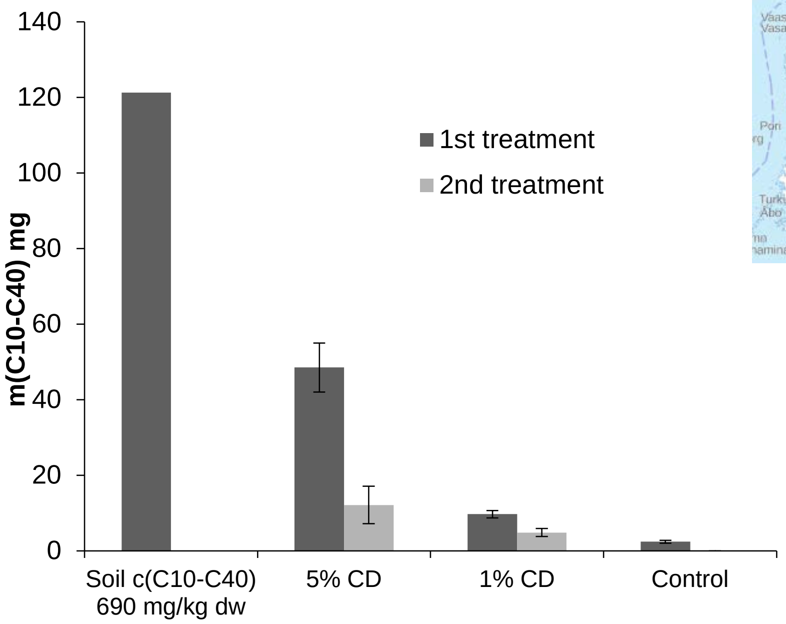
-> can decrease the treatment period but also increase the risks of contaminant mobilization

-> difficult to get permissions even for pilot tests

Site Karjaa

- Oil contaminated residential area
  - Clay/silt soil type
- Soil flushing simulation to test the ability of methyl-b-cyclodextrin (CD) to enhance the bioavailability of oil hydrocarbons
  - Soil received from Karjaa
- Concentration (C10-C40) in the beginning 690 mg/kg dw
- 0.2 kg moist soil, 300 ml treatment solution
  - 3 treatments: 5 % CD, 1 % CD, control
  - Bottles shaken 5 x 1 h (after each a settling period) → 250 ml water sample using a pipette → 2nd treatment: 250 ml of new treatment solution, shaking 5 x 5 h → water samples

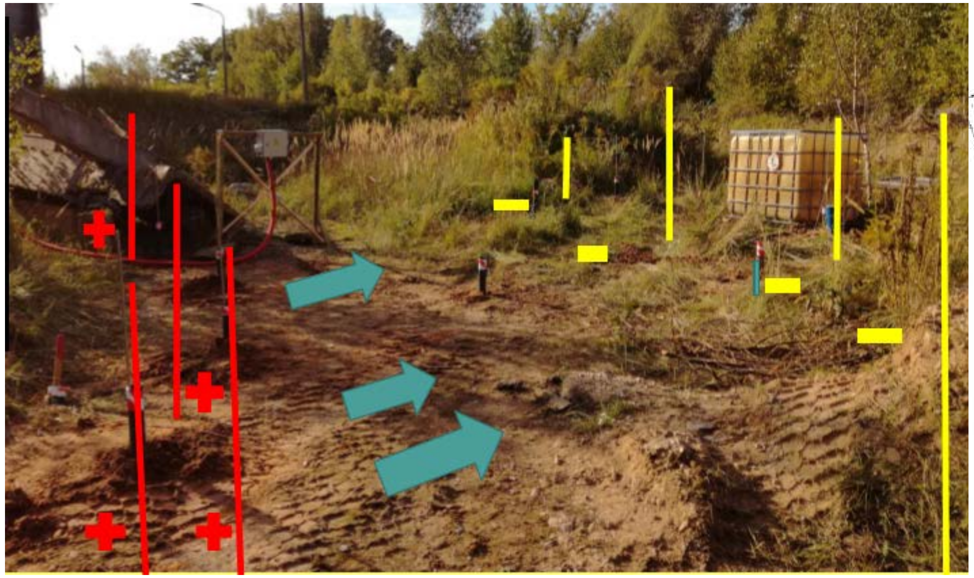
→ The additive could be used either for more effective biological treatment or for soil flushing

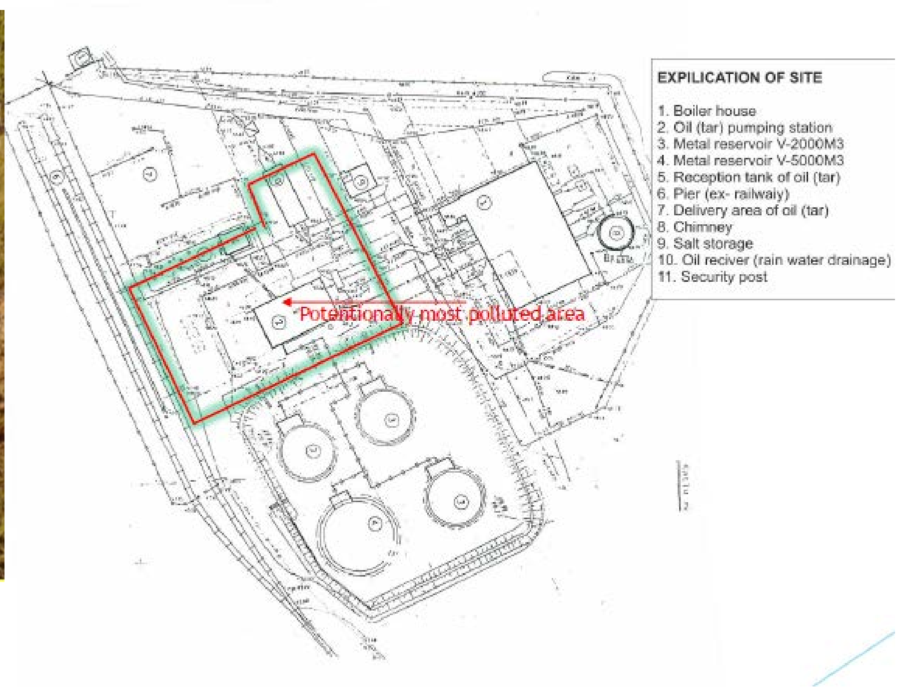


Amount of oil (mg) dissolved in water. On the left is shown the amount of oil in homogenized soil (multiplied with soil dry weight 0.18 kg)

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

Site Valmiera, Latvia





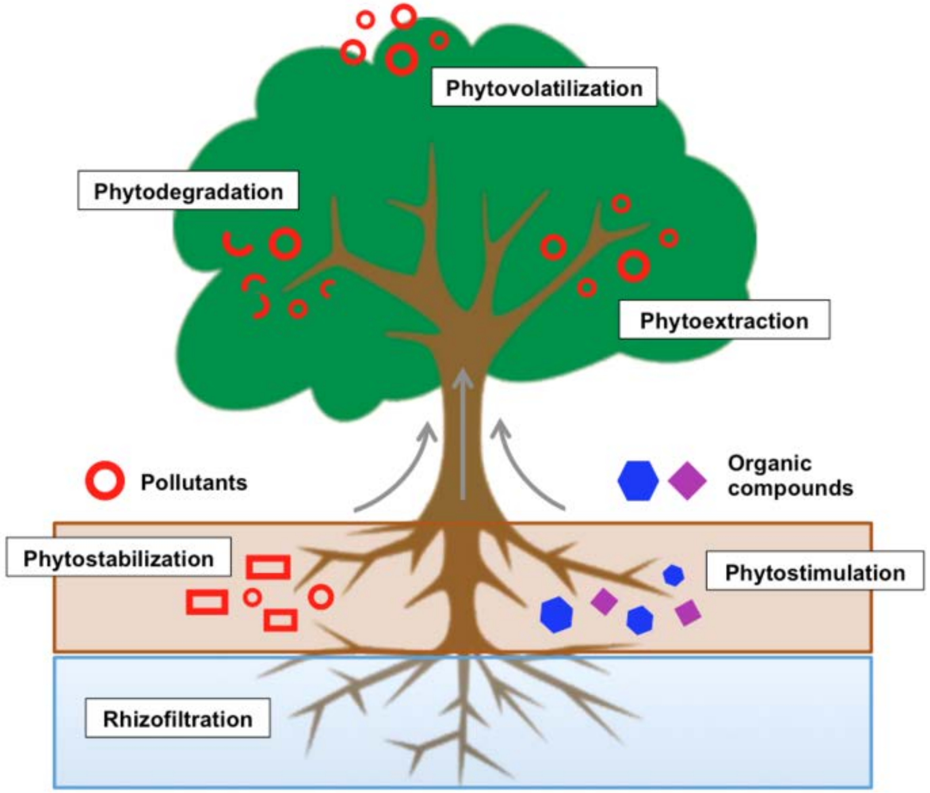
Crude mazut oil contaminated site
treated with biostimulation enhanced with electro-osmosis and cyclodextrin. Treatment on-going (2018-)

Phytoremediation

- Based on the ability of plants to take up, accumulate and/or degrade contaminants that are present in soil and water environments

+ Low costs
+ Minimal environmental disturbance
+ Esthetically pleasant
+ Prevents erosion
+ May enhance soil properties such as soil structure
+ Possibility to recover metals

− Slow process
− Toxicity of contaminants may affect on the survival of the plants
− Not suitable for contaminants located deep under the soil
− Contaminants may enter the food chain



https://commons.wikimedia.org/w/index.php?curid=45235505

Site Virrat

- Old industrial site, contaminated with oil hydrocarbons and heavy metals
- 1200 aspen seedlings in 17 planting blocks planted during 2017
- DNA samples for identification of microbes and bioinformatic analysis to figure out the microbial communities in the contaminated soil
- The site was photographed using a drone in October 2017
- The next sampling in the fall, the treatment will continue until 2028

CHEMICAL AND PHYSICAL REMEDIATION

Chemical remediation

- Chemical oxidation
  - Oxidation of organic contaminants using strong oxidants
  - Ozone, permanganate, H_2O_2...
- Chemical reduction
  - Nanoremediation by zerovalent nanoiron (nZVI)
    - Anaerobic corrosion of nZVI produces H_2 → work as an electron donor for dechlorinating bacteria
    - Add of nutrients or direct current may accelerate the degradation even further
  - Remedial alternative for TCE contaminated site in Motala

Hydrogen peroxide in biological, chemical and physical remediation

- **Biological**: Contaminant is degraded by microbes
  - **H_2O_2**: used as the oxygen source for microbes in low concentrations. Toxic in higher doses.
- **Chemical** – Contaminant is degraded by chemicals
  - **H_2O_2:** breaks into reactive radicals when catalyzed by iron, radicals destroy organic oil hydrocarbons.
- **Physical** – Contaminant is physically removed from the media
  - **H_2O_2:** bubbling and volatilization caused by peroxide breakdown reactions produce an effect comparable to air sparging, could be used to volatize VOCs from groundwater

Chemical oxidation

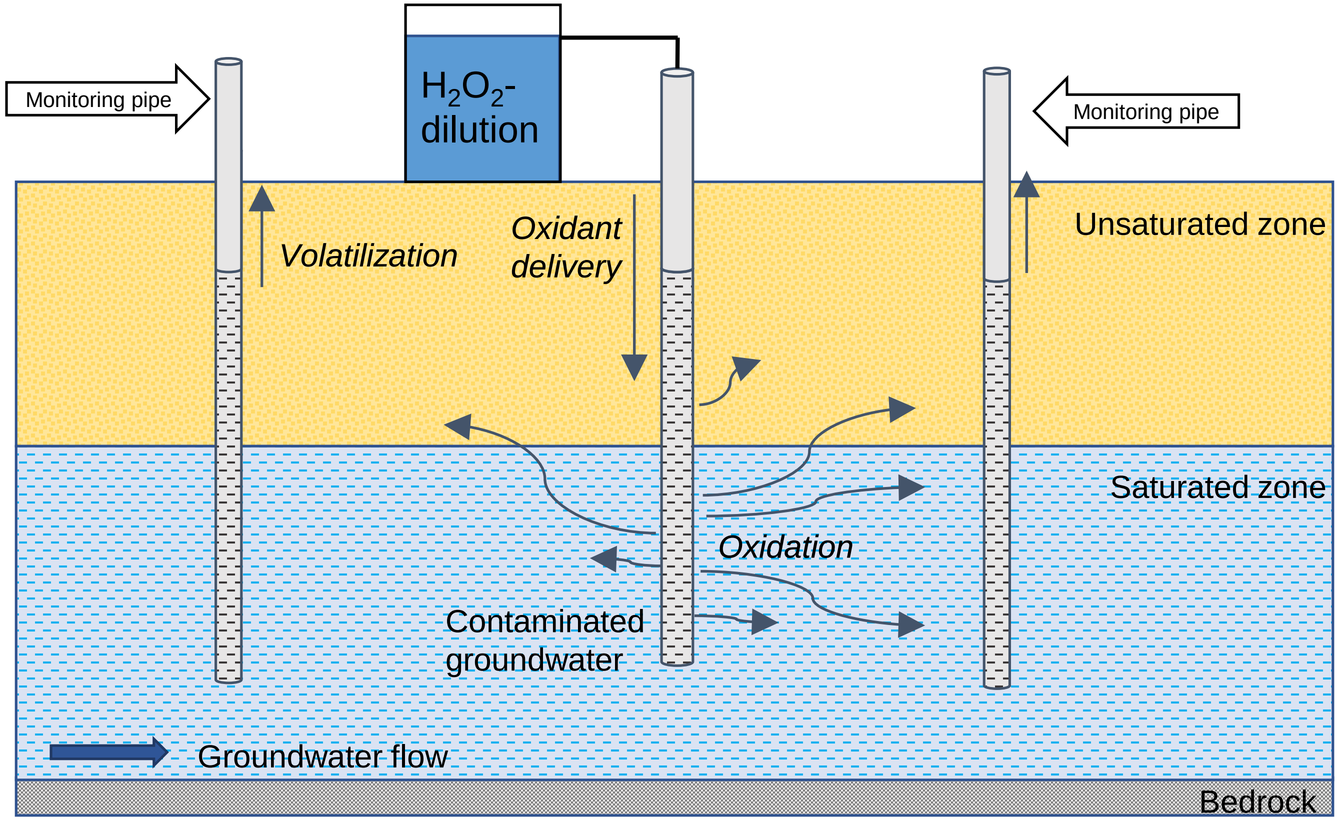
- **Hydrogen peroxide** widely used as an oxidant in chemical oxidation

- Fenton-reaction (Hydrogen peroxide breakdown catalyzed by Fe)
  - $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-}$
  - Radical production is one of the many breakdown routes
  - Requires a low pH to keep iron in soluble form, otherwise ”wasteful” reactions dominate
  - The catalytic capacity of Fe in different oxidation states differ (so does the soil types)
  - By using chelating agents (citrate), iron can be kept soluble near neutral pH (Fenton-like reactions) → Fenton-reaction should be achieved in natural pH

Peroxide sparging

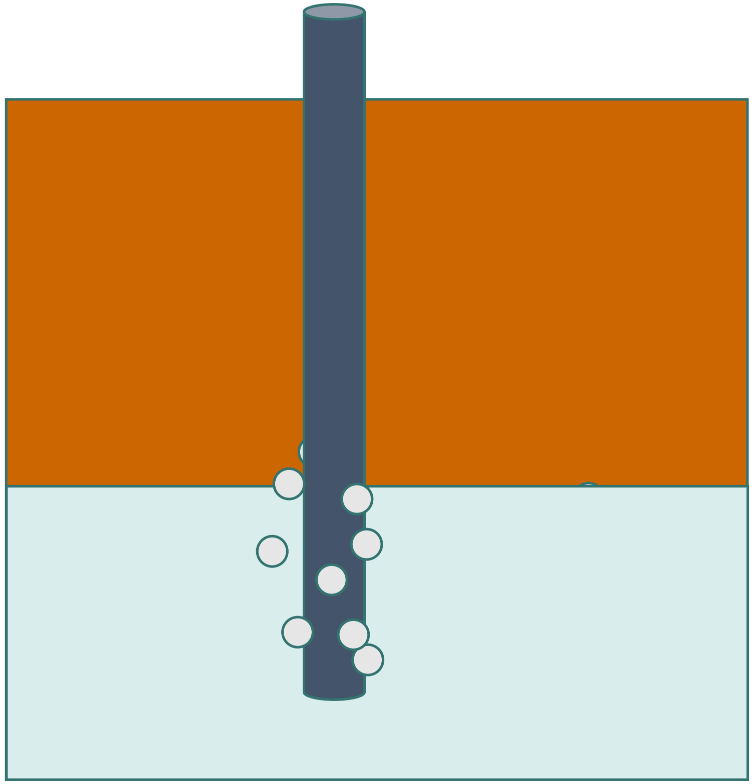
- Catalyzed hydrogen peroxide reactions exothermic → produce heat and gases, O_2 may be produced
- H_2O_2 injected into groundwater → gas produced with slight delay, allowing the diluted peroxide to spread

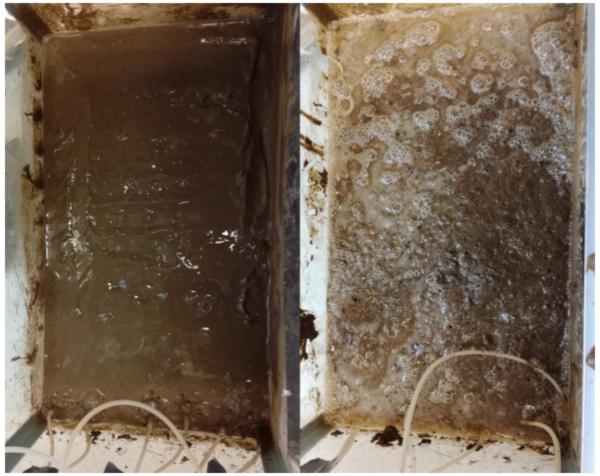
  → Air sparging and stripping-like effects
  → Volatilization and mobilization of VOCs



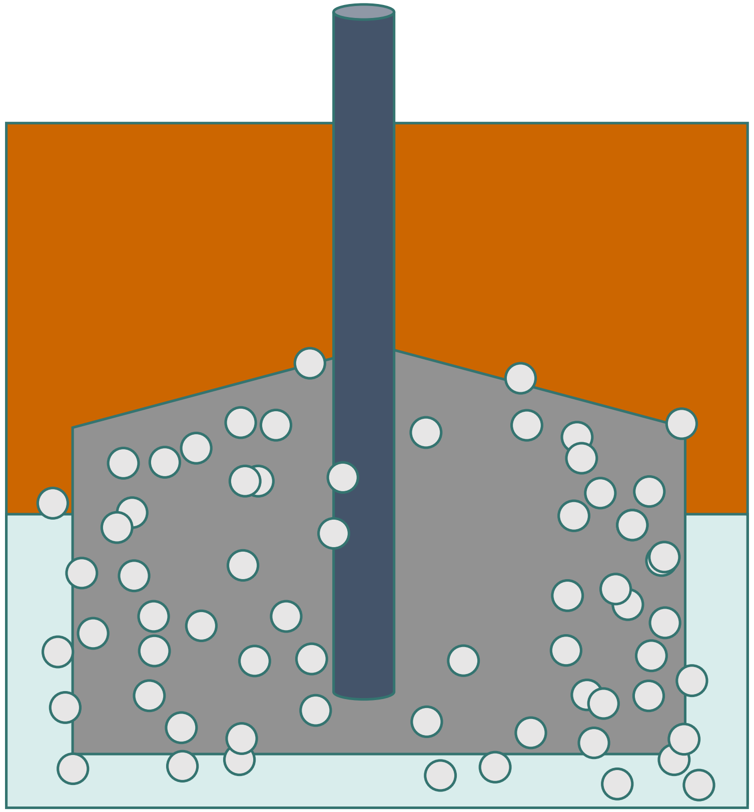
Air escapes from soil via the route of least resistance, liquids should be easier to inject. The peroxide sparging stars after a lag period.

Air Sparging





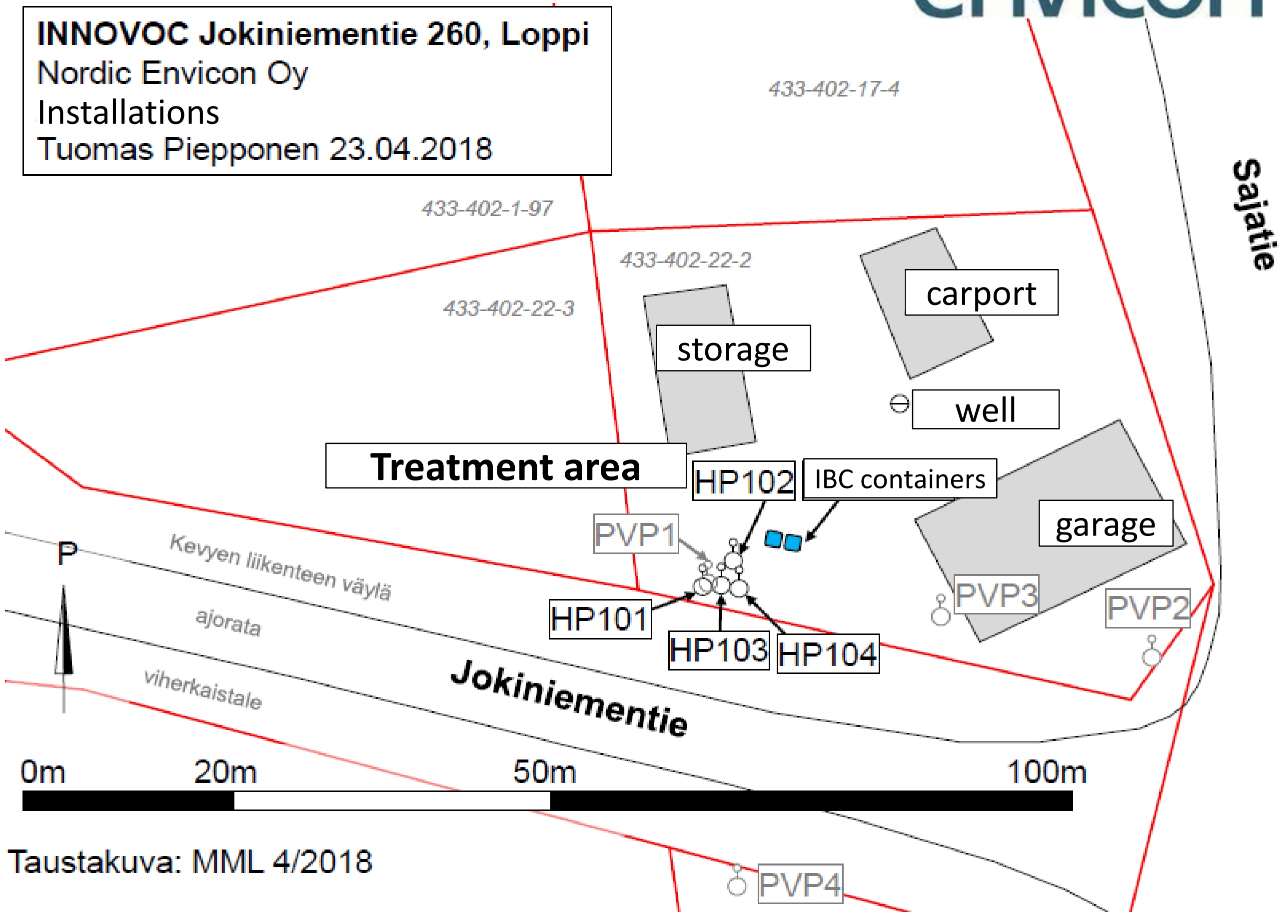
Peroxide Sparging



Site Loppi

- Former gas station, activity ended around 2002
- Soil contaminated with gasoline, diesel and BTEX
- Groundwater contaminated with gasoline and BTEX
  - Groundwater at depth of 3-4 m

- During winter (Feb-March 2018) 1 m^3 of 17 % H_2O_2 into groundwater within the treatment area
- During May-July another 1 m^3 of liquid (25 %) into the treatment area and into a pipe PVP3



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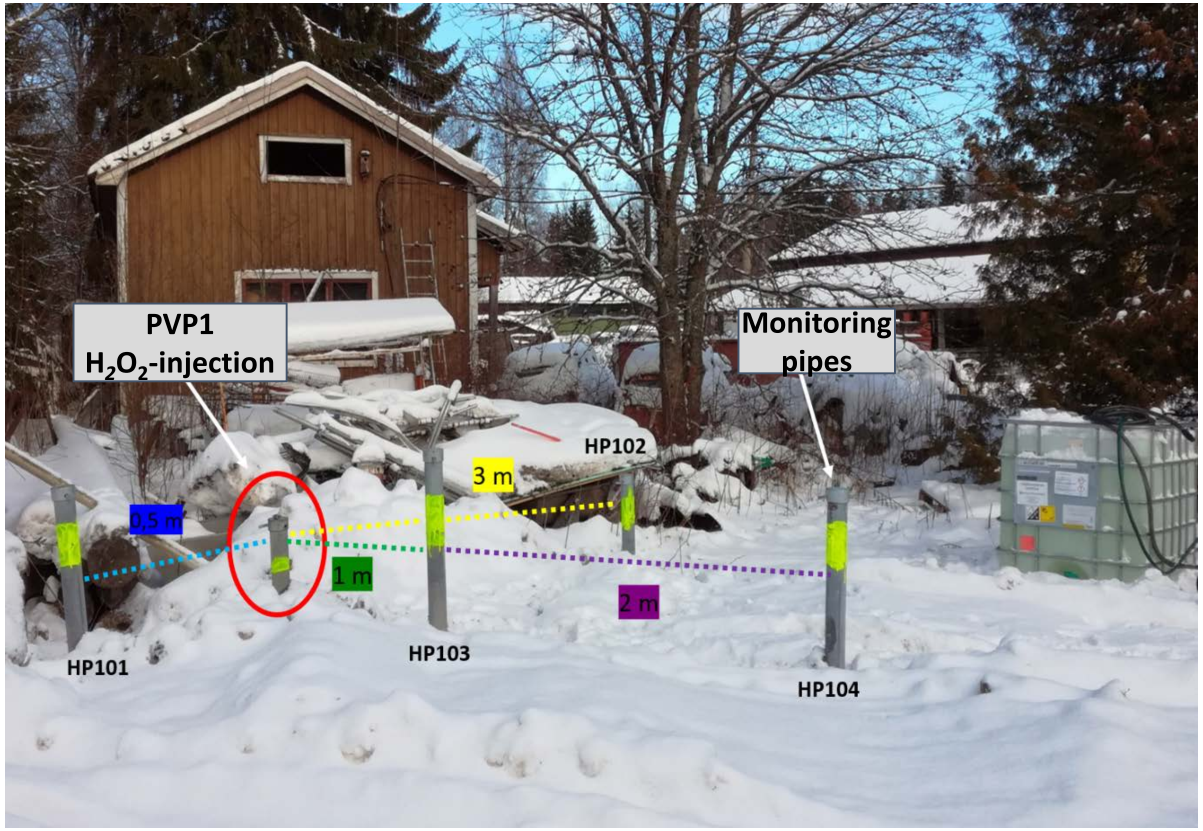
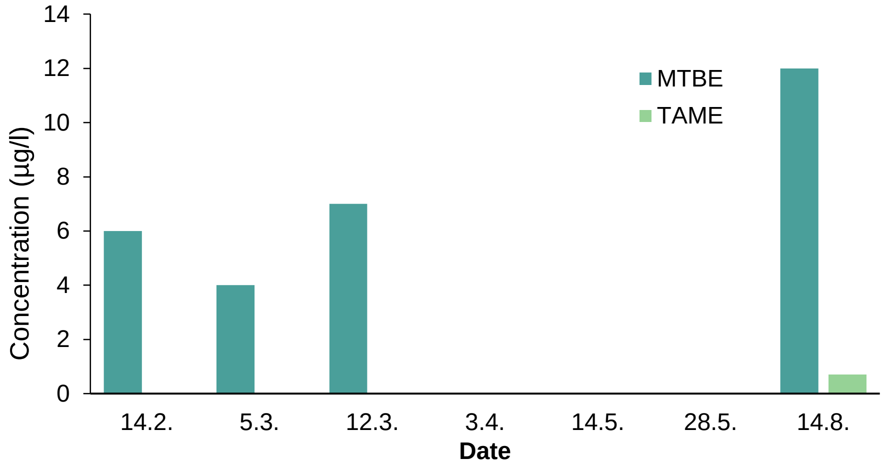
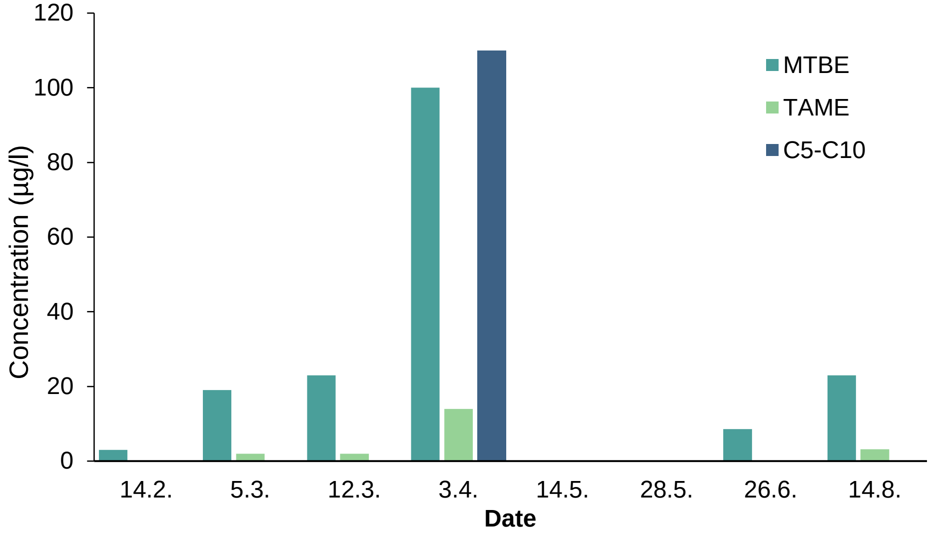
Loppi results



HP101

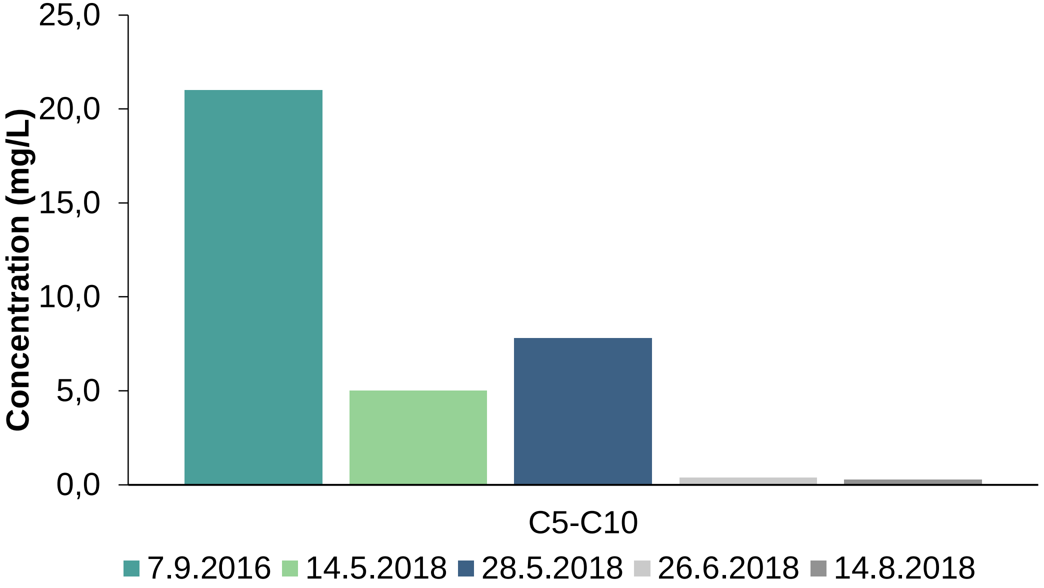


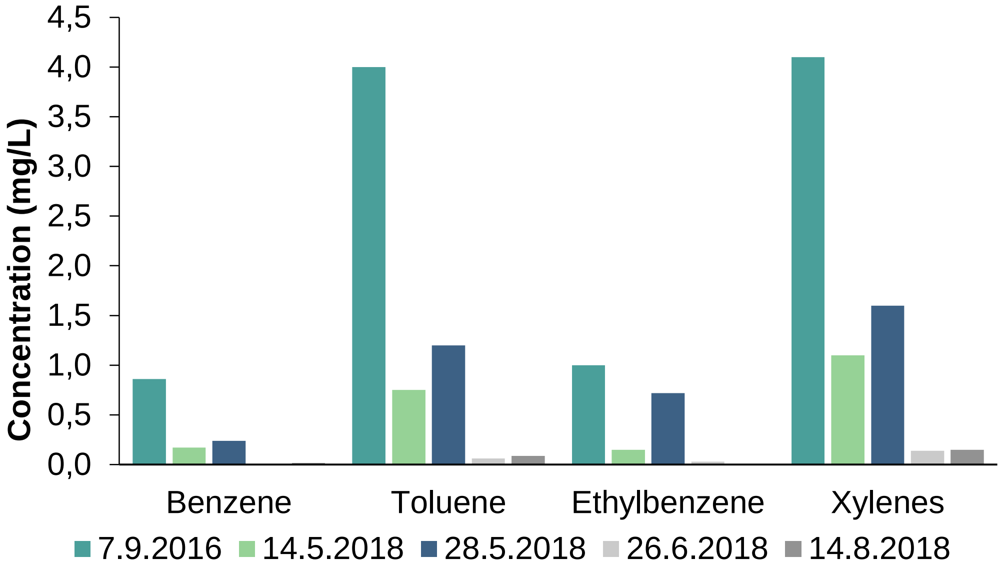
HP104



Results - continued

- Changes in concentrations of BTEX and gasoline (C5-C10) in tube PVP3 were monitored
  - Natural decrease during 2016-2018 (73 – 85 %, depending on the compound)
  - Improved removal during the treatment
    → Reduction (May-August) 88 – 97 %





Site Janakkala

- Phase 1: Fenton → 64% reduction
    - 1,5 m^3 of 15% H_2O_2 infiltrated via oil tank twice with 2-week interval in 2016
- Phase 2: Biostimulation/-augmentation → 90% reduction
    - Soil from previously cleaned site used as inoculum
    - Calcium peroxide and nitrate-ammonium fertilizer to provide O_2 and nutrients (N)
- Phase 3: Continuation of biostimulation
    - Bone meal (REMSOIL®) used as a slow release source of nutrients (N, P, K, Ca)

Site Janakkala

- Sampling in May 2018: biostimulation not reaching deep enough
  → CD (Methyl-b-cyclodextrin) added to enhance the **bioavailability** of oil hydrocarbons
    - H_2O_2 to provide oxygen, bone meal to provide nutrients
- The treatment is on-going

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

Conclusions

Pilot site	Country	Contaminants	Method (B = biological, C = chemical, P = physical)	Status	Lessons learnt?
Nastola	Finland	Oil	Electro-kinetic biostimulation (B)	Finished	Soil was successfully treated
Dzelzcela Street, Valmiera	Latvia	Mazut oil	Electro-kinetic biostimulation, oil bioavailability enhanced with cyclodextrin (CD) (B +C?)	On-going	Chemical composition of mazut varies greatly → difficulties in quantification
Södra stranden, Motala	Sweden	Oil from depot	Electro-kinetic biostimulation (B)	Finished	The remediation took longer than expected
Karjaa	Finland	Heating oil	Bioflushing with CD (B + C?)	Not started	Permission from authorities not easy to get
Virrat	Finland	PAHs, metals	Phytoremediation (B)	On-going	
Loppi	Finland	VOCs in groundwater	Chemical oxidation / peroxide sparging (C + P + B?)	Finished	Concentrations decreased 88–97 %, rebound hindered the efficiency
Janakkala	Finland	Heating oil	Chemical oxidation + bioremediation (C + B)	On-going	Combination of different treatments increased efficiency
Gaides iela, Valmiera	Latvia	...	...	Not started	...

Conclusions

- Efficiency of *in situ* treatment may be site and compound specific
- Combination of different methods may be needed
  - → Requires time
- In some cases, in challenging conditions, sites have been successfully and cost-efficiently remediated
- When risks are low and excavation is impractical, *in situ* is a good choice
- Combination of *in situ* with *ex situ*/on site methods is also worth considering

Thank you!