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RESEARCH ARTICLE

In situ bioremediation of Fenton's reaction–treated oil spill site, with a soil inoculum, slow release additives, and methyl-β-cyclodextrin

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Abstract

A residential lot impacted by spills from a leaking light heating oil tank was treated with a combination of chemical oxidation and bioremediation to avoid technically challenging excavation. The tank left emptied in the ground was used for slow infiltration of the remediation additives to the low permeability, clayey soil. First, hydrogen peroxide and citrate chelate was added for Fenton's reaction–based chemical oxidation, resulting in a ca. 50% reduction from the initial 25,000 mg/kg average oil concentration in the soil below the tank. Part of this was likely achieved through mobilization of oily soil into the tank, which was beneficial in regards to the following biological treatment. By first adding live bacteria in a soil inoculum, and then oxygen and nutrients in different forms, an approximately 90% average reduction was achieved. To further enhance the effect, methyl-β-cyclodextrin surfactant (CD) was added, resulting finally in a 98% reduction from the initial average level. The applicability of the surfactant was based on laboratory-scale tests demonstrating that CD promoted oil degradation and, unlike pine soap, was not utilized by the bacteria as a carbon source, and thus inhibiting degradation of oils regardless of the positive effect on biological activity. The effect of CD on water solubility for different hydrocarbon fractions was tested to serve as the basis for risk assessment requirements for authorizing the use of the surfactant at the site.

Keywords In situ · Bioaugmentation · Surfactant · Methyl-β-cyclodextrin · Bioremediation

Introduction

According to the Finnish Oil Pollution Fund, there are 300,000 heating oil tanks in Finland (Soini 2014). Incidents of spills reported to regional authorities annually count up to hundreds, and may involve a significant portion of individual sites regionally. All in all, these low-profile occurrences amount to the biggest environmental concern in most parts of Finland. In rare cases, these spills are associated with specific accidents, but more commonly result from normal wear and tear of the tank jackets (Puolanne et al. 1994). In these cases, it may take time before the problem becomes noticeable, and large volumes of soil can already have been affected. Excavation of tanks and the contaminated soil tend to be the standard emergency protocol whereas this may be made difficult by buildings or associated underground structures (Dahl et al. 2013). Approximately two thirds of the existing oil tanks are for residential use only (Soini 2014).

Due to the low threshold values for contamination of soil in residential areas, alternative remediation methods are rarely being considered (Sorvari et al. 2009; Reinikainen 2007). It is, however, acknowledged that the current protocol needs to be questioned in the near to immediate future: In Finland, the landfill policies concerning contaminated soil masses are becoming increasingly restrictive (MOTE 2015). Also, globally,

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the push towards sustainable land use and transportation require precautionary principles associated with *in situ* remediation to be re-considered (Smith 2019).

In Finland, natural attenuation is rarely enough for sufficient oil removal (Penttinen 2001). The problem with authorization of active in situ methods is that sites with lowest risks are the ones where low permeability of the soil reduces the possibility of contaminant mobilization. In these particular cases, injection of remediation additives may be difficult and low bioavailability of the contaminant prove to be the primary bottleneck for biological degradation (Martins et al. 2009). Chemical in situ treatment is similarly negatively affected by the extent to which the contaminant occurs as non-aqueous phase liquid or is absorbed into the soil matrix (Wang et al. 2013).

The most used chemical oxidant is hydrogen peroxide. In Fenton's reaction, its breakdown is catalyzed by iron or other transition metals. The resulting hydroxyl radicals start a chain reaction with a capacity to degrade organic compounds such as hydrocarbons (Neyens and Baeyens 2003; Petri et al. 2011). This is dependent on solubility of the catalyst in acidic pH, whereas at higher pH the amount of the catalyst in soluble form can be secured by adding chelating agents (Pham 2012; Kwan and Voelker 2003; Jho et al. 2012; Sun and Pignatello 1992; Venny et al. 2012; Vicente et al. 2011).

The efficiency of Fenton-based chemical oxidation may be compromised by radical reaction inhibition or scavenging by the organic material (Lindsey and Tarr 1999; Miller and Valentine 1999; Pham 2012) or low availability of the contaminant in NAPLs or adsorbed in to soil particles, especially in clayey soils (Sellers 1999; Villa et al. 2010). Even if chemical oxidation is the target mechanism for contaminant removal, a secondary biological mechanism can contribute to the overall efficiency by increasing oxygen availability and contaminant bioavailability, especially if chemical mineralization itself has been insufficient (Talvenmäki et al. 2019; Simpanen et al. 2016; Goi et al. 2006).

In these cases, the balance between different reaction mechanisms may be difficult to define, whereas the role of biodegradation is likely to increase over time. This secondary mechanism may, however, have been impeded by the toxic effects of high H_2O_2, oxygen or radical concentrations, so the degraders themselves may need to be reintroduced (Tarasov et al. 2004; Büyüksönmez et al. 1998). Bioaugmentation performed with pure cultures is often reported to be unsuccessful. This is generally due to competition for limited resources between the imported strains and the native bacteria in undisturbed rather than chemically treated soil conditions (Gentry et al. 2004; Thomassin-Lacroix et al. 2002: Kauppi et al. 2011). Better results have been achieved when the natural microbial community of a particular environment is transferred in its entirety in a soil inoculum. Adaptation of the community is not required if the specific enzymatic pathway can be distributed within the indigenous population horizontally (Sarand et al. 2000). By utilizing treated soil with a similar contamination history as the base, positive results have been achieved for a multitude of organic contaminants, such as herbicides, PAHs, and diesel (Koivula et al. 2004; Kauppi et al. 2012; Sinkkonen et al. 2013).

Availability issues concerning both chemical and biological treatments can be circumvented by introducing surfactants (Chaillan et al. 2006; Martins et al. 2009). Surfactants help to overcome surface charge through changes in the interface between chemical substances of differing polarity (Khalladi et al. 2009). The additive dose should be selected according to whether the contaminant is to be flushed out physically or merely released into the aqueous phase for degradation. This is especially important for biological treatment, as mobilization may outpace bacterial digestion (Simpanen et al. 2016). When selecting the surfactant, biodegradable alternatives are preferable for environmental reasons, whereas it should be noted that highly degradable additives can also interfere with the remediation by acting as a more readily available carbon source than the contaminant itself or by having a reverse effect on bioavailability (Wang et al. 2011; Sen et al. 2012).

In laboratory-scale experiments, the effectiveness of two biodegradable surfactants, pine soap and methyl-β-cyclodextrin, on both hydrocarbon removal and biological activity was studied. Pine soap is made from pine oil, with various resin acids (mainly abietic acid and its isomers) and fatty acids (oleic and linoleic acid) acting as the surface activity–enhancing agents (Biermann 1993; Riistama et al. 2003). Pine soap is inexpensive, easily accessible in small doses, and its negative environmental impacts are considered low. Cyclodextrins are oligosaccharides produced enzymatically from starch containing substances and are able to form guest host–type complexes with many compounds in various chemical states. The hydrophobic inner centrum attaches hydrophobic compounds with van der Waals interaction, and due to the hydrophobic outer rim of the toroid shape the compound becomes water soluble (Del Valle 2004). The effect of methyl-β-cyclodextrin, the surfactant chosen on the basis of a laboratory test for the site treatment, on the water solubility of the different aliphatic and aromatic oil fractions was further examined to direct decisions at the site.

The goal of this research was to study the potential benefits of a combination treatment with Fenton's-based chemical oxidation and a subsequent bioremediation step in situ, with emphasis on how the joint effect could be optimized by targeting the probable bottlenecks, namely the low survival of native bacteria and the low bioavailability of oil. The chosen site exemplifies both the greatest challenges involved with in situ techniques as well as the highest potential rewards: low water permeability of soil hampering infiltration but also lowering the risk of contaminant mobilization, and with only a small hotspot of contamination appearing in a vulnerable location near built structures making excavation a non-preferable procedure. The different approaches were used in combination due to following challenges encountered at the site: (1) Chemical oxidation, regardless of the initial positive results, was not considered an effective way to lower the local high hydrocarbon concentration to the Finnish guideline value levels. (2) Mechanisms leading to the heightened bioavailablity of the contaminant were observed during the chemical treatment, whereas based on the oxidant doses, biological conditions at the site were suggested to have been negatively affected. (3) Conventional biostimulation with oxygen and nutrient addition was ineffective after a certain point, and based on the soil type, low bioavailability was known to be a factor.

Materials and methods

Site characteristics

The study site is located in the Turenki municipality in Finland (Coordinates 60° 55′ N, 024° 38′ E) in a residential area on the premises of a single household. The site is not located within or near a major ground water area and there is no subsurface draining connecting it to neighboring properties. The average air temperature during the 30-month treatment was ca. 5 °C, with eleven of the months below 0 °C and seven above 15 °C.

Preliminary investigations of the site were performed during 2013–2014 by the independent consultant Ramboll Finland Oy. The contamination was found to be the result of oil leakage from a faulty underground heating oil tank with one or more small holes in the tank jacket. The tank is situated approximately 1 m from the north corner of the house, with its bottom at a depth of 2.2–2.5 m. The tank has been cleaned and left intact and its removal has been ruled out due to the vulnerable location near the corner of the house (Fig. 1a and b). The contamination is unevenly distributed but generally residing at the approximate depth of the source, 2.5+ m depth. The permeable soil extends down to 2.8–3.0 m. The soil type in this zone is approximately 60% silt (< 0.063 mm) and 40% sand (0.063–2 mm).

In the preliminary investigations in 2013 by the contractor, C10–C40 concentrations were found to average 1900 mg/kg and vary between < 50 mg/kg dw to 3300 mg/kg dw in the immediate vicinity of the tank. The relative portion of the midrange (C10–C21) fractions in the total hydrocarbon concentrations varied between 66 and 90% suggesting differences in natural attenuation levels between sample points (Kostka et al. 2011; Prince 2010; Rodriguez-Blanco et al. 2010). At this point, no samples were taken directly under the tank. The soil around the tank was found highly impermeable. Approximately 10 L of water could be injected into the soil via a single vertical ground water tube (⌀ 8 cm) within a period of 2 h, and even then, the effect of injection could not be verified from a neighboring receiving tube located 20 cm away.

During the following year, 800 L of ammonium–nitrate–amended water was injected into the soil via five similar tubes during a 3-month period, increasing the nitrogen concentration from 140 mg/kg to approximately 1300 mg/kg**.** This excessive dosage was explained by an erroneous approximation of the radius of influence for a theoretical 100:10 Corg:N addition of nitrogen. The initial phosphorus content in the soil prior to any active remediation measures was 580 mg/kg, which would suggest that biodegradation was not limited by the low availability of either nitrogen or phosphorus. As such excess dose of nitrogen is found to have reverse effects on microbial respiration and hydrocarbon degradation (Fayad and Overton 1995). Since these high local levels were caused by distribution issues, it is likely that the required level was not secured across the contaminated zone. In this initial treatment, the injection of nutrients hence failed to stimulate bioremediation, and so modified and differently targeted in situ protocol was developed.

Outline of site treatment

After the ineffective biostimulation treatment, a combination of chemical and biological treatments was performed at the site as described here. The site was treated first with Fenton's reaction–based chemical oxidation and the biological integrity was then restored by bioaugmentation with a soil inoculant and biostimulation with various oxygen and nutrient sources which were selected based on observed changes in the water saturation conditions. Lastly, biostimulation was enhanced using biosurfactants.

Information on the benefits and risks associated with the surfactant use was collected from two small-scale laboratory tests. In the first one, two possible biosurfactant options, pine soap and methyl-β-cyclodextrin (CD), were surveyed for their effects on oil hydrocarbon removal and biological activity. After the latter was chosen for the site treatment based on the aforementioned results, its effect on the water solubility of different oil hydrocarbon fractions was tested. When the treatment is likely to enhance mobility of the contaminant, authorization of the protocol requires risk assessment based on laboratory-scale model data. For fuels, the risks are associated with particular fractions and their chemical properties, which are recognized by risk assessment tools. In this case, we used the Soilirisk assessment tool, which has been developed by the Finnish Oil Industry Service Center for standardization of the risk assessment process (OISC 2017).

Fig. 1 The study site. above surface view (**a**) and the tank in the original condition (**b**)

Laboratory-scale experiments

Effect of surfactants pine soap and methyl-β-cyclodextrin on hydrocarbon reduction and microbial activity in soil

A preliminary comparison experiment was set up to test whether the chosen surfactants, CD and pine soap, could be expected to increase biological degradation by increasing the bioavailability of the hydrocarbons rather than through acting as alternative carbon sources themselves.

Removal of oil hydrocarbons from soil—either through biodegradation, mobilization or both—as well as biological activity as measured from soil respiration, was studied in an experiment with a recycled aqueous phase. Gravelly soil with aged diesel and engine oil contamination was thoroughly mixed after rocks larger than 1 × 1 cm^2 had been removed with a sieve. This soil, which was coarser than the one found at the site, was chosen to regulate the filtering duration and downplay the role of the edge effect. Soil organic carbon, nitrogen, and phosphorus concentrations were analyzed. Nitrogen content was measured as being below the threshold value and thus the limiting nutrient.

The soil was placed in 18 plastic (⌀ 10 cm, 50 cm) tubes with 3.5 L of soil each, with the aqueous phase of 1.5 L recycled through them (Fig. 2). A thin layer of gravel and a plastic membrane was laid below the soil in the tubes to enable water movement but prevent soil leakage. A small horizontal hole was drilled in the middle of the tubes for sampling.

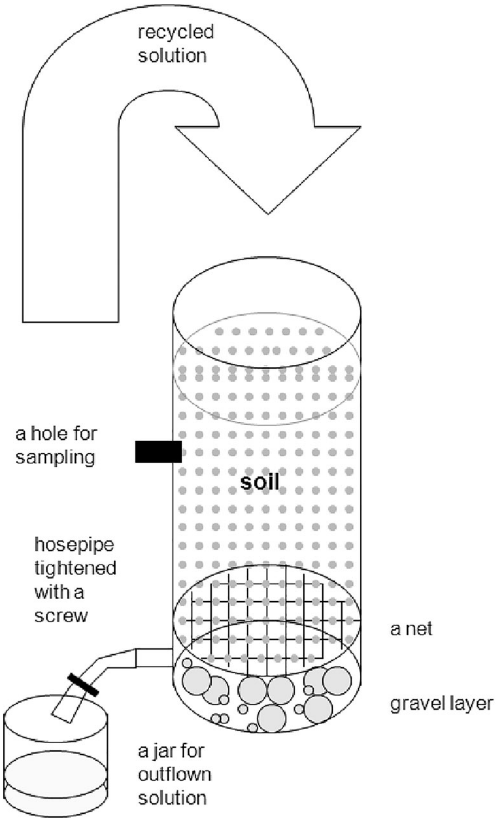


Fig. 2 The construction of experimental cylinders. Height 50 cm, diameter 10 cm

Either nutrients and/or surfactants were added to the recycled water phase. The experiment consisted of six different treatments, all executed as three replicates. The treatments were (i) control without any additions, (ii) liquid pine soap, (iii) liquid pine soap plus nutrients, (iv) nutrients, (v) cyclodextrin and (vi) cyclodextrin plus nutrients.

The surfactant concentration in the solutions was approximately 1%. Nitrogen was added as an ammonium nitrate mix (nitrogen dose 12 mM) and phosphorus as K_2HPO4 + NaH_2PO_4 buffer in dose 710 mg/l (15 mM P). Solutions were adjusted to pH 7 by adding either base (NaOH) or acid (HCl).

The experiment lasted for 13 weeks during which the solutions were recycled trough the soil tubes 22 times. Before returning the solutions that had passed through the soil back into the tubes, pH was determined and the solutions were aerated by vigorous bubbling with aquarium pumps for 1 h. Solutions containing liquid pine soap were not aerated due to foam formation. Samples from the soil were withdrawn four times, 1 week, 3 weeks, 9 weeks, and 13 weeks after the start of the experiment, in ca. 50 g mass.

Oil hydrocarbon concentrations were measured with GC-FID as described in "Analyses" and microbial activity was measured as respiration based on CO_2 production. CO_2 is suggested in this case to result entirely from mineralization of the organic contaminant (Wade 2018; Santruckova 1993). While high respiration values are not always connected to increase in biomass, respiration level itself is a more direct indicator of organic matter decomposition rate (Rui et al. 2016). Respiration was measured from the total carbon in the airspace of the vial was measured with Teledyne Tekmar Apollo 9000 Combustion TOC Analyzer. For this, approximately 20 g of soil was weighed into a glass vial that was capped and left to stand for 30 min. The rate was calculated as the difference in CO_2 concentration in the gaseous phase between measurements at 0 and 3 hours.

Solubilization of hydrocarbon fractions

The efficiency of CD to dissolve aliphatic and aromatic hydrocarbon fractions with the type of soil type found at the site was tested in laboratory scale using clayey soil from an alternative site, with aged heating oil contamination. In situ biostimulation had been performed at the site, suggesting that the more bioavailable fractions had already been degraded, increasing the comparability between the sites. The C_{org}:N:P ratio of this soil was 100:3:11.

The soil was sieved (6×6 mm^2) and thoroughly mixed. The oil content after the homogenization was measured from five replicates. In the experiment, 200 g of soil (dry matter content 88%) was weighed into Erlenmeyer flasks and 300 ml of solution was added. CD was tested in doses of 5% and 1% (w:v), and compared to a water control. All treatments were performed as three replicates. During the first part of the treatment, the flasks were placed in a shaker (150 rpm, 30 mm orbit) for 1-h sessions after which the phases were allowed to separate before the following run. This procedure was repeated five times in total. After the initial sampling, it was repeated in a similar manner but with shaking runs lasting for 5 h. A 250-ml water sample was withdrawn after both of the steps and a compensating treatment solution volume was added.

The results from the test were not presumed to entirely correspond with those from a study or site treatment where the solvent would be instilled or circulated. In this manner, what could be studied was how the addition of CD could enhance the mobilization of non-volatile fractions of oil hydrocarbons in optimal conditions in a thoroughly water-saturated zone. All samples were analyzed for fractions in the C10–C21, C21–C40, and C10–C40 ranges as described in "Analyses." A complete fragment analysis was performed on a single sample per treatment.

Site treatment

Sampling and injection through the tank jacket

The soil immediately below and around the tank was suspected to consist of coarser filling material, and hence act as a continuing contamination source due to the heightened permeability and proximity to the source. Because of these factors, this zone was presumed to respond more favorably to remediation efforts. Due to this higher permeability and the suspected location of the hot spot, sampling and water injections were performed through holes in the tank itself.

For this, five holes (⌀ 4 cm) were drilled (Fig. 3a and b). Three holes were located at the bottom axis and two holes higher up the jacket approximately 15–20 cm from the bottom. Soil samples ca. 60 g in mass were withdrawn with a ⌀ 3.5 cm plastic auger from depths 0–10 cm, 10–20 cm, and 20–30 cm, found to be the maximum depth of the penetrable layer. Higher concentrations of oil hydrocarbons were measured from the initial samples than in any previous investigations, at levels exceeding 10,000 mg/kg (Table 3). All treatments were performed by pumping injection fluids into the tank, from which the fluids slowly could infiltrate the surrounding soil through the holes. Soil mobilization during infiltration allowed subsequent samplings to be performed using the same holes.

Chemical oxidation (4 weeks)

Chemical oxidation required low natural organic matter content in the treated zone, low soil oxidant demand, and conditions in which the catalyst remain in a soluble form (Haselow et al. 2003; Pham 2012; Kwan and Voelker 2003; Jho et al. 2012; Sun and Pignatello 1992; Venny et al. 2012; Vicente

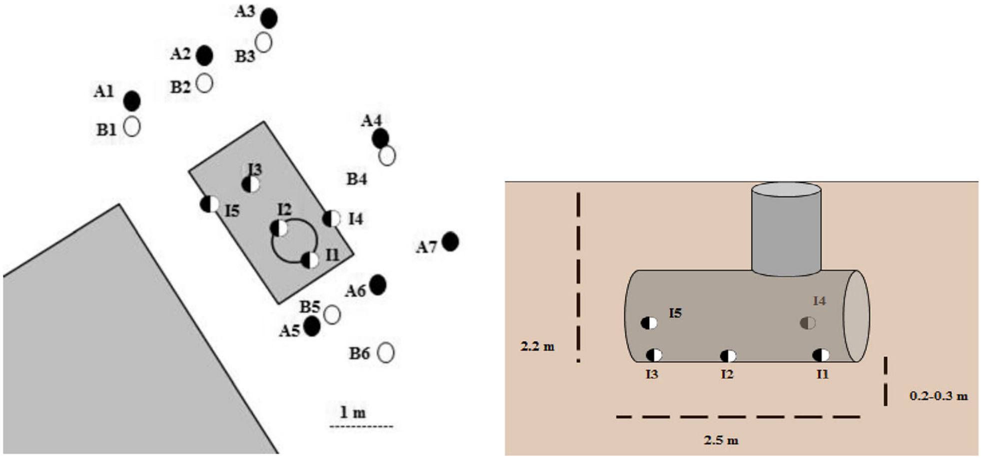


Fig. 3 Technical drawing of the site with sampling spots marked, from above (**a**) and a vertical cut view (**b**). Black sampling spot color indicates sampling performed before remediation activities, white color indicates sampling after or during remediation

et al. 2011). Non-water–saturated conditions were also required as otherwise infiltration of the peroxide may have been limited. Soil oxidant demand was tested as described in Talvenmäki et al. (2019) as surpassing 800 mg $KMnO_4$ /100 g of soil even when visible organic material such as roots had been removed. However, as the majority of the contamination was suggested to appear within a small quantity of soil immediately below the tank, chemical oxidation was still considered an applicable method.

The soil was initially treated with chemical oxidation based on Fenton's reagent, catalyzed by soil minerals alone. The availability of catalyst was tested by mixing soil with H_2O_2. Soil pH 6.7 was found to be too high for non-chelated chemical oxidation, and so citrate chelate was used (Vicente et al. 2011; Lewis et al. 2009). Twenty-five kilograms of tri-sodium citrate was added into the tank with 0.5 m^3 of water (Fig. 4a). One cubic meter of 25% H_2O_2 was then added (Fig. 4b). The injected mixture was found to infiltrate the soil within 12 to 24 h. The H_2O_2 injection was repeated after 2 weeks with soil sampling performed immediately before each infiltration event.

Bioaugmentation with soil inoculum and non-saturated soil biostimulation (10 months)

Since H_2O_2, the released oxygen and the radicals are all known to be toxic in high concentrations, actions were taken to introduce living bacteria following the Fenton's treatment (Tarasov et al. 2004). A 40 kg soil inoculum, consisting of treated, aged diesel–contaminated soil originating from the published study of Liu et al. (2019), was placed into the tank. The inoculum was a 50/50 mix from a control treatment and treatment with CaO_2 in dose 2%. In both treatments, the original oil concentration of 680–800 mg/kg had decreased by 40–61% during a period of 18 weeks (Liu et al. 2019). The suitability of the inoculum was tested by determining the

Fig. 4. Chemical treatment. Addition of citrate (**a**), injection of peroxide (**b**), resulting soil mobilization (**c**)

taxonomic composition of the bacterial community in the two soils by sequence analysis of the 16S rRNA gene pool (described in Hui et al. 2019). The community structure was calculated using Mothur software (Appendix 1 Table 4) as described by Roslund et al. (2019) and Grönroos et al. (2019). Relative abundance of phyla and classes within Proteobacteria were plotted using R as described by Hui et al. (2019).

Nitrogen was added together with the inoculant as 10 kg of agricultural ammonium–nitrate fertilizer (26% total nitrogen, 13% ammonium nitrogen, 13% nitrate nitrogen). Additives were mixed with the soil in the tank, and introduced deeper into the contaminated zone with a 0.2 m^3 dose of water added twice a month by the landowner. This frequency was selected to keep the soil moist but allow for sufficient periods of aerobic conditions in the soil between the additions. The soil was sampled after 2.5, 4, and 10 months.

Low-maintentance biostimulation with slow release compounds (6 months)

Biostimulation was continued in a modified form, with slow release fertilizers allowing for a low-maintenance treatment. A meat industry waste product, meat and bone meal, was used as a slow release source for not only nitrogen but also for phosphorus, potassium, and calcium (Liu et al. 2019). Twenty kilograms of meat and bone meal with ca. 50% protein content was mixed with the soil in the tank. H_2O_2 was added in low concentrations (0.5–1% of the introduced water volume) to increase the oxygen level (Goi et al. 2006; Simpanen et al. 2016). After 6 months, the soil was sampled.

Methyl-β-cyclodextrin enhanced ciostimulation in the saturated zone (12 months)

H_2O_2 was first used as the oxygen source as before. After 2 months, as the contaminated zone was now completely water-saturated, 10 kg of CaO_2 was added to the tank to provide oxygen as in a slow release aquatic zone application (Nykänen et al. 2012). To enhance the efficiency of biostimulation by improving the bioavailability of the contaminant, 10 L of CD was added. The addition resulted in a 5% concentration when diluted of 100 L of water, which was the coarse estimate for the initial water volume in the tank. The use of a biosurfactant was justified through water-saturated conditions leading to slow migration of the aqueous phase and the assumption that bioavailable fractions had been degraded through previous biostimulation phases.

After 12 months, the soil was sampled from the monitoring holes in single 20- to 30-cm soil columns, since water and watery sludge in the tank prevented non-disturbed sampling of distinct soil layers. Oil concentration of the water in the tank was also analyzed. An independent party, Vahanen Oy consultants, performed the final investigations of the area with samples withdrawn from a wider area around the tank, corresponding with previous full area investigations in 2014 (Fig. 3a). A risk assessment was performed based on these results.

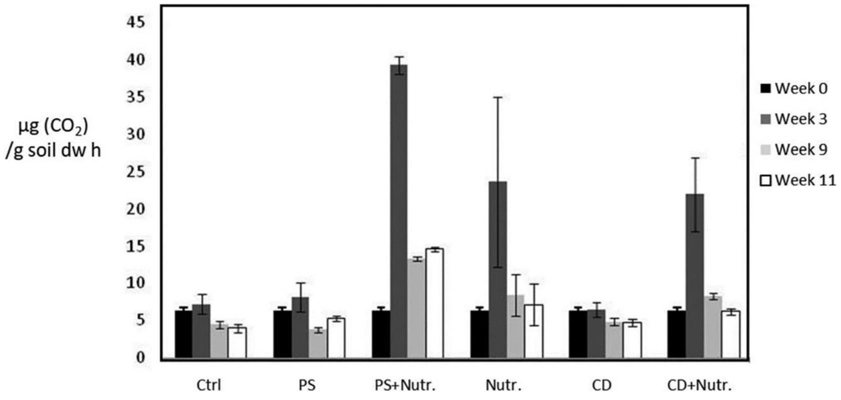
Analyses

In each test, oil hydrocarbons C10–C40 in soil were determined with GC-FID according to standard methods ISO 16703 (soil) and 9377-2 (water) either by the research team (circulation test) or by the accredited lab Synlab Oy, Finland. The analyses connected to the broader site investigations by contractors were executed at various accredited laboratories (Synlab Oy, Eurofins, ALS Finland) with the aforementioned method, or accredited in-house methods based on similar GC-FID technology. Due to the number of laboratories involved, the protocol can be expected to vary within that described in the ISO standard. Inner standards are required in the method for validation of the protocol. The scope of the ISO 16703 standard is all aliphatic and aromatic hydrocarbons with boiling points between those of n-alkanes C10 (n-decane) to C40 (n-tetracontane) (ISO 2004). This range is further separated into midrange and heavy distillates by a C21 marker (n-henicosane). These groupings follow the Finnish threshold and guideline values for oil hydrocarbons (Ministry of Environment 2007). In the analyses performed by the research

Table 1 Between-subjects and within subjects effects in repeated measures ANOVA on microbial activity (μg CO_2/g soil dw h) and in C10–C40 hydrocarbon concentrations (mg/kg soil dw), in mesocosms with treatments of nutrients and pine soap or cyclodextrin. The data has been LOG10 transformed

	Microbial activity			c(C10-C40)		
	F	df	*p*	*F*	df	*p*
Intercept	1497.390	1	< .0005	784.608	1	< .0005
Nutrients	50.781	1	< .0005	68.253	1	< .0005
CD	0.037	1	0.852	6.067	1	0.039
Nutrients × CD	0.303	1	0.599	4.197	1	0.075
Intercept	1652.951	1	< .0005	582.907	1	< .0005
Nutrients	97.276	1	< .0005	24.696	1	.002
PS	10.939	1	0.013	1.666	1	0.238
Nutrients × PS	5.838	1	0.046	0.096	1	0.765
Time	54.522	2	< .0005	47.000	1	< .0005
Time × nutrients	6.958	2	0.008	6.173	1	0.042
Time × PS	2.880	2	0.090	0.101	1	0.760
Time × nutrients × PS	0.404	2	0.675	0.234	1	0.643
Time	64.459	2	< .0005	42.069	1	< .0005
Time × nutrients	16.569	2	< .0005	0.813	1	0.394
Time × CD	0.131	2	0.878	0.647	1	0.448
Time × nutrients × CD	0.429	2	0.659	0.704	1	0.426

Fig. 5 Microbial activity as μg CO_2/g soil dw h produced over time in the different treatments. Standard deviation shown by error bars. Ctrl, control; PS, pine soap; Nutr., nutrients; CD, cyclodextrin



team, 2 ml of hexane-based extraction solution was used for 2 g of soil. Fraction analysis was performed by Synlab Oy with an accredited in-house method.

Nitrogen and phosphorus contents in soil were measured by Eurofins according to accredited in-house methods RA2021 and RA3000 respectively. Organic carbon content was calculated from LOI (550^{o}C) with organic carbon/organic matter ratio 0.50. pH was measured according to standard method ISO 10390, or in the circulation test with a similar procedure but with ultra-pure (mQ) water added in 5:1 water to soil ratio, and with shortened shaking (5 min) and incubation (2 h) periods.

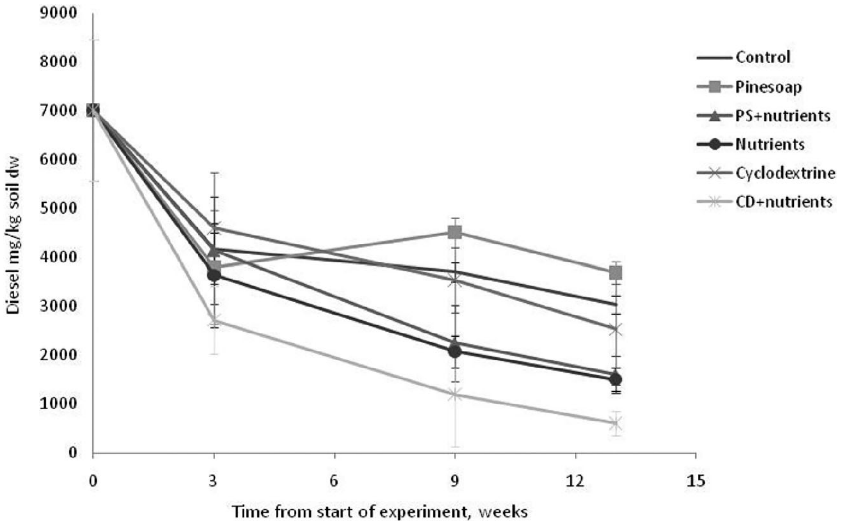
Statistical testing

To test the effects of nutrients, pine soap and cyclodextrin—and especially the nutrients × pine soap and nutrients × cyclodextrin interaction effects—on microbial activity and diesel content in the circulation experiment, log-transformed data was analyzed using two repeated measures ANOVA: One included time, nutrients, and pine soap as explaining variables, the other time, nutrients and cyclodextrin. In the dissolution test for CD, statistical analysis on the effect of treatment on the C10–C21, C21–C40, and C10–C40 concentrations in the aqueous phase was performed with a one-way Anova, and the differences between groups validated with Student-Newman-Keuls post hoc test. The homogeneity of variances was tested with Levene's test. For the rule to apply, results from the initial sampling were log-transformed. Normality was assumed but could not be verified due to low number of measurements

Reagents

Havu pine soap is produced by Henkel Norden Oy. CAVASOL® W7 M TL 50% methyl-β-cyclodextrin was purchased from Wacker Fine Chemicals. H_2O_2 at 35% and 50% solutions was purchased from Bang & Bonsomer Group Oy in Finland and Granular 70CG CaO_2 from Solvay GBU. Nitrogen fertilizers, urea, and Suomensalpietari (ammonium nitrate) were obtained from Yara Suomi Oy, Finland. K_2HPO_4 and NaH_2PO_4*H_2O from Sigma-Aldrich were used for the phosphate buffer. The citrate product applied was W302600-25KG-K sodium citrate dihydrate ≥ 99 from Sigma-Aldrich.

Fig. 6 The changes in diesel concentrations (mg/kg soil dw) in different treatments during the experiment. The last oil content analysis was performed on week 13. Error bars show standard deviation



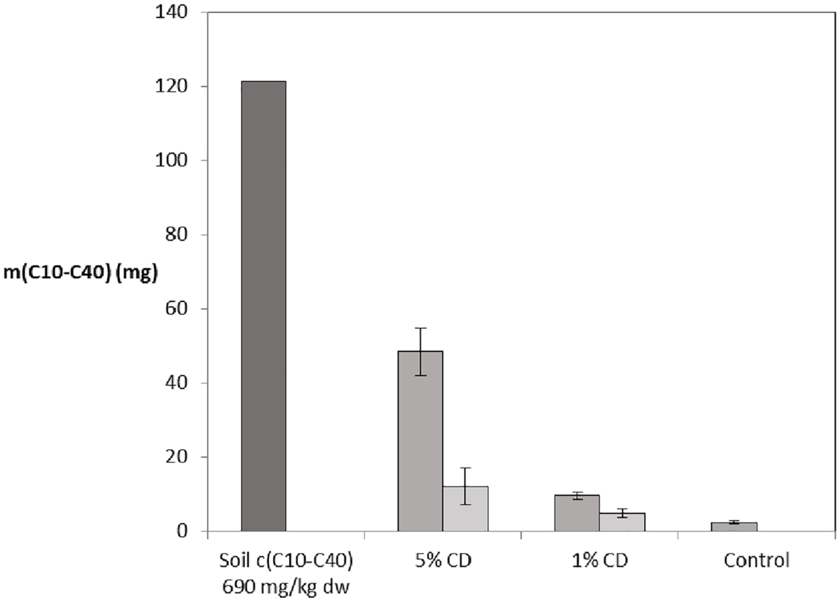


Fig. 7 The portion of C10–C40 in soil originally dissolved into the water phase, after five 1-h periods of shaking, and after subsequent five 5-h periods of shaking. Standard deviation is shown by error bars (*n* = 3)

Results and discussion

Laboratory-scale tests

Preliminary surfactant selection

For the soil used in the circulation experiment, carbon availability was not the rate limiting factor while additional nutrient availability (N, P) apparently was. This is shown by the fact that addition of pine soap alone had no effect on microbial activity as measured by generation of CO_2 at week 3, while nutrients alone had a significant effect on activity (Table 1, Fig. 5). The positive effect of nutrients was increased by pine soap but not by CD, indicating that the former itself may function as a carbon source. This notion is confirmed by the diesel oil degradation data as pine soap alone inhibited diesel degradation in comparison to the control treatment (Fig. 6) apparently by providing an easier source of carbon and energy and by competing for limited resources, while CD alone had no effect observable by increases in emissions compared to nutrients alone. The positive effect of nutrient addition on diesel removal was increased by CD, suggesting that improved bioavailability is a relevant factor, as shown earlier for PAHs (Simpanen et al. 2016)

The stimulatory effect of CD could not be verified statistically, even though the highest reductions were achieved when CD treatment was coupled with nutrient addition. The balance between the two mechanisms, biological and mechanical, was not quantified. In the study by Simpanen et al. (2016), similar 1% dose of CD resulted in biological degradation of PAHs, whereas a 5% dose increased the availability of the contaminant to levels where mobilization appeared to be primary

Table 2 The portion of the soil bound oil hydrocarbon fractions dissolved into the water phase at the two sampling instances (w:w (%)). The results from the second sampling take into account the lowered starting level. The results come from a single sample per treatment. The total reductions in range C10–C40 are comparable with the average results from all three replicas (marked *)

	c. in soil	5% CD			1% CD			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%
*C10–C40 average in 3 replicas		40%	18%	51%	8%	4%	12%	2%	0%	1%

Table 3 Results from the site treatment. * indicate results from a particular depth come from a composite sample. Missing value indicates that a sample could not be withdrawn. For below LOQ values, the LOQ value was used in the calculations. Average values per spot/per depth on gray background. Italicized values imply C10–C21 to C10–C40 ratio below 50% or values below LOQ. Final column indicates total reductions in average values per spot/depth from the initial values (%) and change from the previous sampling (± %). Results are calculated from the three bottom holes. Due to soil mobilization, the spots higher up the tank sides were left hollow and therefore unfit for sampling during the majority of the stages, and these values were excluded

Original level	*I*1	*I*2	*I*3	Average (per depth)	Total reductions in average c per spot/depth (change from the previous stage)
	C10–C21/C10–C40				
0–10 cm	620/1000	20,000/26000	28,000/35000	16,000/21000	
10–20 cm	27,000/31000	38,000/47000	29,000/36000	31,000/38000	
20–30 cm	6100/7000	31,000/37000	5700/6900	14,000/17000	
Average (per spot)	11,000/13000	30,000/37000	21,000/26000	21,000/25000	
1. Chemical treatment					
0–10 cm	*< 50/54*	*< 50/86*	10,000/12000	3300/4000	
10–20 cm	9500/11000	10,000/13000	2200/2800	7200/8900	
20–30 cm	8600/9900	10,000/13000		9300/11000	
Average (per spot)	6100/7000	6700/9000	6100/7400	6500/7900	69/68%
2. chemical treatment					
0–10 cm	430/840	11,000/14000	120/210	3900/5000	
10–20 cm	4100/5100	26,000/31000	*1400/3000*	11,000/13000	
20–30 cm		19,000/23000		19,000/23000	
average (per spot)	2300/2800	19,000/23000	*760/1600*	9300/11000	56/55%
Biostimulation 2, 5 months					(− 43/− 39%)
0–10 cm	230/330	540/750	420/710	390/600	
10–20 cm	*< 50/54*	25,000/29000	460/760	9000/9900	
20–30 cm	*170/690*	20,000/23000		10,000/12000	
Average (per spot)	*150/360*	15,000/17000	440/740	5800/6800	72/73%
Biostimulation 4 months					(38/40%)
0–10 cm	*57/150*	*56/330*	*< 50/170*	*54/210*	
10–20 cm	270/480	4400/5600	3300/4200	2700/3500	
20–30 cm	1300/1800	5300/7000		3300/4400	
Average (per spot)	540/810	3300/4300	1700/2200	1900/2600	91/90%
Biostimulation 10 months					(67/63%)
0–10 cm	*< 50/< 50*	*71/160*	*< 50/130*	*57/150*	
10–20 cm	3400/4100	580/820	730/960	1600/2000	
20–30 cm	3200/3800	2500/3300		2900/3600	
Average (per spot)	2200/2700	1100/1400	390/550	1400/1700	93/93%
Biostimulation 16 months					(26/33%)
0–10 cm	*63/140*	270/520	*75/210*	*140/290*	
10–20 cm	*60/140*	4700/5900	180/290	1600/2100	
20–30 cm	3000/3500	6000/7200		4500/5400	
Average (per spot)	1000/1300	3700/4500	130/250	1900/2300	91/91%
Biostimulation 28 months					(− 36/− 35%)
0–10 cm	*170/480*	*150/450*	*140/370*	*150/430*	
10–20 cm	_170*/480*_	_150/450*_	_140*/370*_	*150/430*	
20–30 cm	_170*/480*_	_150/450*_		*160/470*	
Average (per spot)	*170/480*	*150/450*	*140/370*	*150/440*	99/98% (92/81%)

removal mechanism. Additionally to differences in compounds, this balance between mechanisms would also likely differ for other soil types, as well as for non-disturbed soil. The result could not therefore be extrapolated to field as such. The moderate effect on respiration is likely explained by carbon availability. The effect of contaminant availability is likewise factoring the degree to which the additives will be utilized as carbon sources, whereas already according to the lab scale model, pine soap could be ruled out for in situ applications for contaminated soil of any type.

When the suggested bottleneck of nutrient availability was removed, CD appeared to heighten biodegradation during the initial stages similarly to what has been observed by Molnár et al. (2005) and also lead to lower final concentrations, suggesting higher benefits from surfactant use once the readily available fractions have already been exhausted (Khalladi et al. 2009). Positive effects of CD addition on biodegradation have been noted also by Fenyvesi et al. (2008) and Taccari et al. (2012). Molnár et al. (2005) connect the initial differences to a shortened microbial lag period, but only for soils in which carbon availability is the primary bottleneck. While the peaks in nutrient and nutrient + CD treatments did not differ significantly, the latter phenomenon would require that the period of heightened activity lasts longer. Neither reduced lag periods nor lengthened high activity could be verified from the CO_2 data.

Only minimal variation in organic matter content was observed between treatments and within the survey era. The organic matter content was between 1.3 and 1.9% during the experiment in all the treatments except week 1 in the CD treatment, when an average organic matter content of 3.2% was measured due to a single outlier value.

Methyl-β-cyclodextrin effect on water solubility for different oil hydrocarbon fractions

The concentration of CD was found to affect the solubility of oil hydrocarbons in a significant manner ($p < 0.001$), with apparent differences between all treatments ($p < 0.01$) for all fraction ranges with results from multiple replicates (C10–C21, C21–C40, and C10–C40, Fig. 7). For both the 1% and 5% CD concentrations, a similar amount of contaminant was solubilized per CD concentration during the first stage (32 mg of C10–C40/g of CD).

Similar statistical differences were observed during the subsequent test with significant results between treatments in all fraction ranges. However, an obvious decline in the treatment efficiency was observed, now only ca. 8 and 16 mg of C10–C40/g of CD for the 5% and 1% treatments respectively, in spite of the fivefold shaking time.

The test soil had been withdrawn from a site where biostimulation without surfactants had been performed for several years, and the original concentrations in soil indicated that aliphatic compounds in ranges C12–C16 and C16–C35 had been the most recalcitrant. While the solubility of all aromatic and aliphatic compounds was now affected by CD, no special value in regards to the most hydrophobic compounds was detected (Table 2). The fragment analysis suggested that the largest impact was on compounds in the aromatic C16–C21 range, despite the low initial concentration in soil.

The higher concentration of CD did not only enhance the initial effect, but the total effect as well, as with both 5% and 1% dose more efficient solubilization was achieved during the initial run. This means that the total mass of dissolved fractions was not strictly related to the total amount of CD molecules added. Had that been the case, the efficiency of the 1% CD treatment would not have been negatively affected until a specific threshold was being reached and similar results would be achieved by adding one larger CD dose or a number of smaller doses at different times. Injection of a single large dose therefore proved to be more cost effective whereas in terms of in situ treatments, this choice would likely affect whether or not the dissolved contaminant would be biodegraded rapidly enough so as not to increase the treatment associated risks to an undesired level (Simpanen et al. 2016). The technical grade CD product used in the experiment is only available in 200+ kg amounts, and even with the lowered purity level, it is expensive in comparison to common soaps such as pine oils. Based on this, it is still relevant to test other biosurfactants case-by-case.

Site treatment

The initial chemical oxidation with H_2O_2 and citrate resulted in a decrease in average hydrocarbon concentrations under the tank jacket (Table 3). Mobilization of soil during treatment was found to transport soil from the flanks of the tank, leaving the sides hollow and therefore unfit for sampling.

During the reaction, water and clayey sludge was observed to be transported mainly through the tank itself, as foaming water was rising to the surface visibly through the tank manhole. Furthermore, the treatment had also driven approximately 0.5 m^3 of soil into the tank through the sampling holes (Fig. 4c).

Contaminant reductions in ca. 1/2–2/3 range were achieved with two peroxide injections. The fact that the initial effect could not be repeated, rather on the contrary, suggests that the effect of chemical mineralization alone was limited in this particular situation. The oil hydrocarbon content of the soil in the tank was approximately 600 mg/kg dw. The permeable layer below the tank was only 0.2–0.3 m deep. Considering the exit route of the water through the porous soil, the radius of influence was likely limited to the immediate surroundings of the tank. If also the total mass of the contaminant in the soil was low, which could not be ruled out, oil concentrations under the tank were reduced primarily through soil mixing and dilution. Contaminant-to-oxidant stoichiometry could not be determined as the concentrations were known to be heterogeneously distributed and also the soil mass within the radius of impact remained unknown.

During chemical oxidation, the H_2O_2 concentration in the tank was 17%, and due to the low radius of influence, the concentration in the immediate zone was likely rather close to the initial level. The effect of high peroxide, oxygen, and possibly radical concentrations can be suggested to have impacted the native soil bacteria, although H_2O_2 used in a similar manner did not totally abolish the microbial population in contaminated soil in an earlier pilot scale test (Simpanen et al. 2016). We ensured the presence of a degradation-active microbiome by using an inoculum, i.e., adding soil that had recently been successfully remediated by biostimulation.

In the two soils used, the differences in the final oil concentrations appeared to be related to the increase in relative abundance of bacteroidetes and also of gammaproteobacteria in relation to betaprotebacteria and alpahaprotebacteria within the proteobacteria phylum (Appendix 1 Fig. 8a&b). Both changes have been associated with bioremediation success for oil hydrocarbons (Siles and Margesin 2018). Gammaproteobacteria also constitute the dominant phylotype associated with both the presence and successful remediation of PAHs, especially in low nutrient environments (Parajuli et al. 2017; Roslund et al. 2019; Viñas et al. 2005). The two major families with heightened relative abundance within gammaproteobacteria were *Pseudomonadaceae* and *Xanthomonadaceae* (Appendix Table 4). Many *Pseudomonas* strains are known to utilize a multitude of aliphatic, aromatic and polyaromatic compounds of ecotoxicological concern in diverse nutrient conditions (Palleroni et al. 2010). Also, several genera within *Xanthomonadaceae* are known to be involved with oil hydrocarbon degradation (Chang and Zylstra 2010).

The necessity of bioaugmentation could not, however, be verified as the biological state of the soil was not tested prior or after the augmentation. A reduction in the average oil concentration down to ca. 10% of the initial level was achieved within the first 4 months of biostimulation, whereas only the first 10 cm under the tank jacket was affected. At this depth, the midrange fractions now represented less than 50% of the total hydrocarbons. Alkanes lighter than C21 are known to be biodegraded faster than the heavier fraction and changes in mid-to-heavy range ratio are therefore often used to approximate biodegradation progress (Kostka et al. 2011; Prince 2010; Rodriguez-Blanco et al. 2010). The mobilization of contaminant both within the soil and in the aqueous phase during chemical oxidation can be suggested to have been beneficial for subsequent biodegradation. The latter mechanism has been demonstrated by Talvenmäki et al. (2019), whereas the total effect was now likely negatively affected by the clayey soil type. Regardless of the mobilization mechanism, the contaminant was thus transported to a location with enhanced oxygen and nutrient availability.

Very little or no effect was observed in the time frame of 4 to 10 months, either in average concentrations of relative abundance of midrange fractions. Possible reasons for this were the low availability of hydrocarbons, or insufficient aeration between injections. A strong ammonia odor was also observed thorough the period, suggesting loss of nitrogen through volatilization when using ammonium fertilizers, resulting from increase in pH which may have also inhibited biodegradation.

When meat and bone meal (MBM) was introduced as the alternative nitrogen source, degradation was not visibly affected during the following 6-month period. The soil becoming increasingly water-saturated may have also negatively affected aerobic biodegradation. The addition of low concentrations of H_2O_2 as the oxygen source during this stage may have been insufficient. Peroxide is consumed by organic material, in this case possibly the MBM, before diffusion into deeper soil layers.

During the last bioremediation step, hydrocarbon and oxygen availability were the two factors targeted with the CD and CaO_2 amendments. CaO_2 has been successfully utilized as an oxygen releasing additive in aquatic applications (Nykänen et al. 2012), whereas degradation of the MBM is an oxygen demanding process potentially exceeding the availability from the slow release compound. Also, the effect of CD on solubility of oils has mostly been studied with circulated water phases, and can be expected to decrease with standing water bodies, such as the one found at the site during the later stages of the treatment (Simpanen et al. 2016). Regardless of these potential factors, the remediation effect was found to have reached the bottom of the permeable layer within 12 months and the total contaminant reduction was now 98% of the initial value. Similarly to what was observed during the early months of the biostimulation, the relative abundance of compounds in the C10–C21 range were more heavily affected, dropping to below 40% of the total hydrocarbon concentration in all samples (Table 3). When the effect of poor bioavailability was removed, the slow release compounds for oxygen and nutrients were hence found efficient to support continuous biological degradation, suggesting that bioavailability had been the primary bottleneck.

At the closure of the monitoring period, the C10–C40 concentration in the aqueous phase was 0.67 mg/L. The aqueous phase in the tank could also be removed easily, which was done during soil sampling. Due to the slow infiltration rate, it was suggested that the dissolved contaminant was likely to stay within the vicinity of the tank rather than be transported elsewhere. In this case, the tank conditions provided high enough average temperatures even during the cold season (approx. 0–10 °C), and hence the water was left in the tank. Also, due to the added slow release compounds for oxygen and nutrients, the remediation effect would continue even without active treatment interventions.

In the investigations performed by the contractor, the average C10–C40 concentration at a depth of 2–3 m was approximately 400 mg/kg, with only two out of six samples showing concentrations above 20 mg/kg (2070 mg/kg dw in B5; 149 mg/kg dw in B1, Fig. 3a). In composite samples at three different spots, at depth 2–3 m, 65% of the total concentrations consisted of aliphatic compounds in the C16–C35 range and 19% in the C12–C16 range. These results indicate that local hot spots could still be detected in the soil, and average values would therefore be largely affected by the number of hot spots encountered during sampling. It can also be suggested that due to the low permeability of the soil, the actions performed in the immediate tank area had not affected the entire outer perimeter of the contaminated zone. These soil samples were not water-saturated and because of this, it appears unlikely that the hot spot was caused by contaminant mobilization through preferential flow paths with higher permeability relative to the surrounding soil mass.

According to the verdict of the local authority, the Häme Centre for Economic Development, Transport and the Environment, based on the reports and the risk assessment, the site was no longer found to pose environmental or health risks requiring further treatment.

Conclusion

The sequential in situ treatment of the site resulted in a successful outcome in a limited zone, this result being achieved with the joint effect of the different approaches. The treatment itself affected the site conditions and therefore, also the requirements for the subsequent treatment steps. Laboratory-scale tests were crucial, both in directing the choices of additives at the site, and also in demonstrating the associated risks and benefits to the environmental authorities. The total time for the treatment was considered needlessly long as periods of dormancy could be observed. If, however, slower progress is considered acceptable, the cautionary principle may be applicable, especially when the methods are known to potentially increase the risk level. In this investigation, these ineffective periods could also be considered as control periods during which vital reference data was collected, as similar sites with identical soil type and structure were not available for the study. With accumulating experience on how to combine different in situ techniques and in what order to use them most efficiently, future in situ remediation undertakings can be performed with shorter lag periods, reaching a satisfactory result in a significantly shorter treatment time.

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Authors' contributions All authors contributed to the study conception and design. Material preparation, data collection and analysis of the site treatment was performed by Harri Talvenmäki, who wrote the first draft of the manuscript. The site treatment was designed in collaboration with Martin Romantschuk, Hannu Silvennoinen and Tuomas Piepponen. Niina Saartama, Anna Haukka, Katri Lepikkö, Virpi Pajunen and Milla Punkari executed and reported results from the corresponding small scale models, and wrote some parts associated with these sections. Aki Sinkkonen and Guoyong Yan performed and reported the outcome of the microbial analyses

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Data availability The authors confirm that the data supporting the findings of this study are available within the article.

Compliance with ethical standards

Ethical approval The work was performed in compliance with ethical standards. The landowners and the local authorities were informed of the experimental nature and the associated risks of the site treatment.

Consent to participate All authors and stakeholders were informed about, and agreed to the protocol.

Consent to publish All authors were allowed to read and approve the final manuscript.

Competing interests The authors declare that they have conflict of interest.

Appendix

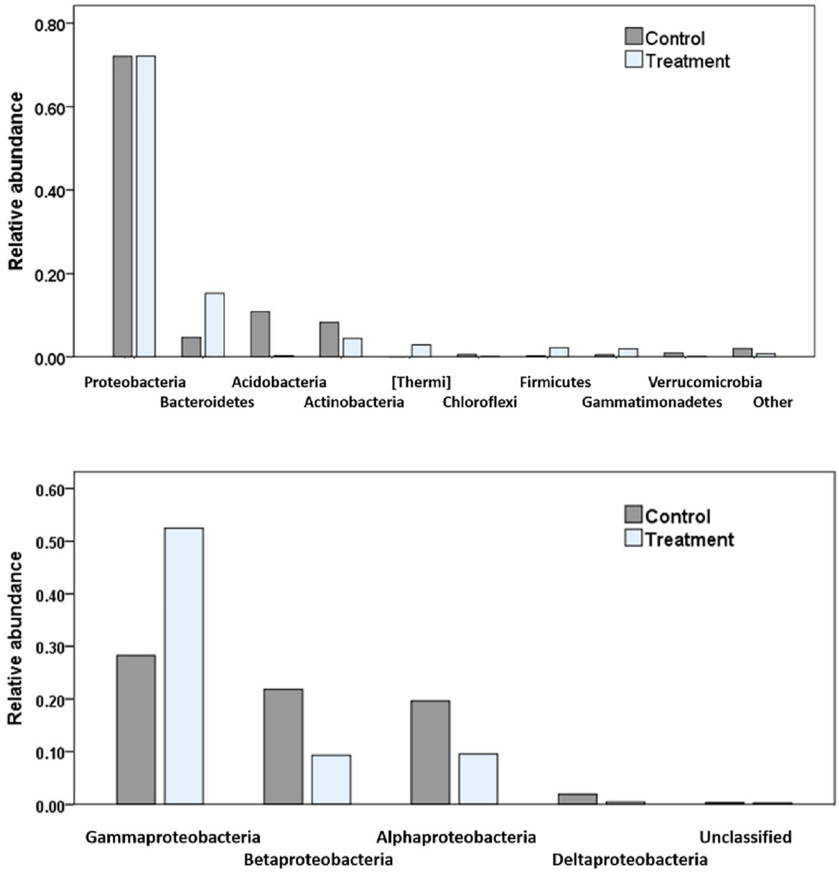

Fig. 8 Bacterial relative abundance within phylum (**a**) and within proteobacteria in the two soils used for the inoculum (**b**) (> 1%)

Table 4 Relative abundance in Class and Order and Family and Genus levels in the two soils used for the inoculum

Class			Order		
	Control	Treatment		Control	Treatment
Gammaproteobacteria	0.283	0.525	Xanthomonadales	0.126	0.323
Betaproteobacteria	0.219	0.093	Sphingomonadales	0.108	0.026
Alphaproteobacteria	0.196	0.095	Alteromonadales	0.102	0.001
Actinobacteria	0.078	0.043	Actinomycetales	0.078	0.043
Holophagae	0.071	0.001	Burkholderiales	0.075	0.084
Flavobacteriia	0.003	0.051	Holophagales	0.070	0.001
Deltaproteobacteria	0.019	0.005	Rhizobiales	0.031	0.023
[Saprospirae]	0.015	0.040	Caulobacterales	0.023	0.042
iii1-8	0.012	0.000	Clostridiales	0.001	0.009
Acidobacteriia	0.010	0.000	Rhodospirillales	0.021	0.001
Gemmatimonadetes	0.004	0.017	PYR10d3	0.021	0.000
Bacteroidia	9.91E-05	0.036	Pseudomonadales	0.017	0.195
[Chloracidobacteria]	0.006	0.000	Sphingobacteriales	0.002	0.017
[Spartobacteria]	0.005	0.001	[Saprospirales]	0.015	0.04
Acidobacteria-6	0.005	0.000	DS-18	0.011	0.000
Sphingobacteriia	0.002	0.017	Acidobacteriales	0.010	0.000

Table 4 (continued)

Class			Order		
	Control	Treatment		Control	Treatment
Bacilli	0.002	0.013	Flavobacteriales	0.003	0.051
Others	0.071	0.064	Myxococcales	0.008	0.002
			Rhodobacterales	0.007	0.000
			Ellin6067	0.007	0.000
			RB41	0.005	0.000
			[Chthoniobacterales]	0.005	0.001
			Bacteroidales	9.91E-05	0.036
			Others	0.254	0.106
Family			Genus		
	Control	Treatment		Control	Treatment
Sphingomonadaceae	0.103	0.026	Arenimonas	0.010	0.000
Alteromonadaceae	0.101	0.001	B-42	0	0.029
Xanthomonadaceae	0.071	0.321	Caulobacter	0.013	0.003
Holophagaceae	0.070	0.001	Flavihumibacter	9.91E-05	0.006
Microbacteriaceae	0.062	0.023	Gelidibacter	0	0.027
Sinobacteraceae	0.049	0.001	Geothrix	0.070	0.001
Comamonadaceae	0.046	0.046	HB2-32-21	0.101	0.001
Oxalobacteraceae	0.026	0.002	Kaistobacter	0.005	0.000
Caulobacteraceae	0.023	0.042	Kaistobacter	0.007	0
Chitinophagaceae	0.0145	0.040	Kaistobacter	0.006	0
Moraxellaceae	0.013	0.002	Lysobacter	0	0.091
Acetobacteraceae	0.011	0.000	Lysobacter	0	0.005
Rhodospirillaceae	0.009	0.001	Novosphingobium	0.015	0
Bradyrhizobiaceae	0.007	0.001	Perlucidibaca	0.012	0.001
Rhodobacteraceae	0.007	0.000	Petrimonas	0	0.011
Hyphomicrobiaceae	0.007	0.002	Pseudomonas	0.003	0.015
Koribacteraceae	0.006	0.000	Pseudoxanthomonas	0.005	0.005
[Chthoniobacteraceae]	0.005	0.001	Rhodanobacter	0.001	0.080
Pseudomonadaceae	0.004	0.192	Roseococcus	0.007	0.000
Flavobacteriaceae	0.003	0.043	Sediminibacterium	0.013	0
Alcaligenaceae	0.001	0.035	Serpens	0	0.055
Porphyromonadaceae	0	0.035	Sinobacter	0.008	0
Trueperaceae	0	0.029	Sinobacter	0.006	0
Sphingobacteriaceae	0.002	0.017	Sinobacter	0.008	0
Phyllobacteriaceae	0.001	0.006	Sphingomonas	0.010	0.001
[Weeksellaceae]	0	0.005	Thermomonas	0	0.016
Clostridiaceae	0	0.005	Others	0.700	0.652
Others	0.355	0.121			

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SUSTAINABLE RISK MANAGEMENT OF CONTAMINATED LAND AND SEDIMENT - NORDROCS 2016

Soil vapor extraction of wet gasoline-contaminated soil made possible by electroosmotic dewatering–lab simulations applied at a field site

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Abstract

Purpose Soil restoration is still mainly carried out ex situ by excavating and replacing the contaminated soil. In situ remediation would reduce the costs of soil transportation and this way, the problem is not merely transferred elsewhere. The present study introduces a field case where the aged, oil-contaminated soil in a former fuel station in Finland was treated in situ sequentially with different methods.

Materials and methods Several approaches, including soil vapor extraction and biostimulation with electrokinetic pumping, were performed in the field. After these treatments, the dense original portion of the soil beneath the gasoline pump location, ca 100 m^3, was still contaminated with petroleum-derived volatile organic compounds (VOCs), with concentrations of nearly 10,000 mg kg^{-1} measured at some hotspots. After a period of electroosmotic water circulation, the electrical field (0.5 V cm^{-1}, DC) was kept connected for 6 months without addition of water, leading to dewatering and warming of the soil.

Results and discussion In contrast to the situation with the original wet soil, VOCs, in lab conditions, were found to volatilize very efficiently from the dewatered soil. When the soil vapor extraction treatment was renewed using perforated tubing installed horizontally at ca 1 m depth in the dewatered soil at the contaminated site, the treatment was efficient and the soil was decontaminated in 5 months. The final VOC concentrations were on average 190 mg kg^{-1} ($n = 13$) with the highest value of 700 mg kg^{-1} at one hotspot. After a risk evaluation, the site was concluded to be sufficiently clean for industrial use.

Conclusions Since with many former fuel stations, the contamination consists of both volatile fractions that are difficult to degrade by biological means and heavier compounds for which biostimulation is often suitable, a combination of different methods may be worth pursuing.

Keywords Oil hydrocarbon contamination · Soil remediation · Electrokinetic remediation

Abbreviations

BTEX	Benzene, toluene, ethylbenzene, and xylenes
PHCs	Petroleum hydrocarbons
SVE	Soil vapor extraction
VOCs	Volatile organic compounds

1 Introduction

The soil at most if not all old fuel stations in Finland is contaminated with gasoline, diesel fuel, and other petroleum hydrocarbons (PHCs) (Pyy et al. 2013). Even normal fuel station practices result in small repeating discharges of fuel and lubricating oil that when infiltrated into the soil may result in high contaminant levels, posing a threat to the ground water and the local environment in general (Puolanne et al. 1994). Because of the low soil temperature in Finland and similar regions,

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natural attenuation does not remove the oil with sufficient velocity (Romantschuk et al. 2000), even if the natural microbial community has the capacity to perform the degradation (Kauppi et al. 2011). Diesel fuel is biologically readily degraded when bottlenecks for microbial activity—low temperature, lack of nutrients, etc.—are removed (Kauppi et al. 2011). Although BTEX (benzene, toluene, ethylbenzene, and xylenes) compounds, aromatic components of gasoline, are biodegradable, the removal efficiency is lower than for many of the aliphatic diesel fuel components (Soares et al. 2010; Soares et al. 2012). On the other hand, BTEX compounds are volatile and, similarly to the Volatile organic compounds (VOCs), can be easily removed by soil vapor extraction (SVE) if the conditions are suitable (Farhan et al. 2001; Boudouch et al. 2012). The SVE does not work well in wet or otherwise impermeable soil (Garcia-Gerruzo et al. 1994; Farhan et al. 2001) and is considerably slower in cold than in warm conditions (Garcia-Gerruzo et al. 1994; Huon et al. 2012). Here, we describe an approach where electroosmotic treatment of the soil at a former fuel station resulted in warming and dewatering of the contaminated soil, from which gasoline-derived VOC compounds then could be efficiently removed by SVE.

2 Materials and methods

2.1 Site description and electrokinetic remediation

The site was a former fuel station in the Jalasjärvi municipality (coordinates, N6235, E2284) that had been in use from the late 1950s until the beginning of 1990s. In the middle of 2000s, the contamination levels were such that active cleaning of the site was demanded by authorities. The contaminated area was 5 m wide and 6 m long, with the contaminants, mostly heterogeneously distributed C_6–C_{10} residues, peaking at 3000–4000 mg kg^{-1}. Maximum depth of the contaminated volume was 6 m. The soil directly beneath the location of the former fuel pumps was course sand that had been introduced during construction of the station, but beneath a depth of 1.5 m, under a layer of Styrofoam plates, the natural soil was dense wet silty soil. The first remediation effort was started in 2006 using SVE for 8 months but the treatment had been found ineffective by regular photoionization detector (PID) monitoring of the extracted air. Electroremediation-based soil cleaning was started in autumn 2007. First, stainless steel rods (1 cm in diameter) were installed as electrodes in drilled holes inside perforated plastic tubes down to a depth of 5 to 6 m. A row of four anodes was installed in parallel at ca. 2 m intervals, and a row of cathodes was installed in a similar manner 5 m from the anode row (Fig. 1). Anodes and cathodes, respectively, were connected in parallel with copper cable to a transformer serving as a power supply and set to 270 V DC resulting in a voltage of ca. 0.54 V cm^{-1}. The maximum current capacity of the transformer was 40 A, which clearly exceeded the maximum current recorded at the site.

At initial stages of the in situ treatment, water amended with nutrients had been infiltrated via the anode cavities and from the top through holes in the asphalt. The top layer of course sand was decontaminated during this treatment from all PHC components, while the deeper layers consisting of dense natural soil was still found to be heavily contaminated with VOC components. The period of biostimulation was followed by continued electrokinetic treatment for 6 months during the winter but with no addition of liquids. After the discontinuation of addition of water, the electricity consumption fell first rapidly from the maximum level of 7 A (1.9 kW) within 1 day to 2 A (540 W) and then gradually to a level below 0.5 A (135 W) when the treatment was discontinued. When soil samples were collected in December 2008 (after a 2-month period of electrokinetic drying), the soil was warm and dry at all depths influenced by the electric field. The consumption of electricity for the total site treatment including the circulation of nutrient-rich water and the dewatering phase was about 20,000 kWh leading to expenses of less than 1000 €. The dewatering phase of the electrokinetic treatment consumed less than 1000 kWh costing less than 50€.

2.2 Laboratory simulation

Laboratory scale VOC evaporation test was performed with contaminated soil taken from 1.5–2.0 m depth of the Jalasjärvi site after the electrokinetic drying. The volume of 0.5 L glass bottles was filled with 800 g of soil. The mass was assumed to correlate positively with the VOC removal time. The soil density achieved was still assumed to be lower than in the field, so that spontaneous evaporation in the flasks roughly would reflect SVE in the field. The soils were wetted to the saturation degree of 0% (equal to electrokinetically dried soil, no water added) 40, 70, or 100% saturated with water). Each saturation degree was tested as three replicates. Saturation degree was kept constant by following the mass of soil and adding water when needed. A capped bottle with soil of 0% saturation degree was included as a control. Bottles were placed in a fume hood at ambient temperature of +18 °C and incubated for 9 weeks. The VOCs were recorded with a PID by closing the bottle with a parafilm for 1 hour, after which the air space of the bottle was measured. Measurements were done 32 times during the 9-week incubation period. Hydrocarbon C_5–C_{10} concentrations (including BTEX compounds) were analyzed from the soil samples (100 g) at the start of the experiment and after 3 and 9 weeks of incubation.

2.3 Soil vapor extraction field treatment

Based on the result of lab simulation, the SVE treatment was started in the field again. A trench (1.5 m depth, 5 m length, and 0.4 m width) was dug with the narrow scoop of a front loader for installation of SVE tubing so that it was located ca. 20 cm into the dense-contaminated soil. The perforated 50-mm SVE tube was installed at the bottom of the trench and hooked up to a vacuum pump via sealed plastic tubing. The tubing at the bottom of the trench was covered with a plastic sheet and sand in order to direct the vacuum effect downwards. The extracted vapors were collected in activated charcoal before release of the cleaned soil air. Approximate vapor PHC concentrations were monitored with a handheld PID analyzer. When concentrations based on PID analyses had dropped significantly, the soil was sampled down to a depth of 5 m at all previously identified hotspots. The total time for SVE pumping was 5 months, the pumping power being 100 m^3/h.

2.4 Sampling

Soil core samples (10 cm in diameter) were taken by the Destia Ltd. with a drilling machine down to a depth of 6 m. At each sampling, soil cores were taken from the four sampling points in the area of contamination (Fig. 1) and two controls outside the area. Soil columns were divided into roughly 0.5–1-m sections for further analysis. Samples were also taken from the ground water beneath the contaminated soil and downstream of the site. In the field, thorough sampling for VOC analyses was done three times, after electrokinetic enhanced biostimulation and electrokinetic drying on December 2008 and after electrokinetic drying and soil vapor extraction on August 2009 and at the end of treatments on October 2009 (Table 1).

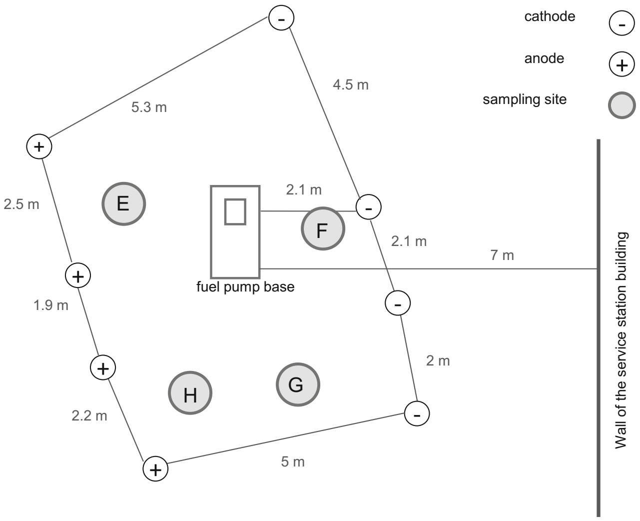

Fig. 1 *Top view* of the treated fuel station area. The rows of anodes and cathodes are indicated. The contaminated area lies between these rows and extends down to 5 m below ground. The central part beneath the concrete fuel pump base (*rectangle* in the middle) consisted of ca 20 m^3 of course sand down to 1.5 m below ground. This section (ca 4 × 3.5 m) was readily infiltrated by nutrient-rich water introduced to achieve biostimulation. The rest of the 200 m^3 polluted soil was dense natural soil. The *capital letters* indicate sections where initial sampling had recorded high concentrations of TPH

2.5 Physical and chemical analyses

Temperature of the soil was recorded immediately after soil lifting. Dry matter content was determined by drying 2–6 g soil sample overnight at 105 °C and the organic matter content was measured as loss on ignition (4 h in 550 °C). VOCs, including the total C_5–C_{10} fractions, BTEX compounds, and oxygenates (MTBE, TAME), were analyzed with a method based on standards EPA Method 8260B, EPA Method 5021, and ISO/DIS 22155. Analysis was done using methanol extraction and determination was done with a static headspace technique using gas chromatography/mass spectrometry (HS/GC/MS). Total C_{10}–C_{40} fractions were analyzed according to standards ISO16703 using hexane-acetone extraction and gas chromatography/flame ionization detector. Analyses were performed at Ramboll Analytics Ltd. in Lahti, Finland.

2.6 Statistical methods

Univariate analysis of variance with Tukey's post hoc tests was used to analyze the data in IBM SPSS Statistics 23. C_5–C_{10} concentrations (mg kg^{-1}) in soil were analyzed on week 3 and week 9. Volatile organic compounds in the air (ppm) were analyzed first as single-day PID values on days 0, 1, and 3 to distinguish differences in the rapid volatilization of the most volatile low molecular weight compounds. Thereafter, differences in the cumulative values of PID measurements were compared between different treatments. The first cumulative PID period preceded the second oil hydrocarbon measurement (days 7–21, PID values were measured every third day) and the second PID period covered days 23–75. As PID values in closed bottles are not comparable with those in open bottles and as PID values in the closed control bottles stayed at 0 day values over the whole experimental period, the treatment was excluded for the PID analysis.

3 Results and discussion

In this study, the soil at a former fuel station was treated with a set of in situ methods in order to remove PHC derived from gasoline, diesel fuel, and lubricating oil that had seeped into the soil during decades of normal use with no major accidents recorded. First treatment with SVE had been found nonfunctional in the initially wet untreated soil presumably since VOCs are less volatile in wet conditions (data not shown). Electrokinetically enhanced biostimulation, using methods described for PAHs by Suni et al. (2007), removed efficiently diesel compounds (initial C_{10}-C_{40} concentration ca.

Table 1 Hydrocarbon C_5–C_{10} and C_{10}–C_{40} concentrations in samples taken from the fuel station site. SVE treatment started in May 2009

Sampling time	Treatments before sampling	Sampling site	Sampling epth	C_5–C_{10} mg kg^{-1}	C_{10}–C_{40} mg kg^{-1}
December 2008	Biostimulation with electrokinetic pumping for 1 year, electrokinetic drying for 2 months	E	0.5–1.5 m	49	91
			1.5–2.5 m	9000	474
			2.5–3.5 m	2300	50
		F	0.5–1.5 m	61	63
			1.5–2.5 m	8700	339
			2.5–3.5 m	3400	124
			3.5–4.5 m	660	31
			4.5–5.5 m	40	8
		G	0.5–1.5 m	45	19
			1.5–2.5 m	4800	80
			2.5–3.5 m	110	23
			3.5–4.5 m	8.1	5
		H	0.5–1.5 m	27	38
			1.5–2.5 m	350	43
			2.5–3.5 m	0.5	7
August 2009	Electrokinetic drying for 4 months, soil vapor extraction for 2 months	E	1.2 m	8.6	
			1.5 m	8000	
		F	0.8–1 m	31–67	
			1.5 m	590	
		H	1.2 m	150	
			1.4 m	26,000	
October 2009	Soil vapor extraction for extra months	E	0.1–1.2 m	400	
			2.1–2.4 m	460	
			2.6–3.2 m	8	
		F	1–1.4 m	5	
			1.4–1.6 m	5	
			2–2.8 m	5	
			2.8–3.4 m	5	
		G–H	0.8–1.4 m	640	
			1.8–2.2 m	700	
			2.2–2.8 m	7	
			2.8–3.4 m	280	

2700 mg kg^{-1} before the start of biostimulation) but had very little effect on gasoline-derived VOCs in the natural dense soil beneath the installation (Table 1). During the liquid circulation soil moisture was ca. 15% and a maximum current of 7 A was recorded, but mostly, 1.0–2.0 A was in use. As the electroosmotic pumping was continued at 270 V without addition of water, the current dropped to below 0.5A where it remained for 6 months, over the winter in 2008–2009. Apparently, this was due to low conductivity in the dry soil. The area was sampled in December 2008 and found still to be heavily contaminated with hydrocarbons C_5–C_{10} in hot spots within the dense soil regions (Table 1.), but as opposed to earlier observations, the soil moisture had dropped to 5–8%. At that time, the soil temperature was 15–20 °C below the depth of 1.5 m, and a strong smell of gasoline could be observed, whereas no such smell was observed with the same soil using the earlier, wet samples. This was likely the result of increased VOC volatilization from the dried soil, which gave us the idea to test hydrocarbon evaporation at different soil moisture levels.

Evaporation experiments in lab conditions were performed with dried soil and with a set of soils wetted to different levels, one of the levels representing the original moisture level. A clear difference between soils with different moisture levels was observed in the recorded PID values from the head space of the flasks after day 0. On day 0, PID values were equal in all treatments (Fig. 2a; mean ± SE = 965 ± 29; $F = 3.6$, df = 3, 8, $p > 0.05$). The capped control retained a high PID value of over 1000 ppm, while very low PID values were observed in

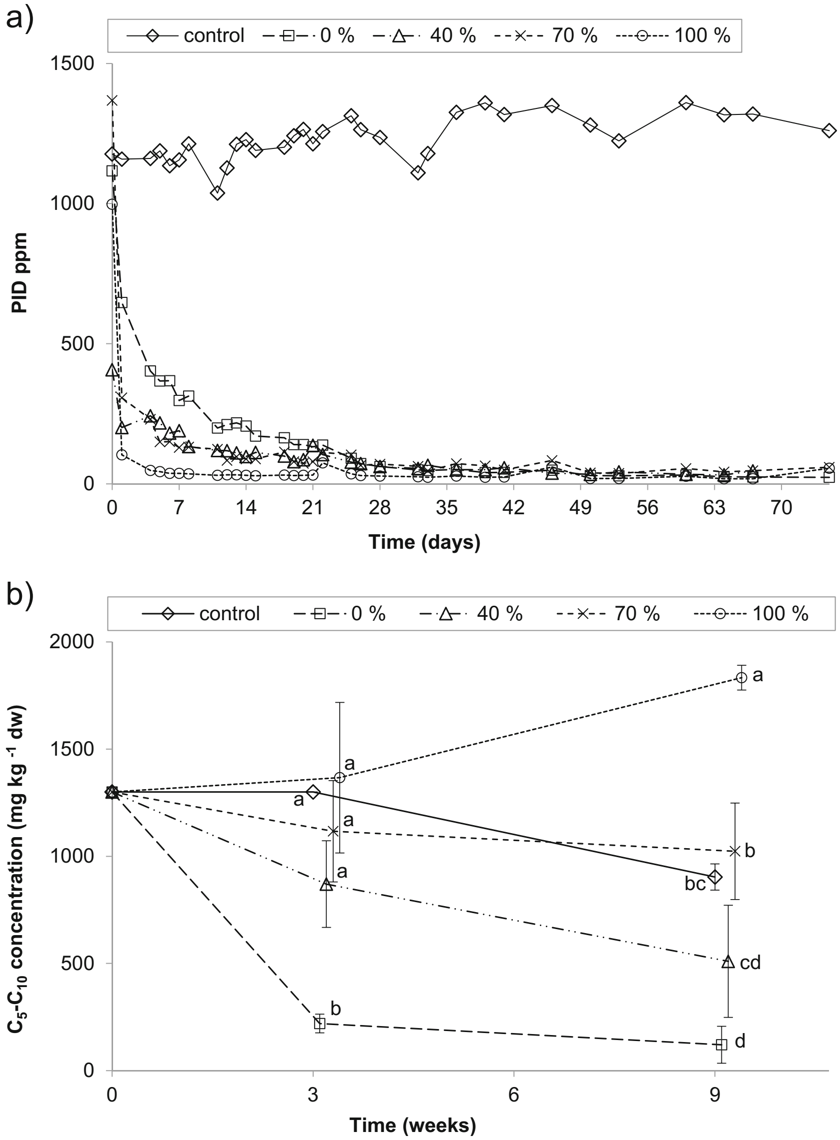

Fig. 2 Volatile organic carbon (*VOC*) concentrations in the laboratory experiment measured from **a** the air space of the bottle with the photoionization detector and from **b** the soil samples (mean ± SD) taken at the start of the experiment and after 3 and 9 weeks of incubation. Soil water content is shown as percentages of saturation degree (100% is saturated with water and 0% without water amendment, equal to electrokinetically dried soil). In **b**, *letters* indicate homogenous subsets in Tukey's post hoc tests

the 100% saturation degree flasks (Fig. 2a). The dried, field moisture soil (0% saturation degree) flask produced higher VOC vapors for the first 22 days, while the soil of 40 and 70% levels of saturation degree was found between the extremes (Fig. 2a). In more detail, on days 1 and 3, PID values dropped steadily in all noncapped treatments (Fig. 2a) and values in the dried, field moisture soil (0% saturation degree) were higher than those in the 100% saturation degree treatment ($F \geq 8.3$, df = 3, 8, $p \leq 0.018$). On days 7–21, the cumulative PID value was the highest at 0% saturation degree treatment and the lowest in the 100% saturation degree treatment (Fig. S1a in the Electronic Supplementary Material, $F = 75.8$, df = 3, 8, $p < 0.0005$). After a 23-day incubation the VOC concentration in the head space was very low in all flasks except the capped control. On days 23–75, the cumulative PID value was smaller in the 100% saturation degree treatment than in 40 and 70% saturation degree treatments, and the 0% saturation degree treatment (open bottles) was not different from any other treatment (Fig. S1b in the Electronic Supplementary Material, $F = 6.6$, df = 3, 8, $p = 0.015$).

As gasoline concentrations in soil were equal on day 0, we compared the concentrations on weeks 3 and 9 (Fig. 2b). On week 3, gasoline concentration in soil was lower in 0% saturation degree treatment (open bottles) than in the other treatments (Fig. 2b; $F = 14.5$, df = 4, 10, $p < 0.0005$). The other saturation level treatments had similar concentrations ($p > 0.05$). On week 9, gasoline concentration was the lowest in the 0% saturation degree treatment and the highest in 100% saturation degree treatment (Fig. 2b; $F = 46.2$, df = 4, 10, $p < 0.0005$). The results indicate that the lower the saturation degree is, the faster is the evaporation of gasoline compounds from soil. Combined with PID results, we report that gasoline compounds evaporated to a significant degree and that the evaporation was enhanced in dry conditions.

The lab experience was applied to the field conditions starting in May 2009. At this point, the electrokinetic treatment was stopped and SVE tubing was installed as described in Section 2.3. The approximate VOC concentration in the vapors pumped from the ground was monitored biweekly using a handheld PID device before and after the air passed through an activated charcoal filter (data not shown). The SVE treatment was stopped at the end of October 2009 and the area, including previous hot spots, was sampled (Table 1). The soil temperature was still on average 18 °C at the depth of the tubing, but the VOC odors were almost indistinguishable. The samples were shown to have residues of C_5–C_{10} PHCs that were below the required target concentrations (higher guideline value for industrial use 500 mg kg^{-1}) at most of the sampled spots (Table 1). Since some fractions were found in concentrations above the target value, a site-specific risk assessment was performed quantitatively with the SOILIRISK model. With no changes in land use, the site was found to be in acceptable condition requiring neither further remediative actions nor monitoring.

The sequential approach towards achieving in situ remediation had thus led to the desired result. In this process, the method development and technical modeling in the lab were crucial, both for understanding the phenomena observed and for a proper application of the methods developed. The total treatment time at the site was rather long—over 2 years—but a great portion of this time could have been saved with a more systematic use of lab pretesting, in particular at the onset of the treatment. The efficient and active phases of the treatment represented about half of the total time, and based on experience gained at Jalasjärvi and other typical former fuel station sites, similar new cases could be treated in a substantially shorter time, using the best suited combination of methods in an optimal order.

Investments in equipment had been done earlier, before the Jalasjärvi project and during the biostimulation phase of the project. Costs connected specifically to the dewatering and SVE phase reported here are the electricity consumption during the electrokinetic dewatering and the SVE vacuum pumping. The electricity price during the time of these treatments fluctuated around 0.09€ kWh^{-1} and is still comparable to that level, although the fluctuations are wider now. Calculating with an average power 135 W (270 V, 0.5 A) and a treatment time of 9 months, the estimated total electricity consumption during the dewatering phase was ca 1400 kWh costing ca 130€. The electricity consumption by the vacuum pump running for 3 months raises the total price for the electricity to ca 200€. Sampling, analyzing, and installing of the perforated SVE tubing generated far more expenses than the soil dewatering and SVE activities. The volume of the treated soil was approximately 130 m^3 taking into account the depth from 1.5 m below ground down to 6 m below ground and assuming that the area influenced by the electrokinetic dewatering was the area between the rows of electrodes. All soil above the 1.5 m depth had been cleaned previously. This should be compared to the volume 180 m^3 (6 × 5 × 6 m) in case of using excavation; since then, also the cleaned top layer would have been removed. In addition, such excavation would also have required removal of the constructions on top of the ground.

4 Conclusions

In all, a novel combination of existing methods for in situ remediation of soil contaminated with volatile recalcitrant substances is presented. Once the methods were applied in correct sequence, light fraction PHC components including BTEX were readily removed in a cost-efficient manner. Based on the experience gathered here, the remediation of similar sites can be planned to be executed in less than 1 year, at total costs that are competitive with excavation and other more invasive procedures. It is envisioned that other volatile water-insoluble compounds could be removed in a similar manner and that sites larger in area could be treated with similar sequence of methods, although compound properties and site-specific matters have to be taken into account.

Acknowledgments This work was supported by Tekes—the Finnish Funding Agency for Innovation. Additional funding was obtained from the Finnish Cultural Foundation's Päijät-Häme Regional Fund and via the EU Baltic Central project INSURE. The Jalasjärvi Voluntary Fire Brigade is acknowledged for technical help.

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European achievements in soil remediation and brownfield redevelopment

A report of the European Information
and Observation Network's
National Reference Centres
for Soil (Eionet NRC Soil)

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European achievements in soil remediation and brownfield redevelopment

“ Essentially,
all life depends
upon the soil...
there can be no life
without soil and no
soil without life;
they have evolved
together. ”

Charles Kellogg 1938

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Foreword

Industrialization over the past 200 years has created much wealth and opportunities for human beings. We have seen how the overall quality of life has risen as has the improved transport of goods, facilitated communications, and increased the productivity of agriculture. However, this progress has been accompanied by numerous side effects that society is only beginning to notice today. These include releases of hazardous chemicals that are polluting the air, water and soil, noise from the various means of transport, and impacts on the planet's climate due to greenhouse gases emissions. There are many more examples. Future life on Earth will rely on the ability of human beings to protect its natural resources. A significant threat comes from soil pollution arising either from industrial contamination or from inappropriate land management practices. This concern is reflected by recent developments associated with the Sustainable Development Goals, which includes targets for tackling the issue of soil pollution on human health. A reinforcement of the SDG aims was also evident during the G7 Presidency Summit in Taormina (Italy) on 26-27 May 2017, where a major recommendation of the Summit in relation to global trade governance, was to give priority to remediate contaminated sites. The final declaration of the meeting declared that the Group aims to "allow business to deploy its full potential in polluted site remediation". By managing polluted site remediation, business would actively pursue resource efficiency objectives and preserve natural assets. We call on the G7 to incentivize on-site remediation technologies that are more economically efficient and more environmentally effective." This general concern about soil contamination will also be addressed by a Global Symposium on Soil Contamination and Pollution, which will be organized by the Global Soil Partnership in April 2018.

However, the recently published "Inventory of Soil Protection Policy Instruments in EU Member States"[1] reports a high variability among national legislation and a knowledge gap in methodologies to manage contaminated land. Industrialised countries such as The Netherlands, Germany, France, Belgium, Italy and United Kingdom, have more than 25 years experience in looking for ways to restore polluted soils, with legislation in place and a strong technical expertise in decontamination activities. In many other countries, this, and with comprehensive inventories, is lacking.

It is in this context that this monograph aims to highlight inspirational examples of brownfield redevelopment that supports the trend towards the objective of 'no net land take'. These include the 2012 London Olympic Park, the new residential area of Penttilänranta in Finland which is constructed after the restoration of a former industrial site that was active over a period of 100 years, the restoration of the heavily polluted industrial area in Bilbao into the Guggenheim Museum and green areas for the citizens. These examples represent valuable achievements in soil remediation and brownfield redevelopment, and how to manage contaminated sites that originated from industrial plants, urbanization or by accidents. The cases here demonstrate progress in research and innovative technologies, novel approaches to soil remediation management, the beneficial integration of stakeholders in decision-making and fruitful progress in raising public awareness and citizen science.

The engagement of each one of us is vital for the protection of our limited natural resources like the soil, by doing simple daily actions we can contribute to ending extreme poverty, fighting inequality and injustice and fixing climate change with a result of creating a better world for the future generations.

Dr. Giovanni De Santi
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[1] http://ec.europa.eu/environment/soil/pdf/Soil_inventory_report.pdf

Executive summary

Over 200 years of industrialisation have caused soil contamination to be widespread in Europe. Decision makers, scientists, businesses and individual citizens generally accept and understand the impacts of air and water pollution on human health and environment, but the impacts of soil contamination have a much lower profile. Soil contamination is very often perceived as a burden for policy makers and public administration and as a potential threat for citizens' health and environment.

From the 1980s until today Europe has developed numerous laws to reduce and remediate the adverse effects of soil pollution. Each country has gathered very valuable information and published their own work in the national language (normally not accessible and not known by other countries), on how to manage contaminated sites that were originated from industrial settlements, urbanization or by accidents.

This document and its predecessor, The Remediated sites and brownfields. Success stories in Europe, were published at the initiative of EIONET NRC Soil, which established in 2015 an ad-hoc working group on contaminated sites and brownfields in Europe. The objective was to collect cases and European achievements of remediated sites and brownfields, harmonise and facilitate exchanges of information on contaminated soils and soil remediation between the Eionet contributing countries. These cases aims to raise awareness about the huge efforts already made in this ambitious endeavour. as well as to contribute to a better understanding of the remediation of contaminated sites and brownfields rehabilitation while sharing best practices and new techniques in soil remediation and management.

This document presents examples of success stories of remediation of contaminated soils in various contexts and different European countries. It is not meant to provide an exhaustive inventory of remediated sites in all countries Eight countries present a total of 17 cases which illustrate how soil and brownfields remediation along with sustainable land management have become essential for reversing the trend of soil degradation and ensuring the provision of ecosystem services by soil.

The cases show progress in research and innovative technologies of soil remediation, new outstanding approaches to soil remediation management, beneficial integration of stakeholders in decision-making and fruitful progress in raising public awareness and citizen science. These stories have also achieved the restoration, safeguarding and longterm ensurance of some of the most widely recognized functions of soils, such as support for water regulation and purification, provision of new habitat for organisms, food, fibre and fuel, promotion of cultural and recreation areas and foundation for human infrastructure.

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International	Josiane Masson	DG Environment European Commission

List of abreviations

Acronyms	Terminology
%	Percentage
˚C	Degrees celsius
˚F	Degrees fahrenheit
µg (mc)	Microgram (10^{-6} g)
ADEME	The French Environment and Energy Management Agency
AMD	Acid mine drainage
ARPA Umbria	Environmental Protection Agency of the Umbria region
ARPAE	Environmental Protection and Energy Agency of Emilia Romagna region
AS	Air sparging
ASTM	American Society for Testing Materials
B €	Billion Euros
BTEX	Benzene, Toluene, Ethylbenzene and Xylenes
BTEX	Benzene, Toluene, Ethylbenzene, Xilene
CEO	Chief Executive Officer
cm	Centimeter
cm^2	Square centimeter
EOX	Organic halogen compounds
EPFL	Public Land Establishment of Lorraine
ERA	Ecological Risk Assessment
ERDF	European Regional Development Fund
g	Gram
g/L	Gram per litre
GAC	Granulated Activated Carbon
ha	Hectare
INAIL	National Institute for Insurance against Accidents at Work
ISPRA	Italian National Institute for Environmental Protection and Research

List of abreviations

KAC	Environmental Protection Fund Appropriation
Kárinfo	Remediation Information Subsystem
KEOP	Environment and Energy Operative Programme
kg	Kilogram (103 g)
KIOP	Environmental Protection and Infrastructure Operative Programme
KKA	Central Environmental Fund
km	Kilometer
km^2	Square kilometer
l	Liter
m	Meter
M €	Million Euros
m^2	Square meters
m^3	Cubic meters
mg	Milligrams (10^{-3} g)
mm	Millimeter (10^{-3} m)
NGR	Generic Reference Level
O&M	Operation and Maintenance
OKKP	National Environmental Remediation Programme
OVAM	Public Waste Agency of Flanders
P&T	Pump and Treat
PAH	Polycyclic Aromatic Hydrocarbon
POPs	Persistent Organic Pollutants
RBCA	Risk-Based Corrective Actions
ROI	Radius of Influence
SME	Small and Medium-sized Enterprise
SVE	Soil Vapour Extraction
t	Tonnes (106 g)

Introduction: background on Soil Contamination and remediation in Europe

About Eionet NRC Soil

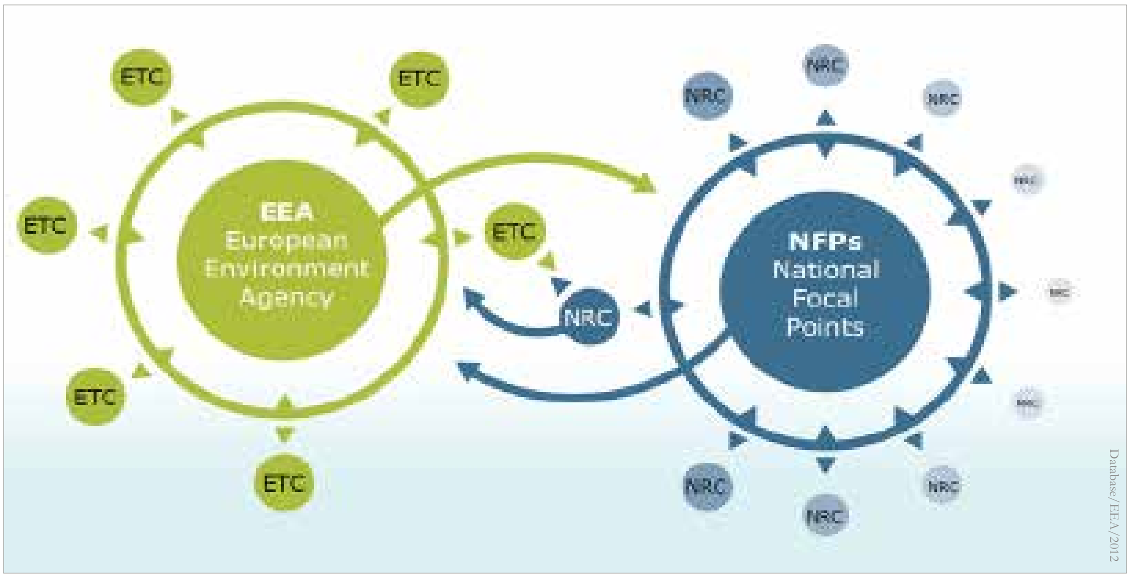
The European Environment Information and Observation Network's (Eionet) is a partnership liaison of the EEA and its member and cooperating countries. It consists of the EEA itself, a number of European Topic Centres (ETCs) and a network of around 1 500 experts from 39 countries in up to 400 national bodies dealing with environmental information. These experts are designated as National Focal Points (NFPs) and National Reference Centres (NRC).

Eionet NRC are individuals or groups with relevant expertise in a national environmental organisation nominated and funded by the country to work with the EEA and relevant ETCs. NRC are located in organisations which are regular collectors or suppliers of environmental data at the national level and/or possess relevant knowledge regarding various environmental issues, monitoring or modelling. NRC are organised around specific environmental areas - for example soil.
The overall NRC structure, including the identification of relevant environmental themes, varies in accordance with the requirements and priorities of the EEA multi-annual work programme. Through Eionet, the EEA brings together environmental information from individual countries concentrating on the delivery of timely, nationally validated, high-qualiy data. This knowledge is made available through the EEA website and forms the basis of both thematic and integrated environmental assessments. The European Commission, the European Parliament, national and regional authorities in the Eionet

Database/EEA / 2012

Eionet member countries and cooperating countries.
More information at EEA brochure

> “Throught the European Soil Data Center, the JRC is interacting with the Eionet NRC for Soil for the management of soil data and information.”



Database/EEA/2012

Cooperation between National Focal Points (NFPs), The European Environment Agency (EEA) and European Topic Centres (ETCs). Eionet Connects. Sharing environmental information in Europe.

countries, the scientific world and a wide range of non-governmentalorganisations among the regular users of the databases and information products.

In the area of soil, the European Commission's Joint Research Centre (JRC) has the responsibility for the European Soil Data Centre, the thematic centre for soil-related data in Europe. In that capacity JRC is interacting with the Eionet NRC for Soil for the management of soil data and information.

For a full picture of the role of Eionet, please consult this EEA brochure.

Soil policy context

In September 2006 the Commission adopted a Soil Thematic Strategy[1] including a proposal for a Soil Framework Directive[2]. This was originated from the need to ensure a sustainable use of soils and protect their function in a comprehensive manner in a context of increasing pressure and degradation of soils across the EU.

Taking note that the proposal has been pending for almost eight years without a qualified majority in the Council in its favour, the Commission decided to withdraw the proposal, opening the way for an alternative initiative in the next mandate[3]. In withdrawing the proposal for a Soil Framework Directive, the Commission indicated that "The Commission remains committed to the objective of the protection of soil and will examine options on how to best achieve this. Any further initiative in this respect will however have to be considered by the next college[4v]."

The commitment to sustainable soil use is in line with the Seventh Environment Action Programme (7th EAP)[5] which provides that by 2020 "land is managed sustainably in the Union, soil is adequately protected and the remediation of contaminated sites is well underway" and commits the EU and its Member States to "increasing efforts to reduce soil erosion and increase organic matter, to remediate contaminated sites and to enhance the integration of land use aspects into coordinated decision-making, involving all relevant levels of government, supported by the adoption of targets on soil and of objectives land as a resource and land planning". It also states that "The Union and its Member States

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[1] COM(2006)231.

[2] COM(2006)232.

[3] OJ C 163, 21.5.2014, p. 4.

[4] OJ C 163, 28.5.2014, p. 15.

[5] Decision N° 1386/3013/EU of the European Parliament and of the Council of 20 November 2013 on a General Union Environment Action Programme to 2020 "Living well, within the limit of our planet" (OJ L 354, 28.12.2013, p. 171-200).

should also reflect as soon as possible on how soil quality issues could be addressed using a targeted and proportionate risk-based approach within a binding legal framework”.

The 2012 Commission reports on the implementation of the Soil Thematic Strategy and ongoing activities[6] and on the State of Soil in Europe[7] highlighting the continuous degradation of soils in Europe. The European environment- state and outlook 2015 (SOER 2015)[8] underlines that “soil stores, filters and transforms a range of substances including nutrients, contaminants and water. In parallel, this function in itself implies potential trade-offs: a high capacity to store contaminants may prevent groundwater contamination, but this retention of contaminants may be harmful for biota. The issue of contamination is crucial for this function as both diffuse and point source pollution can impact human health and ecosystem services, thus affecting a soil’s capacity to “regenerate”.

Database/Authors

European legislation and policy instruments related to the protection of the soil environment

> “**Soil** *Framework Directive is needed to ensure a sustainable use and protection of soils in a context of increasing pressure and degradation of soils across the* **EU**”

To date, soil is not subject to a comprehensive and coherent set of rules in the Union. The protection and sustainable use of soil[9] is scattered in different Community policies contributing in various degrees to mainly indirect protection of soil, for example through environmental policies on waste, water, chemicals, industrial pollution prevention, nature protection and biodiversity, nitrates and pesticides, sewage sludge, forestry strategy, climate change adaptation and mitigation, and biofuels. For soil contamination 13 different pieces of EU legislation apply, for example:

Directive 1999/31/EC on the landfill of waste[10] addresses the presence of toxic substances resulting from a land-filling operation, on the condition that it had not been

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[6] COM(2012) 46.

[7] The State of Soil in Europe, EUR 25186 EN.

[8] http://www.eea.europa.eu/soer-2015/europe/soil

[9] As mentioned in the Soil Thematic Strategy as overall objective

[10] OJ L 182, 16.07.1999, p. 1

closed and covered before 16 July 1999. Directive 2004/35/EC on environmental liability[11] requests liable operators to undertake the necessary preventive and remedial action for a range of polluting activities, provided that serious pollution was caused after April 2007 Directive 2010/75/EU on Industrial Emissions[12] aims to ensure that the operation of an industrial installation does not lead to the deterioration in the quality of soil (and groundwater), and requires establishing, through baseline reports, the state of soil and groundwater contamination. However, a large number of installations do not fall under the scope of the directive.

The EU Cohesion Policy plays a role for the rehabilitation of certain industrial sites and contaminated land: in the period 2007-2013, 3.1 B € have been allocated to eligible regions (mostly in Hungary, Czech Republic and Germany). The Cohesion Funds and the European Regional Development Fund (ERDF) continue to support the regeneration of brownfield sites under the current programming period 2014-2020.

Within Regional Policy Investment priorities relating to the environment (Art.5(6) ERDF and Art. 3(c) CF the following is included:

a) Protecting and restoring biodiversity, soil protection and restoration and promoting ecosystem services including NATURA 2000 and green infrastructures.
b) Action to improve the urban environment, revitalisation of cities, [...] regeneration and decontamination of brownfield sites (including conversion areas), reduction of air pollution and promotion of noise-reduction measures.
c) Limiting land take on greenfields and recycling of land, including remediation of contaminated sites. Complementary state aids for the remediation of soil contamination can be granted under the Environmental Aid Guidelines provided that the 'polluter pay principle' is respected.

At national level the situation varies a lot from one Member State to the other; only a few Member States have specific and comprehensive legislation on soil protection, very often national soil legislation is limited to soil contamination and soil sealing. The others rely on provisions on soil protection in the environmental legal acquis.

At national level the situation varies a lot from one Member State to the other. Only a few Member States have specific and comprehensive legislation on soil protection, very often national soil legislation is limited to soil contamination and soil sealing. The others rely on provisions on soil protection in the environmental legal acquis. A range of EU policy documents indirectly addresses soil contamination, but due to the lack of a European legal framework that encompasses all regulations, countries operate along national policies. That legal vacuum is evidenced by the permanence of 215 national and/or regional legal tools explicitly addressing this issue, many of them not linked with any EU policy (go on see Graph 1 in page 17). Other 85 national legal instruments address soil contamination in an indirect way. About 44% of Member States' legal tools are addressing industrial and point source contamination of land (Frelih-Larsen, et al., 2016)[1].

On the basis of non-harmonised national inventories, local soil contamination in the EEA-33 plus the 6 cooperating countries has recently been estimated at 2.5 million potentially contaminated sites. About one third of an estimated total of 342 000 contaminated sites in the EEA-33 plus the 6 cooperating countries have already been identified and about 15% of these have been remediated. It is still insufficient but the remediation market is growing.

Nowadays, every European Member State has a national policy that includes the "polluters pay principle", either a specific one or regulations included in a more generalist environmental code. They also include contamination-related definitions, threshold values, risk reduction

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[11] OJ L 143, 30.4.2004, p. 56

[12] OJ L 334, 17.12.2010, p. 17

[1] Frelih-Larsen, A., Bowyer, C., Albrecht, S., Keenleyside, C., Kemper, M., Nanni, S., . . . Vidaurre, R. (2016). Updated Inventory and Assessment of Soil Protection Policy Instruments in EU Member States. Final Report to DG Environment. Berlin: Ecologic Institute.

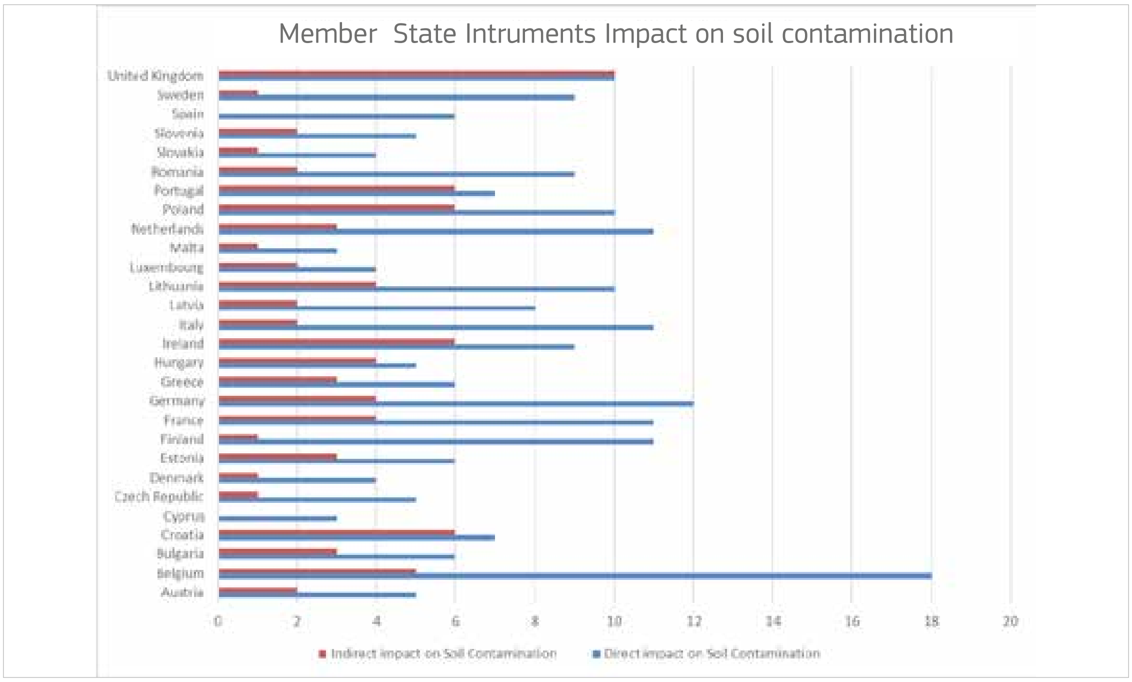
measures and guidelines to site identification.

Generally, all these regulations aim to prevent harmful changes in the soil and the rehabilitation of contaminated soils and groundwater, which is in many cases considered as part of the soil system or to be intimately related to it. In some cases, preventing air contamination by emissions is also considered under specific legislation on soil contamination (Paya Perez & Rodriguez Eugenio, 2017)[2].

Monitoring the management of contaminated sites

In the area of soil contamination, the Soil Thematic Strategy (COM(2006) 231) proposed that Member States draw up a list of sites polluted by dangerous substances with concentration levels posing a significant risk to human health and the environment, and of sites where potentially polluting activities have been carried out (landfills, airports, ports, military sites, petrol and filling stations, etc.). The proposal for a Soil Framework Directive (COM(2006) 232) lists such potentially polluting activities. The indicator Progress in management of contaminated sites (LSI 003), which is part of the thematic cluster of land and soil indicators (LSIs) of the EEA, has been agreed by the Eionet NRC Soil more than a decade ago. It is used to track progress in the management of local soil contamination in Europe, and is also used for reporting on the State of the Environment (SOER). Six data collection exercises have been completed since 2001 to support reporting by the EEA of the indicator CSI015 Progress in the management of contaminated sites.

The Progress in the management of Contaminated Sites in Europe (2014) report, produced by the JRC in collaboration with the EEA and its 39 member and cooperating countries, presented the state of knowledge about such progress (based on data collected in 2011-2012). However, differences between countries remained considerable because of lack of consensus in defining potentially polluting activities and the absences of political support to develop systematic analysis and inventories. On year 2015 the Ad-hoc Working Group on Contaminated Sites and Brownfields underT EIONET NRCs Soil initiated a revision of the indicator on "the progress in the management of contaminated sites". Thus, a new Land and Soil Indicator (LSI003) was proposed and refers to a thematic cluster of



Graph 1. Number of national policies that explicitly or indirectly address contamination industrial point source (CIPS) by country (based on information provided in the Soil-Wiki platform).

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[2] Paya Perez, A.B. & Rodriguez Eugenio, N. (2017) Status of local soil contamination in Europe. JRC Technical Report JRC107508

land and soil indicators (under development).

In the 2016 data collection exercise[2], LSI003 is based in site status, depending on its management step. Six-site status area considered:

- Status 1 – sites where polluting activities took place
- Status 2 - sites in need of investigation/still to be investigated or under investigation where there is a clear suspicion of contamination
- Status 3 – sites that have been investigated, but no remediation needed
- Status 4 – sites that need or might need remediation or risk-reduction measures (RRM), including natural attenuation
- Status 5 - sites under/with on-going remediation or RRMs
- Status 6 – site remediation or RRMs completed or sites under after-care measures.

The LSI003 indicator aims to present the progress made in the management of contaminated sites, including available policy tools, by each Member State and cooperating countries. According to the new JRC report (JRC107508, 2017)[2], a tentative extrapolation to the whole of Europe (39 countries), considering the average density of contaminated sites depending on the surveyed countries' population, produces an estimate of 3.3 million sites where polluting activities took place. However, whether extrapolations are made based on countries artificial surface extension (km^2), an estimate of 2.7 million sites where polluting activities took place is obtained. Until end of year 2016 significant progress has been achieved regarding identification of sites where polluting activities took place, since circa 45% (627 251 sites) of estimated sites where polluting activities took place are already identified and registered in national and/or regional inventories. Of them, more than 263 695 sites are in need of detailed investigation in order to define whether pollution is creating a significant risk to human health and environment (Site Status 2). Of the 23 countries who responded to this question, 30% said they have 1 000 or more sites are still requiring detailed inspection and the other 30% have more than 10 000 sites that need further investigation. Around 8% of registered sites need or might need remediation or risk-reduction measures (RRM), including natural attenuation (Site status 4). Nevertheless, a significant effort is been made to reduce or remediate these polluted sites with more than 14 360 sites under remediation or risk-reduction measures (Site status 5) across surveyed countries[2]. Regarding those sites where there were a suspicion of soil contamination but after the accomplishment of detailed investigation risk reduction measures or remediation are not needed, 21 of 27 countries that return the questionnaire have reported 82 798 sites in Status 3, but an estimate of circa 140 000 sites in the whole Europe might be in this situation[2].

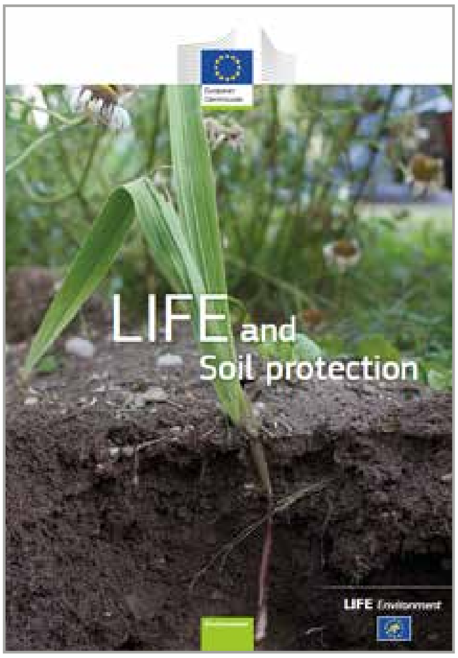
The research and development

The EU Research and innovation programmes, such as Horizon 2020 and LIFE+ projects18, are contributing to improving the knowledge base on soils and soil protection measures, along with the JRC which hosts the European Soil Data Centre. The publication LIFE and Soil protection (2014) provides information on 23 LIFE projects on soil contamination. In these projects diverse pollution activities like landfills and waste treatment plants, industrial pollution – mainly heavy metals and mineral oil- mining, quarrying and military use are addressed.

The Research Framework Programme FP7 has financed 7 projects for a total budget of 28 460 484 M €. In 2014-2015, two calls for proposals were launched under the Horizon 2020 "Societal Challenges 5 on Climate Action, Environment, Resource Efficiency and Raw Materials":

1. SC5-8-2014: Preparing and promoting innovation procurement for soil decontamination (2 M €)
2. SC5-10-2014/2015: Coordinating and supporting research and innovation for the management of natural resources (9 M €).

More recently the H2020-SCC-2016-2017 Research Framework Programme is financing projects for "demonstrating innovative nature-based solutions in cities" and on the call for Societal Challenge 5 'Climate action, environment, resource efficiency and raw materials', specifically the action on SC5-26-2017: Pre-commercial procurement on soil decontamination (5 M €) aims to find common innovative and sustainable solutions for soil decontamination/remediation, avoiding 'dig and dump'. The proposal is expected to bring radical and innovative improvements to the quality and efficiency of public soil decontamination services, processes and products. Considering the important role soils play on human health and environmental preservation, nowadays, public and private organizations are producing more evidence of the current and long-term impacts on human health and the environment from exposure to contaminants from soil and groundwater. This is very relevant at the local level, around contaminated sites, but has also implications at regional and national level. Following the initiative of the WHO meeting in Syracuse (2011) and Catania (2012) a COST Action of Industrially Contaminated Sites and Health Network (ICSHNet) was launched in May 2015 aiming to identify the knowledge gaps and research priorities, and propose harmonized methodologies and guidance on the environmental health issues related to industrially contaminated sites in Europe. The Action is focusing on four main Tasks, strictly interconnected to each other, and 4 Working Groups (WGs) will perform these tasks and will contribute to the completion of the Action objectives:



WG1: Environment and health data - Identification of needs and priorities to guide the collection and organization of environment and health data concerning industrially contaminated sites;
WG2: Methods and tools for exposure assessment - Identification of needs and priorities on the design of strategies to evaluate exposures to environmental contaminants in populations residing in industrial contaminated sites;
WG3: Methods and tools for health risk and health impact assessment - Identification and evaluation of methods and tools to guide health risk and health impact assessment in industrially contaminated sites;
WG4: Risk management and communication - Development of guidance on risk management and risk communication on environmental health risks in industrially contaminated sites.

In all these areas (industrial contamination, landfilling, innovative restoration technologies, education, and others…) there is a need to improve or update the knowledge base through a continuous dialogue with stakeholders using existing platforms (NICOLE, Common Forum, CLAIRE, EUGRIS, Eionet NRC Soil, etc.) and Research Institutions (Agencies, Research Councils and Universities) across Europe.

WHO (2013) report of two Workshops on Contaminated Sites and Health: Syracuse (Italy) 2011 and Catania (Italy) 2012. www.euro.who.int

EC (2013) – In depth report " Soil Contamination: Impacts on Human Health", Science for Environmental Policy, September 2013 Issue 5. http://ec.europa.eu/science-environment-policy

Van Liedekerke M. (2014) – Progress in the management of contaminated sites in Europe, 70 pp. EUR 26376 EN

Paganos P., Van Liedekerke M., Yigini Y., and Montanarella L. (2013) - Contaminated sites in Europe: Review of the current situation based on data collected through a European Network. J. of Environmental and Public Health, article ID 158764.

EEA (2014) - Environmental Indicator Report 2014 Environmental Impacts of Production - Consumption Systems in Europe.

http://www.eea.europa.eu/publications/environmental-indicator-report-2014

EEA (2015) - SOER 2015 - The European environment - state and outlook 2015:

http://www.eea.europa.eu/soer

ESDAC – European Soil Data Centre: http://esdac.jrc.ec.europa.eu/

> “*The word Homo, the genus that comprises the specie Homo sapiens, is derived from the Latin humus, meaning of the soil.*”
>
> Arwyn Jones, 2015.

Summaries

BELGIUM

FINLAND

FRANCE

HUNGARY

ITALY

POLAND

SPAIN

UNITED KINGDOM

Newton SME Park in Anderlecht.

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BELGIUM

Clean-up of soil contamination is essential, because it allows many abandoned sites in Brussels to be rehabilitated, giving them a second chance by repurposing them for new economic, residential and recreational activities. Consider the example of the new Newton SME (Small and Medium Enterprise) Park in Anderlecht, which in 2006 was found to be affected by significant soil and groundwater pollution by chlorinated solvents. It was then that the idea of building an SME park on this site took shape. This type of example therefore proves that a contaminated parcel of land can be turned into an opportunity for the installation and development of new projects that have a positive impact on the region. The Flemish soil remediation policy features very strict and enforceable investigation and remediation obligations, it also offers room for flexibility and margin for negotiation when necessary. In this regard they describe two flexible instruments: the company-specific agreement which allows better planning and scheduling of soil investigations and remediation in line with the company's priorities and possibilities; and the acquisition of contaminated blackfields for one symbolic euro from bankrupt companies according to the protocol agreement between OVAM and the Flemish Bar Council. Finally, it is also briefly described the clean-up of the Carcoke site, which still is the most expensive remediation in Flanders ever.

> *“SME park stands as an example of a contaminated parcel of land turned into an opportunity for the installation and development of new projects that have a positive impact on the region.”*

Penttilänranta area during works, Joensuu, Finland.

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FINLAND

There have been two major national remediation programmes for oil-polluted sites in Finland. The first was SOILI 1997-2015 and the second is JASKA 2012-today. More than 1 200 sites have been investigated and about 800 sites have been remediated during these national programmes. Project funding comes from the Finnish Oil Pollution Compensation Fund, which is administered by the Ministry of the Environment. The primary aim of the Finnish national remediation programmes is to eliminate environmental and health hazards by utilising cost-effective and high-quality methods. All of the programmes' remediation contracts and other services are put out to bid. The contract format, which has been used for in situ remediation is so called a turnkey contract, where the contractor is committed to reaching the target values within a fixed price. Moreover, there is also a condition in the bidding documents which states that, before the contract agreement, the chosen contractor shall conduct their own investigation of the site to confirm the applicability of the offered in situ method and the required extent of the remediation. Total cost savings from the 72 sites remediated by in situ methods have been approximately 40% (savings of about 3.2 M €, VAT 0) over conventional 'dig and dump' treatment. The clean-up cases of Lintuvaara, Halikko, Jalasjarvi and Penttilanranta are presented. The restoration of Penttilanranta area has been converted into a new high quality residential zone with about 3 000 inhabitants and new industrial locations with expected investments of 400 M € during the period of 2010-2040.

> *“The primary aim of the Finnish national remediation programmes is to eliminate environmental and health hazards by utilising cost-effective and high-quality methods.”*

In situ biosensors (Remwatch R&D project).

© Florian Philippon

FRANCE

Preventing risks of any kind arising from a plant classified for the protection of the environment is the responsibility of the site's operator in France. Should it remain unidentified (disappearance) or insolvent, would the site be considered as orphan, or site defaulting responsible. The SUTE site located in the centre of Pont-à-Mousson, nearby the most visited tourist site in the Lorraine region the so called "Abbaye des Prémontrés" abbey, is classified as cultural heritage building. That's why the SUTE site was entrusted to the French Environment and Energy Management Agency (ADEME), which ensured the management of setting health and environmental safety. As part of the main principles of the management of contaminated sites approach set up in France, ADEME implemented a management plan after the diagnosis step carried out in close connection with EPFL (Public Land Establishment of Lorraine). The management plan had identified the need to treat the sources. The land reclamation project is now finished, and the municipality is assessing several reuse options, of which a formal parking area and some green space. The JEC site remediation located in Quincieux, in the Rhône County faced several constraints. The groundwater table directly below the site is at least 8 meters thick. JEC Industries Company used to manufacture metal office furniture from cold rolled sheets since the end 50's on this site. By now, several treatment options are recommended by combining excavation or thermal treatment of soil located above the aquifer with an in situ biological treatment or zero valent Iron. Costs are estimated between 1 and 1.5 M €.

> *"The reclaimed area is ready to be used either as a green area or as a parking space."*

Cleaning works in Budafok, Hungary.

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HUNGARY

After the withdrawal of the Soviet military troops, Hungary started an environmental remediation programme called National Environmental Remediation Programme (OKKP). The number of potentially contaminated sites requiring investigation was estimated at 35 000, with remediation tasks set to last 50-60 years at a cost of HUF 1 000 billion. The leader of the ministry responsible for the environment controls the OKKP and coordinates its subprograms. As national recording progressed, the number of areas needed remediation reduced to 2 000. So far, intervention of State responsibilities has occurred in 580 cases, and there are 2 000 areas needing future actions. The data collected from these projects are added to a database, available for general public. The programme was financed by governmental sources, but following Hungary's European Union accession EU sources are also used. In the framework of the National Environmental Protection and Remediation Programme 1996-1997 in Budapest, the remediation of cave homes polluted by disposal of the gas cleaning paste has been implemented. There were four sources in Budatétény and two more in Budafok. The hazardous materials have been found in two different phases. The amount of previously disposed of harvested solid gas paste was 77 344 t of liquid phase, 559 t leachate and 3 000 t of dilute sludge. The real estates on the remediated area are built-up, inhabited or non-built-up with weekend houses and gardens, or industrial estates or public areas and roads with public utilities. The target of the technical intervention was the thorough decontamination of the area.

> *"The technical interventions resulted in a healthy environment ready to be used as agricultural lands."*

Ritorto creek, Tuscany, Italy. High concentration of Iron causes the reddish colouring of waters.

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ITALY

Confindustria, the lead organization representing the manufacturing, construction, energy, transportation, ITC, tourism and services industries in Italy presents a working paper providing an assessment of the environmental policy for land remediation in Italy from the regulatory/procedural standpoint, as well as from the technological and economic point of view, identifying, a number of key factors to foster remediation and to re-launch economic and industrial activities. The second case presented, Reconnet, the Italian network for the management and remediation of contaminated sites is the main multi stakeholder network operating in Italy in the field of contaminated sites, counting around 60 members among universities, scientific institutes, research centres, consultants, regional environmental agencies, trade associations and large private companies. It is shown, as third article, the case of Cava Pirata, where the intervention was to achieve the site remediation of all the matrixes involved: bioremediation (bio-pile) for soils, soil vapour extraction for soil gases, air sparring for groundwater. The last one is Torrente Ritorto in Colline Metallifere (Tuscany) with constructed wetlands for remediation of acid mine drainage.

> *“Reconnet, the Italian network for the management and remediation of contaminated sites is the main multi stakeholder network operating in Italy in the field of contaminated sites.”*

Barren smelter wasteland in Piekary before the reclamation.

© courtesy of authors/Photostock

POLAND

The study case presents the decommissioned Zinc and Lead ore smelting plant located in Piekary Slaskie, Poland. The wasteland had wastes from two different smelting processes — Welz and Doerschel. Both wastes contained extremely high loads of Zinc (up to 128 g kg^{-1}), Lead (up to 40.6 g kg^{-1}), Cadmium (up to 3.46 g kg^{-1}) and Arsenic (0.76 g kg^{-1}). The pilot reclamation of smelter waste sites was performed within the framework of the Silesia project. The project was a joint effort by local government, industry and national or international research institutions and agencies: the US Environmental Protection Agency (USEPA), the Centre for Research and Control of the Environment (OBIKS), Virginia Polytechnic Institute, USDA-ARS in Beltsville and the Institute of Soil Science and Plant Cultivation (IUNG). The main objective of the Silesia project was the development of guidelines for the effective and safe use of bio-solids for the reclamation of degraded lands and waste sites.

> *“Silesia project which joins effort by local goverment, industry and national or international research institutions and agencies pursues the development of guidelines for the reclamation of degraded lands and waste sites.”*

Aerial view of The Guggenheim Museum Bilbao, along the Nervión River in central Bilbao after the remediation works.
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SPAIN

In Europe the brownfields phenomenon has a clear aim in the creation of initiatives of revitalisation and redevelopment for contaminated/abandoned/derelict areas. A qualitative comparison between three cases of brownfields in Spain, looking for the identification of factors of success in the process of redevelopment of the affected areas is presented. One of the articles focuses in four lines of analysis: the current general situation of the brownfields phenomenon in Spain; the explanation and justification of the figures of the factors of success; the possible convergences and divergences that may exist between brownfield cases with different status of redevelopment; and finally how the potential findings can influence future perspectives of the phenomenon across the Spanish territory. The Autonomous Community of the Basque Country provides an overview of what they consider to be the key points of their policy, the inspiration for which comes from those earlier policies in the task of protecting the land, in the hope that others may likewise benefit from their experience. A study case describes two performances made in Andalusia for the remediation of soils contaminated by hydrocarbons in industrial locations, employing two different techniques.

> *“Three cases of brownfields in Spain that aim for the identification of factors of success in the process of redevelopment of contaminated, abandoned or derelict areas.”*

Contamination in the Queen Elizabeth Olympic Park before remediation works.
© courtesy of authors/Photostock

UNITED KINDGOM

When London won the right to host the 2012 Olympic and Paralympic Games, it provided a catalyst to regenerate a former industrial area covering approximately 250 ha in Stratford, East London. The Olympic Delivery Authority (ODA) was established to manage the creation of the Olympic Park, which later became the Queen Elizabeth Olympic Park (QEOP). The creation of the Queen Elizabeth Olympic Park (QEOP) set a challenge to remediate a large, derelict site with a long industrial heritage close to central London. The study case tells the geo-environmental story of the Enabling Works project, which was responsible for the design and implementation of the earthworks and remediation package. Site teams embraced a sustainable remediation approach, which focused on the treatment and re-use of site won materials to minimise off-site disposal of soils to landfill. In doing so, they demonstrated that achieving high re-use targets can also provide the most cost effective solution.

> *“The creation of the Queen Elizabeth Olympic Park (QEOP) set a challenge to remediate a large, derelict site with a long industrial heritage applying the most cost effective solution.”*

HISTORICAL ACHIEVEMENTS

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1. Hungary: the Hungarian National Environmental Remediation Programme
2. Spain: making a virtue of necessity. The case of a small region: the Basque Country
3. Italy: from remediation to re-industrialization: State of play in Italy, problems and proposals

Historical achievements

1. The hungarian national environmental remediation programme (OKKP)

LOCATION	Various, Hungary
POLLUTANT	Halogenated volatile organic compounds (HVOC)
SOURCE	Carcass pit, pesticides and poisons warehouses, industiral waste sites, spoil-bank, fly-ash and slurry dump, militiary and mining sites
GENERAL CLEAN UP OBJECTIVES	Protection of human health, drinking water and soil, water reservoir and enviroment, remediation of contaminated areas
REMEDIATION ACTIONS	Unspecified
SITE/END USE	Industrial, commercial, reisdential
SOCIAL-LEGAL ISSUES	Various national decrees
KEY LEARNING/ EXPERIENCE TO SHARE	Development of a register with public access to the data sheets

Author's profile

Norbert Baross is an environmental expert at the Herman Ottó Institute Nonprofit Ltd. with a post gradual master course in Environmental Engineering in 2010 at Szent István University. He started his work as an engineer assistant at the National Institute for Environment. He was in charge for surface water management tasks of the Budapest Regional Branch, for three years. In 2014, he got into the environmental remediation workgroup. He has considerable experience with GIS programs. He used to attend training courses and conferences regularly. He has participated in a numberof international projects and also in publication of professional articles.

Miklós Hollósy is a professional leader of environmental remediation at ÉMI Non-Profit Llc. He received a Ph.D. in Chemical Engineering at the Technical University of Budapest. He began his professional environmental work in 1982, working in the field of hazardous waste management. His main interest focus on remediation technologies. He has worked for different companies as an environmental expert. He has significant laboratory practice, experience in controlling and proficiency in implementation of projects. He has good organizational and leadership skills. He has published about 20 papers to journals and conference proceedings.

The Hungarian National Environmental Remediation Programme (OKKP)

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After the withdrawal of the Soviet military troops, Hungary started an environmental remediation programme called OKKP. The number of potentially contaminated sites requiring investigation was estimated at 35 000, with remediation tasks set to last 50-60 years at a cost of HUF 1 000 billion. The leader of the ministry responsible for the environment controls the OKKP and coordinates its subprograms. As national recording progressed, the number of areas needed remediation reduced to 2 000. So far, intervention of State responsibilities has occurred in 580 cases, and there are 2 000 areas needing future actions. The data collected from these projects are added to a database, which has an interface for the general public. At the start the programme was financed by governmental sources, but following Hungary's European Union accession EU sources are also used.

Keywords: *Contamination, remediation, database, environmental protection, legislation, remediation programme.*

Introduction

The beginning of the OKKP was closely related to the withdrawal of the Soviet military troops that had been stationed in the country since the end of World War II. After they left the government developed a short- and a middle-term environmental programme, including the main tasks relating to the contaminated sites left behind. During this period the draft of the general rules for environmental protection was formulated and codified. Legislation on the definition and restoration of environmental damage and an environmental quality limit system did not exist in Hungarian law at that time.

Hungary first began an environmental remediation programme in the Middle European region. The package of measures was adopted by the government in 1996. The developers of the programme pointed to the damaging risks to human health by the contaminated areas, the effects of damage to the environment and the risk to drinking water and the land use restriction that prevent economic development. The number of potentially contaminated sites requiring investigation was estimated at 35 000, with remediation tasks set to last 50-60 years at a cost of HUF 1 000 B € (approximatly 3 234 M €).

During preparation, using the then-available databases and records, all solid and liquid waste disposal, carcass pit, pesticide and poison warehouses, industrial waste sites, spoil banks, fly ash and slurry dumps, as well as potentially contaminated industrial, military and mining objects were featured.

OKKP priorities.

1. Protection of human health.
2. Protection of drinking water, water reservoirs.
3. Protection of soil, water and the living environment.
4. Remediation of contaminated areas.

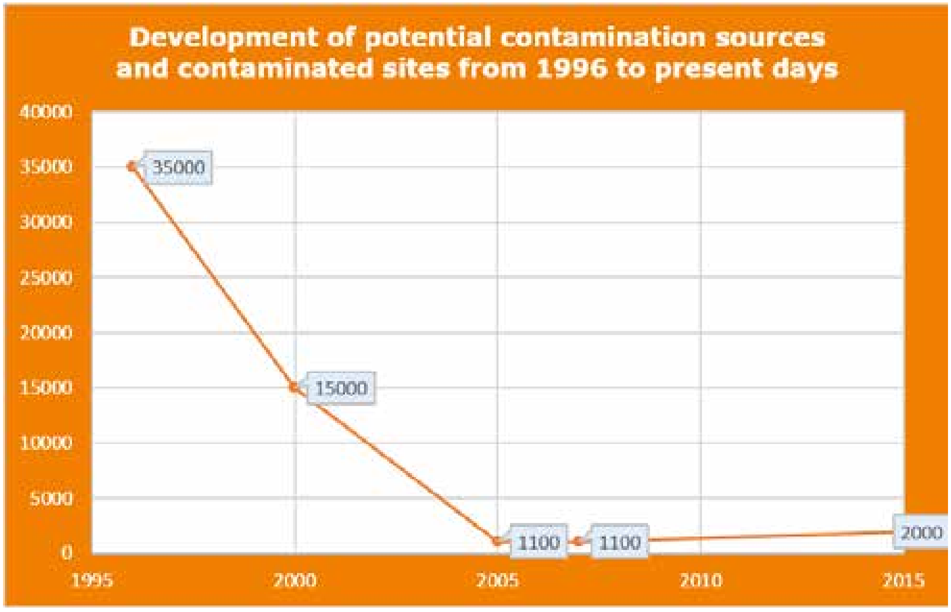
The leader of the ministry responsible for the environment controls the OKKP and coordinates its subprogrammes. This includes the national, general and specific tasks of the operation of the OKKP, such as:

- Ensuring continuous development of legal and technical regulations.
- International relations.
- Harmonisation with EU regulations.
- Data collection, registration and ranking of contaminated sites independent of responsibilities.
- The provision of domestic and international data services based on the register.
- The supply and coordination of monitoring of the remediated contaminated sites.
- R&D and innovation activities providing professional development.
- Helping social awareness and access to information.
- The creation and operation of coordinating organisations.
- Professional control and development of the functioning of OKKP.

The Strategy

Legal Bases

The liability issues related to environmental damage and the government remediation related tasks set by the LIII Act on Protection of the Environment in 1995. 219/2004 (VII.21.) government decree on the protection of groundwater comprises the rules of the remediation processes and the tasks of the OKKP. The environmental quality limit values are in the 6/2009 decree on limit values and the measurement of pollutants to protect geological formations and groundwater from pollution. The 14/2005 decree contains the rules for the screening of remediation site investigations. The 18/2008 decree on the provision of data for the groundwater and geological medium environmental registration system set the rules for the data collection and record-keeping processes for contaminated sites and remediation tasks.

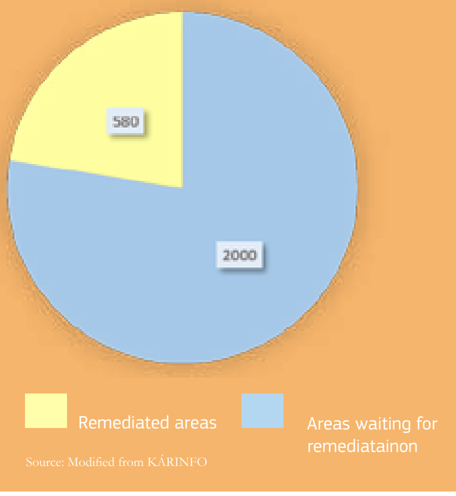


Source: Modified from KÁRINFO

The number of areas needing remediation

As national recording progressed, the previously estimated figure (35 000 sites) halved thanks to on-site surveys by authorities and fact-finding

Distribution of contaminated sites



Source: Modified from KÁRINFO

> *“So far, intervention of State responsibilities has occurred in 580 cases, and there are 2 000 areas needing future actions.”*

inspections carried out within the framework of the OKKP. Some 15 000 potentially contaminated and contaminated areas have been registered in the Kárinfo database created by the first phase of a national accounting process. During additional monitoring and review the number of registered contaminated sites decreased to 1 100 by 2005.

In 2007 the renewed Kárinfo received new data sheets from new areas. At present nearly 2 000 contaminated and potentially contaminated sites are registered that require some level of remedial work.

Remediation tasks undertaken so far on the responsibility of the government (580), and the present state of knowledge of the proportion of areas requiring further remediation tasks (2 000) are illustrated in the diagram below, which is based on data recorded in the Kárinfo database.

The national census of contaminated areas, pollution sources and areas needing remediation started with the involvement of environmental inspectorates and regional research centres after the start of the OKKP. For the national recording, inventory and ranking of the areas needed to remediation, the National Environmental Information System (OKIR) has an information subsystem, called Kárinfo.

The 6/2009 government decree on protection of the groundwater provides that each section of the remediation requires data reporting. The reporting must contain data prescribed by the 18/2007 decree on data provision of groundwater and geological medium.

The decree’s:

- 4th Annex specifies the data content of the ‘Datasheet of data before investigation’ (B1 datasheet)
- 5th Annex specifies the data content of the ‘Datasheet of data after investigation’ (B2 datasheet)
- 6th Annex specifies the data content of the ‘Datasheet of data after technological intervention’ (B3 datasheet).

Public access to the datasheets and the data contained in the register is via the website of the OKIR, under the subtitle ‘Protection of groundwater and geological formation’ in the data query menu.
The contaminated areas can be grouped by further categories, such as:

- Extension of the contaminated area (from 0.1 ha to hundreds of has).
- Main pollutants (heavy metals, oil products,

organic solvents, pesticides, etc.).
- Type of pollution source (mining, metallurgy, metal processing, chemical industry, pharmaceutical industry, etc.).
- Risk to human health.
- Hazardous impact to water and degree of risk (e.g. water resources).
- Protected areas, species, habitats.

Financial sources

When it started, part of the funding for the programme came from privatising state properties and corporations, then from the Central Environmental Fund (KKA) and the Environmental Protection Fund Appropriation (KAC). After the latter merged into the central budget, it was decided that the ministry responsible for the environment would have targeted financial resources for implementing the targets of the OKKP. This was deleted from the budget in 2011, and in the absence of resources for the implementation of tasks, the OKKP's progress has stalled.
At the same time as the accession to the European Union, the ministry responsible for the environment take the lead for using Cohesion Funds in remediation duties. In the first financial period (2004-2006), under the KIOP , six projects and a major priority project (Üröm-Csókavár) were launched. In the 2007-2013 financial period 23 remediation interventions were carried out, to the value of HUF 39.3 billion. HUF 22.8 billion is available for the third period of KEOP (2014-2020) for remediation -tasks under governmental responsibility, which only take place within narrow limits: essential conditions enforce the polluter-pays principle and the implementation of the government's role in statutory and regulatory decisions, as well as the proper preparation of the project, the spatial delineation of the contamination, the cost-effective feasibility of the intervention and the social usefulness of the results.

Further readings

Relevant websites

http://web.okir.hu/hu/tart/index/43/Adatok_lekerdezese

http://www.kvvm.hu/szakmai/karmentes/kiadvanyok/remediation2002/index.htm

Historical achievements

2. Making a virtue of necessity — the case of a small region: the Basque Country

LOCATION	Bilbao river estuary, Basque Country, Spain
POLLUTANT	Unspecified
SOURCE	Industrial waste
GENERAL CLEAN UP OBJECTIVES	Reduge groundwater and soil contamination
REMEDIATION ACTIONS	Excavation, catalitic dechlorination plant, in situ confinement
SITE/END USE	Commercial, industrial activities, residential zones, community spaces, exploratory study
SOCIAL-LEGAL ISSUES	A new policy: the Prevention and Correction of Land Contamination Act
KEY LEARNING/ EXPERIENCE TO SHARE	Private sector engagement, investigation and advanced remediation techniques, new legislation on contaminated land

Author's profile

Ihobe is the public agency of environment, belonging to the Department of the Environment, Territorial Planning and Housing of the Basque Government. Ihobe's mission is to support the Basque Government in developing environmental policy and spreading the culture of environmental sustainability in the Basque Country.

After 30 years of experience in the field, the public agency Ihobe has consolidated its position in the field of environmental management and protection. Although it was initially created to promote environmental infrastructures, nowadays it is the Basque Country's official environment agency and a crucial instrument of the Basque Government's Department of the Environment and Territorial Policy, collaborating with the different units of the Environment Office to implement environmental policy in the fields of soil and air quality, waste, natural environment and public-private partnerships. It also assists the Environment Office in developing strategic projects involving different organisations, such as the Udalsarea 21 network of municipalities and the Eco-Efficiency Programme, and in projects related to ecodesign, environmental planning, climate change, international cooperation and responsible procurement.

Making a virtue of necessity – the case of a small region: the Basque Country

Ministry Office of the Environment, *Department of the Environment and Territorial Policy, Basque government*
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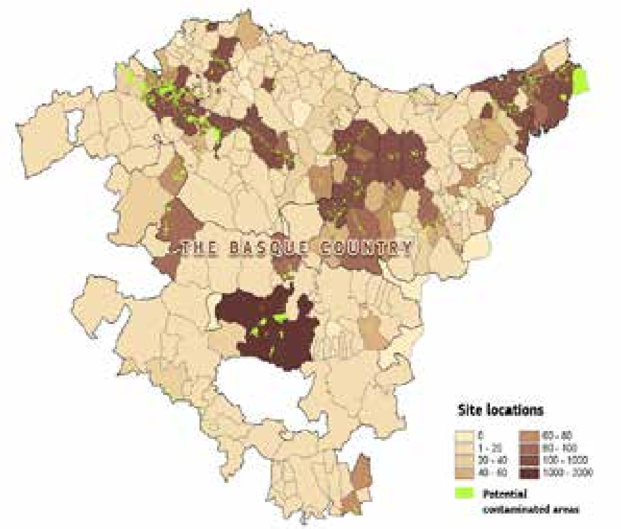
The Autonomous Community of the Basque Country is a small region in the north of Spain with a significant industrial legacy in the form of contaminated land. Ever since the first serious case was detected, numerous sites have been investigated and remediated and whose problems could be described as part of this document. Nonetheless, we have opted to try to provide an overview of what we consider to be the key points of our policy, the inspiration for which comes from those earlier policies in the task of protecting the land, in the hope that others may likewise benefit from our experience.

Keywords: *Basque Country, Bilbao River Estuary, contaminated sites policy, industrial estates, lindane.*

Introduction

With a surface area of 7 235 km^2 and just over 2 million inhabitants, the Basque Country can be considered as an example in how to manage contaminated land at regional level. That management is based on a policy that emerged out of the need for revival and for reinvention after a deep economic crisis that during the 1980s led to the dismantling of much of the industry, particularly the heavy industry, on which the economy had been based up until then. We were only able to see the tip of the iceberg at that time, but the very nature of our country allowed us to sense that this issue could be sufficiently large to require a specific policy. Early industrialisation based on metallurgy, a lack of environmental awareness up until then, mountainous terrain that leaves little space for uses to be developed and disorderly urban planning resulted in a land degradation scenario that could have hindered the economic upturn. The Basque Country's industrial past and present has left a negative legacy of 12 351 potentially contaminated sites that cover 9 337 ha, i.e. 1.1% of the total surface area and 67% of the land occupied by economic activities

Twenty-five years later, we can now claim that the miracle of regenerating the main degraded zones has been successful, although there are still challenges that need to be addressed. Not a single one of the envisaged measures has come to a standstill due to a lack of viable solutions. Many of them would be worthy of special mention. However, if there is something that we can share it is not the way measures have been taken at specific sites, but rather what we consider to be the keys to the success of an environmental policy that has not been straightforward to implement. We have sought to classify our problems in sufficient detail, extract their specifics, look around in search of solutions, adapt them to our situation and design flexible solutions. We have not invented anything — we do not have huge resources to do so — but we have managed to make some progress, often with the help of other countries and regions that



The Basque Country's industrial past and present has left a negative legacy of 12 351 potentially contaminated sites that cover 9 337 ha

are ahead of us in this task to protect our main asset, the land. Our thanks go to all of them.

The strategy

The fundamental points/best practices of the contaminated land managemnt policy in Basque Country

Twenty-five years of work, from when the first serious case of what we now call 'land contamination' was identified, has taken the Basque Country to a point where highly important events have come together for the future of the policy to protect and efficiently use this resource. First of all, a new Prevention and Correction of Land Contamination Act was passed on 25 June 2015, 10 years after the enactment of the first specific Basque legislation in this area. Second, we have embarked on the preparation of a new plan on a timeline for 2020 and 2030. Finally, there is the government's mandate to prepare a strategy to protect, conserve and restore the natural functions and use of the land. These may be considered as modest advances. Nonetheless, reflection on the key issues that have brought the Basque Country to this scenario, and some examples of which are considered briefly below, could encourage others to address the challenge of protecting the land and the services that it provides us.

The results

Legislation endorsed by experience

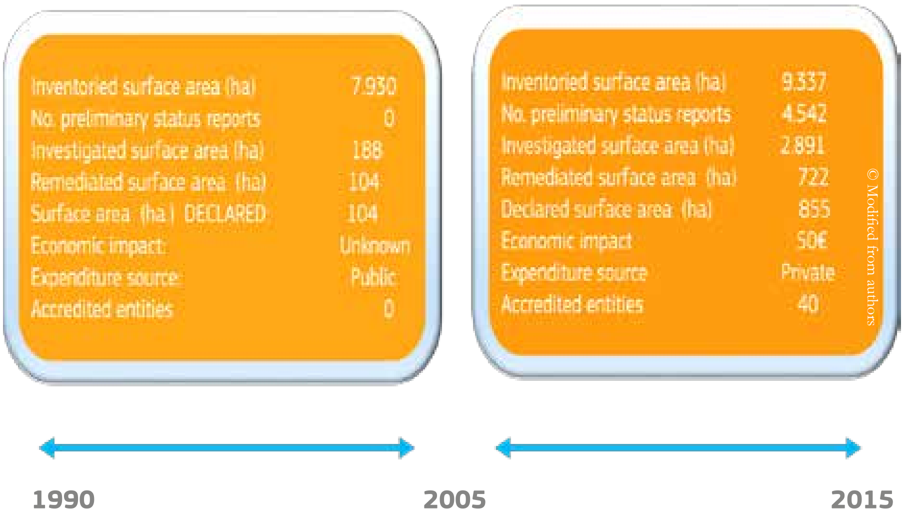
We needed 10 years to produce a comprehensive legal text that could be submitted to the parliament for its approval. For a long time, the interventions on contaminated land and the routine work led to contributions that seemed as if they were never going to enable us to fulfil the goal of producing legislation that was eternally at the draft stage. Requiring intervention at potentially contaminated sites without the support of legislation is hard and sometimes disheartening work. However, the specific characteristics of this setting and, specifically, the fact of being the only environmental compartment subject to private property, permit something that is unthinkable in other areas of the environment: progress in a scenario outside the law exclusively using market dynamics.

The 10-year perspective after the passing of the first Basque legislation in this area has enabled us to understand that legislation would have been of little use without the guarantee of experience and reflection that requires solutions to be found for problems that are so different and varied that it is difficult to systematise them. Just as it would not have been of use without many other management, economic and technical instruments where the different stakeholders and, above all, those that had the expertise, provided input for their preparation right from the start.

Solution adapted to the essence of each set of problems

There are clearly many ways in which to classify the problems and, according to those ways, the strategies and tools developed will also be different. The three classic dimensions are proving to be lacking to describe a system where numerous variables come into play. An attempt could be made to design a set of tools as complex as the problem. However, in the case of the Basque Country, the decision was made for an initial, very simple classification, but one which has proved to be very useful at least in the medium term. On the one hand, the aim is to address in a different fashion those sites earmarked for urban development purposes, where the introduction of new uses will allow the investigation and remediation work to be financed, and, on the other hand, to deal with those other non-market sites where only the intervention of the public authorities may lead to their remediation. In the first of the cases, its success lies in the introducing in the legislation of required automatic mechanisms at the start of the land declaration procedure (investigation).

BEFORE AND AFTER THE PASSING OF THE ACT



Inventoried surface area (ha)	7.930
No. preliminary status reports	0
Investigated surface area (ha)	188
Remediated surface area (ha)	104
Surface area (ha) DECLARED	104
Economic impact:	Unknown
Expenditure source:	Public
Accredited entities	0

Inventoried surface area (ha)	9.337
No. preliminary status reports	4.542
Investigated surface area (ha)	2.891
Remediated surface area (ha)	722
Declared surface area (ha)	855
Economic impact	50€
Expenditure source	Private
Accredited entities	40

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> “So far, *is the government’s mandate to prepare a strategy to protect, conserve and restore the natural functions and use of the land.*”

The change of use, the intention to expand or establish a new activity, earth movement/excavation or the end of the potentially contaminating activities are some of the cases where the mechanism is triggered without the intervention of the environmental authority being necessary. This mechanism, linked to the local councils being prohibited from issuing the relevant planning permission if the declaration has not been submitted, led at the very time of passing the legislation to an exponential increase in the sites investigated and remediated.

When the potentially contaminated sites are in rural settings that are not of interest for urban development, mainly illegal landfills that are currently abandoned, the solution requires a more systematic and gradual approach supported by the authorities. In short, this approach has included the following aspects:

- The legal status of the abandoned former landfills as contaminated land, which thus allows the application of more flexible tools than those laid down by landfill legislation, such as risk analysis or remediation techniques.
- The classification of the landfills according to a multicriteria prioritisation system in two independent lists according to the type of property, whether it is public or private.
- The research and design of risk reduction measures (if necessary) for the public landfills that are the priority for the environmental authority. Subsidies have been set up for the local authorities owning those landfills to guarantee the adoption of the measures.
- The implementation of monitoring and control campaigns for the private priority landfills by the environmental authority in order to obtain data in order to demand responsibility from polluters and owners.

Land protection criteria integrated in other policies

Despite the progress regarding the policy to manage contaminated land in recent years, including integration of areas with track record and deployment, it is still needed a better integration an cost-effective mechanisms.Special mention should be made of the following examples.

This way of working involves great coordination in order to move past a single approach to land protection from the environmental perspective towards a multiple approach involving numerous agents from different spheres, such as health, water protection, food safety, urban development, etc. The path for cooperation is slow and not without difficulties, but the results more than compensate for them. The key is to initially identify common goals without imposing a unilateral approach.

INTEGRAL SOLUTION SUMMARY

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> ***"Multiple approach** involving numerous agents from different spheres, such as health, water protection, food safety, urban development, etc."*

Integral solutions for problems with shared common characteristics

Even though a significant part of the interventions on potentially contaminated land have been carried out on an individualised basis, problems requiring integral/global solutions have emerged throughout the history of the contaminated-land policy of the Basque Country. The design of these solutions has involved a greater degree of reflection and involvement in a process from which lessons learnt have been extracted that could be extrapolated to other situations. Some examples that they share are mentioned below.

A geographical location: Bilbao river estuary.

The industrial crisis of the 1980s left Bilbao, and specifically along its river estuary and in its metropolitan area, with the highest concentration of potentially contaminated sites in the Basque Country. The plans

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Bilbao river estuary at the height of its industrial activity

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designed at that time to become the drivers of the urban and economic regeneration of the Gran Bilbao greater metropolitan district clashed with this circumstance when major economic initiatives exposed a problem that had been largely ignored up until then.

The construction of the Guggenheim Museum, the new Conference Centre and Music Hall, the expansion of the airport, shopping centres and new industrial areas dedicated to technological activities or the then new compact steelworks, among other initiatives, required measures that would ensure that the land was able to host the new uses. Yet what were the key points that made that measure possible?

- The political impetus emerged out of the need that led to broad and efficient interinstitutional cooperation (Basque government, provincial councils, local councils, publicly owned companies, etc.).
- The setting-up of an organisation dedicated to regenerating the zone that aligned interests, but that also identified the opportunities and resources that the different parties, both public and private, involved could contribute to the success of the project.
- A combination of 'productive' uses in order to obtain funds to finance the environmental regeneration and other community uses of services that revealed the possibility of using urban development as a source of funding.
- Large-scale showcasing of the benefits of environmental intervention.

The current economic crisis has slowed down city construction and therefore the remediation of the contaminated sites. The action time has been extended in zones where there are still interesting initiatives such as Zorrozaurre, with a master plan after which the design of the architect Zaha Hadid was chosen, with 30 ha in which approximately 70 potentially contaminated plots were located. Current economic circumstances have given us time, something that was scarce at other times of hectic urban development. This is time that

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Area showing waste industrial material.

has to be used to look for new solutions; in this case, to consider innovative procurement strategies seeking the agreement of the largest number of stakeholders involved in this case.

A major type of contamination; waste from the production of the pesticide lindane

Two plants used to produce the pesticide lindane for over 40 years were responsible for generating over 80 000 t of waste, which, except for the 5 000 t in its pure state discovered in one of the plants after it closed, was dumped haphazardly at an indefinite number of sites. The identification of this as a key problem to protect the environment of the Basque Country resulted in the preparation of a global work strategy that included the following tasks:

- An exhaustive inventory of the possible dumping points that detected 33 very different hotspots.
- Detailed characterisation of each and every one of the sites.
- Research and development to look for the best solutions.
- Designing, constructing and commissioning of a basic catalytic dechlorination plant to treat 5 000 t of waste in its pure form.
- The construction of two safety cells that house the waste mixed with soil and other types of waste from three sites in one of them and from four in the other. In situ confinement was carried out in five cases, while monitoring and control plans were designed for the remaining 11 once it was established that there were no unacceptable risks.
- Defining a financing strategy that included obtaining funds from different sources (polluters, owners of the land, the EU and the Basque government) by means of mechanisms that were innovative at the time in some cases, such as deferred payments by means of capital gains for those owners of sites where productive use is not foreseen in the short-term but is foreseen in the future. This mechanism meant involving the local councils that had not tried it out up until then.
- A participation and communication strategy for the stakeholders, including the general public.

A management problem; industrial estates

The disappearance of heavy industry after the economic crisis in the 1980s caused a significant change to the structure of the Basque industrial fabric. To understand this change, it should be remembered that 95% of companies overall can be classified as micro-companies (0-9 workers). Industrial land that was home to heavy industry in the past and even some landfills located in peri-urban areas have been replaced by industrial estates which are home to many of these small and medium-sized companies. The legal obligation to obtain a soil-quality declaration at the start of the activity, failing which the relevant planning permission will not be granted, led to the discovery and in some cases the remediation of small plots within those industrial estates. It could soon be seen that the environmental improvement of these actions was irrelevant for most of the potentially contaminated area, as well as being a disproportionate economic burden for the owners, most of whom were not the polluters. Given this situation, the Basque government designed and funded an investigation programme for industrial estates built before the Prevention and Correction of Land Contamination Act 1/2005 came into force, which has led to the streamlining of the formalities to set up new industrial activities once the quality of their land has been declared on 32 of those estates deemed to be priority.

An approach based on protecting sensitive areas

The urban regeneration policy that is followed sometimes produces a feeling that other sites —located in eminently natural areas with the potential to affect priority protection targets such as consumption of water or protected natural area ecosystems — are being abandoned. This is a perspective that requires greater intervention by the administration and that has slowed down in the Basque Country due to the economic crisis, but that nonetheless remains as one of the priority approaches for

Area of intervention before remediation works, Bilbao river stuary.

Area of intervention after remediation works, Bilbao river stuary.

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the planning of new land protection measures. Nonetheless, several sites have so far been returned to the natural environment once decontaminated. One such example is a large hydrocarbon storage area that has recovered its saltmarsh status, with the ensuing recovery of the local ecosystem from prior to the implementation of the industrial activity.

The conclusions

Despite the limitations and the key areas for improvement in the sphere of managing contaminated land, the policy implemented in the Basque Country has driven the intervention in 2 072 sites, leading to 855 ha being authorised for new uses, 75% of that area being for new commercial and industrial activities, 12% for residential zones and 7% for community spaces. Some 53% of land found to be suitable for a use is based on an exploratory study (1 098 investigations) and 47% on a detailed investigation (998 investigations), and remediation work has been necessary in 35% of the cases (722 sites). In addition, 27% of the sites where action has taken place are located in areas of hydrogeological interest. Regarding artificialised land, even though there has been a relative growth of 30% in this period, land reuse has enabled this growth to be cut by 5%. Beyond the exclusively environmental results, the activity in this area has allowed a sector to be established that has created 365 direct and 450 indirect jobs in the Basque Country, fundamentally by means of the investigation and remediation of contaminated land. New instruments, mainly legislation, have led to a new scheme for expense sharing in which the private sector assumes a very high percentage of the investigation and remediation costs. These are only modest numbers, but they are part of the Basque environmental policy for more ambitious targets that go beyond managing contaminated land. The efficient use of land as a resource, its integral management and the consideration of the services of the ecosystems in relation to other policies will undoubtedly be the basic concepts underpinning our next steps.

Further readings

Relevant websites:

http://www.ingurumena.ejgv.euskadi.eus/r49-579/es
https://www.ihobe.eus

Historical achievements

3. From remediation to re-industrialization: state of play in Italy, problems and proposals

LOCATION	Italy
POLLUTANT	Unspecified
SOURCE	Industrial waste
GENERAL CLEAN UP OBJECTIVES	Reduce soil contamination
REMEDIATION ACTIONS	Biopile, ECRT, phytoremediation, TPE, inerting, ISCO, MPE, soil vapor extraction, soil flushing, thermal desorbtion, bioventing land farming, soil washing, biosparging, excavation and disposal
SITE/END USE	Industrial activities, exploratory study, research, supporting legislation
SOCIAL-LEGAL ISSUES	Land remediation, relaunch economic and industrial activities
KEY LEARNING/ EXPERIENCE TO SHARE	Private sector engagement, investigation and advanced remediation techniques, cost-effective remediation solutions

Author's profile

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Giulio Molinaro is currently working at the Industrial Affairs Department of Confindustria, the main association representing manufacturing and service companies in Italy. He holds a professional Master's Programme (2nd level) in "Engineering and environmental economy and territory" and a Master's degree (second cycle) in "Environment, development and territory economics" – with honor - from university of Rome "Roma Tre" .

From remediation to re-industrialization: state of play in Italy, problems and proposals

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Confindustria published in September 2016 a working paper providing an assessment of the environmental policy for land remediation in Italy from the regulatory/procedural standpoint (Chapter 1), as well as from the technological and economic point of view (Chapter 2 and 3), identifying, in the final Chapter 4, a number of key factors to foster remediation and to relaunch economic and industrial activities.

Keywords: *remediation, technology, Italy, impact assessment, Site of National Interest (SIN), Site of Regional Interest (SIR).*

Introduction

Since 2009 Confindustria, the main Italian business Association, has carried out studies in order to give its contribution to overcome the critical issues that have prevented the progress of land remediation in Italy and, as a consequence, the achievement of a good level of environmental protection and citizens' health as well as the activity and the development of the Italian industrial system. More recently, Confindustria has published in September 2016 a new working paper providing an assessment of the environmental policy for land remediation in Italy from the regulatory/procedural standpoint, even with respect to the proposals made at the time (Chapter 1). Furthermore, this new positioning paper is distinguished by a new "multi-disciplinary" approach that aims at broadening the analysis also to the technological and economic / financial aspects (Chapter 2 and Chapter 3) to better value, in new regulatory/procedural proposals (Chapter 4), the opportunities for industrial development and innovation resulting from the remediation policies of polluted sites.

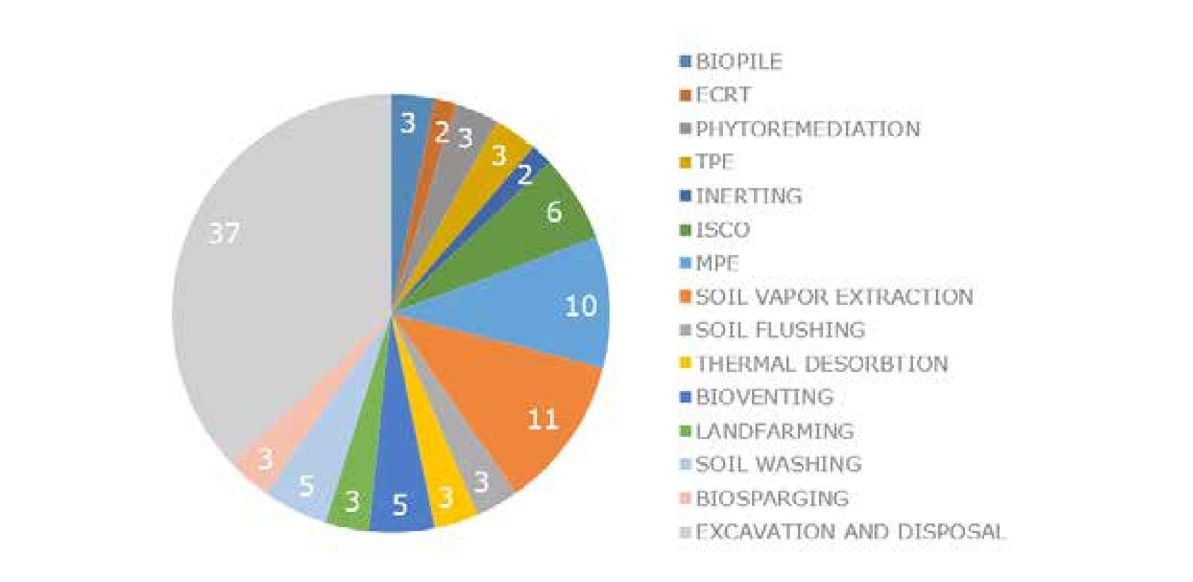
The strategy

Regulatory framework on land remediation in Italy

In Chapter 1, the paper analyzes the latest regulatory framework concerning land remediation which, in line with the proposals made by Confindustria, pursues the objective of revitalizing the processes of remediation and re-industrialization, in coherence with the concept of sustainability. The regulatory measures introduced up to now in Italy in terms of simplification and compatibility between production and remediation activities have begun the regulatory framework reform process, which, however, cannot be said to be completed. Therefore, this document defines some legislative proposals, with the hope to give a useful contribution to the identification of the critical issues faced by operators and the relative proposals in order to overcome such issues.

State of play technologies

In Chapter 2, the document briefly analyzes



Percentage of different remediation activities in the reference sample

the state of play of the dissemination of technologies used in Italy for the remediation of the Sites of National Interest (SIN), in order to provide evidence of the Italian industrial system positioning in the technological innovation road-map and in the practical application of the know-how that has been achieved in this field (Paragraph 2.1).

Within a national context where the progress of remediation procedures in the SINs appears to be diversified, but mostly to be implemented (paragraph 2.2), Confindustria has made a survey of the kind of actions undertaken in these sites with the contribution of its associations and enterprises.

According to the reference sample (about 11% of the total area within the industrial SIN) more than 50% of the remediation activities is located ex situ, mainly through excavation and disposal (see piechart page 49 and 50): a choice that is ineffective from an environmental perspective and inefficient from an economic point of view, but which is currently widespread due to some of its benefits such as, above all, a reduced implementation time with regard to, for example, in situ technologies (Section 2.2.2 and Section 2.4 – See graph above page 51).

Hence, the hope is that, thanks to this first analysis, Confindustria will be able to contribute in promoting effective technologies having less impact and minor costs in comparison with the use of disposal operations, relying on the high weight of made in Italy in the chain of remediation activities (see Table page 53).

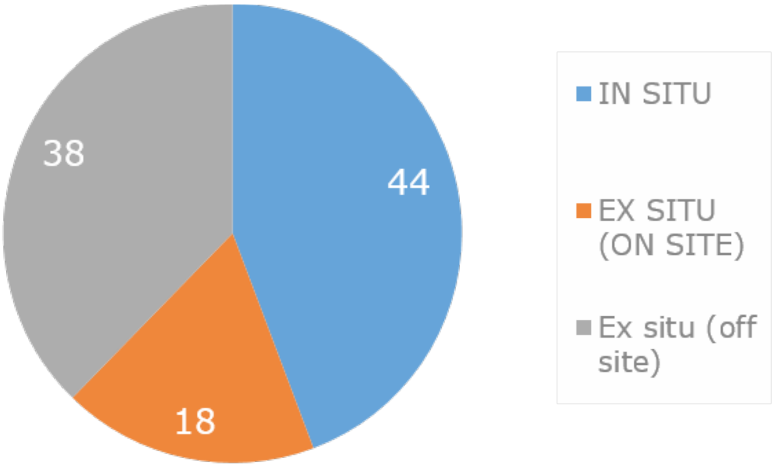
Economic impact assessment of investments in remediation

The objective of this analysis is to highlight the net social cost of remediation investments considering the positive effects in terms of increase of output growth and added value, impact on employment and the benefits in terms of public revenue from direct and indirect taxes and social contributions.

Net social cost is a monetary measure of social well-being to which benefits deriving from the recovery of contaminated areas, re-use for economic and social purposes, and health benefits must be added.

This theoretical exercise proposes an estimation of the net social cost for the remediation of almost all SINs (Chapter 3, Paragraph 3.1).

In order to estimate this net social cost, the study starts from an estimation of the total cost of remediation investments for all the considered industrial areas (about 6.6 B € for about 31 000 ha) and public areas (a total cost of about 3.1 B € for approximately 15 000 ha). Over the next 5 years, according to Confindustria



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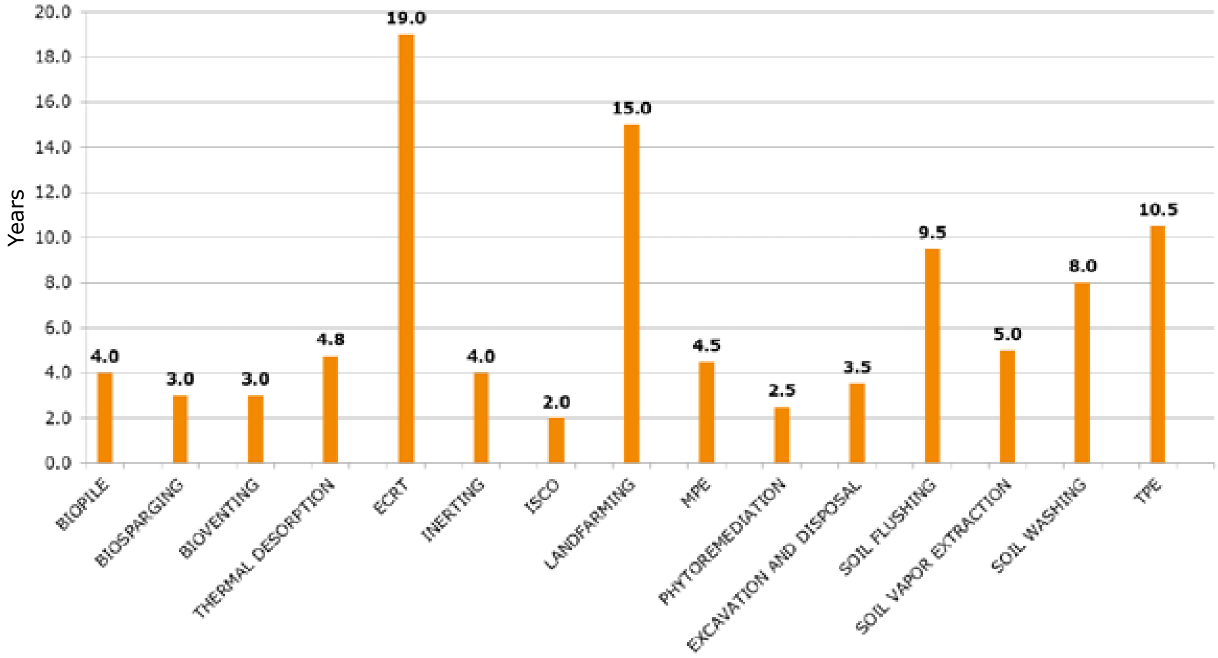
Percentage of different kind of remediation activities (in situ, ex situ (on-site), ex situ (off site))in the reference sample

Economic research Department, this investment could generate an increase of the output of over 20 B € and an increase of the overall added value of about 10 B €. In addition, the model estimates an increase of about 200 000 standard work units. These macroeconomic effects can be translated in an annual average variation around 0.13% for the production and 0.136% for the added value. Taking into account that the average growth of Italian industrial production and of added value were roughly negative over the last five years (-1.27% and -0.6% understood as average annual changes), a widespread revival of remediation investment could provide a definitely positive economic impact. Furthermore, the effects in terms of revenue for the government were considered. In the period taken into account, the financial impact in terms of overall revenue could be estimated in more than 1.6 B € in terms of direct taxes and about 1.7 B € in terms of indirect taxation, plus a total increase of more



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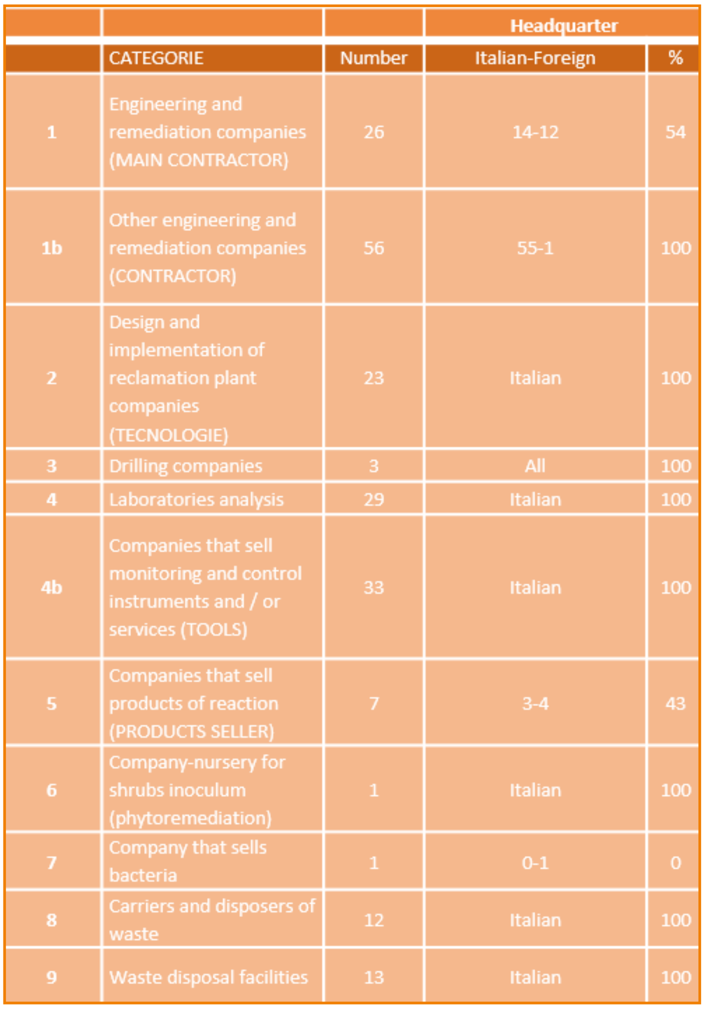
Average implementation time (end of remediation procedure) for each remediation activities in the reference sample (years).



			Headquarter	
	CATEGORIE	Number	Italian-Foreign	%
1	Engineering and remediation companies (MAIN CONTRACTOR)	26	14-12	54
1b	Other engineering and remediation companies (CONTRACTOR)	56	55-1	100
2	Design and implementation of reclamation plant companies (TECNOLOGIE)	23	Italian	100
3	Drilling companies	3	All	100
4	Laboratories analysis	29	Italian	100
4b	Companies that sell monitoring and control instruments and / or services (TOOLS)	33	Italian	100
5	Companies that sell products of reaction (PRODUCTS SELLER)	7	3-4	43
6	Company-nursery for shrubs inoculum (phytoremediation)	1	Italian	100
7	Company that sells bacteria	1	0-1	0
8	Carriers and disposers of waste	12	Italian	100
9	Waste disposal facilities	13	Italian	100

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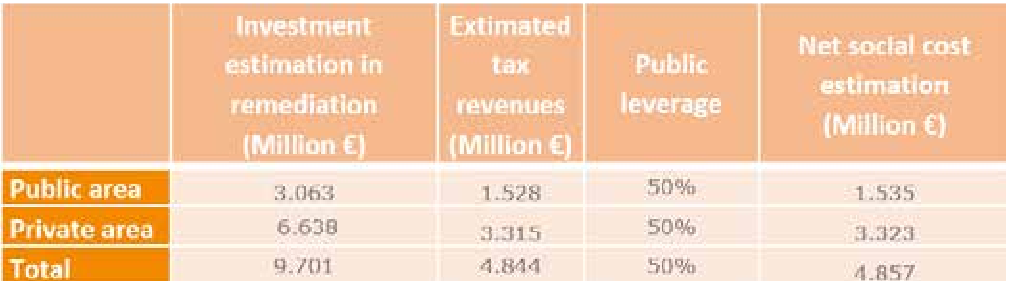
Qualitative examination of the chain of reclamation in the reference sample.

than 1.4 B € in terms of social contributions. Therefore, a social cost for remediation investments of about 10 B € could generate approximately 5 B € of public revenues. If we consider that this investment is made by the government, we estimated that the actual net cost to the community almost halved is equal to about 5 B €. In other words, for every euro of investment in clean-up activities, the public sector will obtain a value of about 0.50 € (see table above).

For sake of clarity, it is important to underline that this analysis does not take in account social benefits arising from the environmental recovery of the contaminated areas and the potential for further economic development that would result in terms of redevelopment, industrial reconversion and reindustrialization.

At the same time, this study is focused on collecting useful data to provide economic evidence for approximately 1 B € about the will of the industry to boost industrial or economic activity (Section 3.2). Furthermore, the study contains an overview about some public financial instruments (European as well as national) put in place in order to support remediation and relaunch of economic/ industrial activities (paragraph 3.3): it highlights the need of an afterthought in the public-private relations to target the resources needed. Indeed, in addition to being characterized by some limiting factors from a procedural point of view (summarized in Chapter 4), these tools should be more proportionate to the necessary resources which, for the single phase of the SIN remediation (without taking into account sites of regional competence - SIR), are estimated, as already seen, at about 10 B €.



	Investment estimation in remediation (Million €)	Extimated tax revenues (Million €)	Public leverage	Net social cost estimation (Million €)
Public area	3.063	1.528	50%	1.535
Private area	6.638	3.315	50%	3.323
Total	9.701	4.844	50%	4.857

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Private/public economic evidence related to the investment in remediation.

Conclusions

In the conclusion chapter (Chapter 4), the study identifies a number of key factors to foster remediation and to relaunch economic and industrial activities, that is:

1. Taking into account the supply of financial resources, thinking of incentive mechanisms that the government could make available to the private sector for the phase of remediation and relaunch of economic/industrial activities production (Section 4.1).
2. Take action on the demand of financial resources, through proposals that make recovery easier in order to reuse the contaminated areas (section 4.2).
3. Proposals for rationalization and simplification of remediation and reindustrialization procedures (section 4.3).
4. Proposals to promote the use of in situ and innovative technologies other than excavation and disposal (section 4.4).

Further reading

- Relazione sugli interventi di sostegno alle attività economiche e produttive - Ministero dello Sviluppo Economico - Direzione generale per gli incentivi alle imprese – DGIAI (settembre 2015).
  SuRF Italy (2015), Libro Bianco "Sostenibilità nelle Bonifiche in Italia":
  http://www.surfitaly.it/documenti/SuRF_Italy_Libro_Bianco_rev_Ottobre2015.pdf

Relevant websites

http://www.bonifiche.minambiente.it/decisorie_2012_.html
https://frtr.gov/matrix2/section3/table3_2.pdf
http://www.bonifiche.minambiente.it/contenuti/Iter/Presentazione_2016_W_30_062016.pdf
http://www.bonifiche.minambiente.it/page_adp_SIN.html
http://www.claire.co.uk/projects-and-initiatives/surf-uk
http://www.confindustria.it/wps/wcm/myconnect/
http://www.confindustria.it
http://ec.europa.eu/eurostat/en/web/products-datasets/-/ENV_AC_EXP2
http://www.invitalia.it/site/new/home/cosa-facciamo/rilanciamo-le-aree-di-crisi-industriale.html
http://www.isprambiente.gov.it/files/temi/matrice-tecnologie-ispra-rev050908.pdf
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http://www.nicole.org
http://www.surfitaly.it/
http://www.sustainableremediation.org/
http://www.umweltbundesamt.at/eurodemo

BROWNFIELDS

BROWNFIELDS

1. Belgium: paepsem Newton - Park.
2. Belgium: from one euro to the most expensive remediation case in Flanders ever
3. Finland: restoration of Penttilänranta area, Joensuu, methods in national programs
4. France: securing a polluted site by removing and treating the source of pollution, in the town centre of Pont-à-Mousson
5. Spain: remediation technologies of contaminated soils, developed in Andalusia
6. United Kingdom: sustainable remediation building the London Olympic Park

Brownfields

1. Belgium: Paepsem Newton – Park

LOCATION	Anderlecht, Belgium
POLLUTANT	Chlorinated solvents
SOURCE	Industrial battery production facilities
GENERAL CLEAN UP OBJECTIVES	Reduge groundwater and soil contamination
REMEDIATION ACTIONS	Non specified
SITE/END USE	Enterprise park for SME and offices supply, cultural and recreational activities
SOCIAL-LEGAL ISSUES	Polluters unknown, bankrupt or otherwise unable to clean
KEY LEARNING/ EXPERIENCE TO SHARE	Successful formula where project sponsors receive subsidies for depolluting the land as well as integrated business support

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Saïd El Fadil, PhD in geochemistry and geology from University of Brussels. First advisor for Tauw and now Manager of the soil division at Brussels Environment.

Paepsem – Newton Park, Belgium

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Clean-up of soil contamination is essential, because it allows many abandoned sites in Brussels to be rehabilitated, giving them a second chance by repurposing them for new economic, residential and recreational activities. Consider the example of the new Newton SME Park in Anderlecht, which in 2006 was found to be affected by significant soil and groundwater pollution by chlorinated solvents.
It was then that the idea of building an SME park on this site took shape, and Citydev.brussels wasted no time in initiating the process that would make this project a reality.
This type of example therefore proves that a contaminated parcel of land can be turned into an opportunity for the installation and development of new projects that have a positive impact on the region.

Keywords: *Contaminated soils, economic development, social development, remediation, pollution, Brussels, environmental performance, brownfields, ERDF.*

Introduction

We all know that soil contamination currently constitutes a significant problem, particularly within the Brussels Capital Region. Indeed, the industrial era in Brussels resulted in a considerable number of contaminated parcels of land. The soil inventory carried out by Brussels Environment at the end of 2015 recorded 14 193 parcels of land, 9 091 of which are potentially contaminated, 2 870 contaminated, 1 193 mildly contaminated and 1 039 uncontaminated.
This situation sometimes leads to the delay or hindrance of real estate transactions or economic projects, thereby impeding the region's social and economic development. This is why the clean-up of soil contamination is essential, because it allows many abandoned sites in Brussels to be rehabilitated, giving them a second chance by repurposing them for new economic, residential and recreational activities. Consider the example of the new Newton SME Park in Anderlecht, which in 2006 was found to be affected by significant soil and groundwater pollution by chlorinated


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Inside area of a battery production facility.


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Industrial wasteland before the Paepsem development

solvents. At the time, the site was an industrial brownfield owned by the Public Social Welfare Centre of Brussels and rented by Citydev. brussels. It measured just under 38 000 m² and had been used as a battery production facility. It was then that the idea of building an SME park on this site took shape, and Citydev. brussels wasted no time in initiating the process that would make this project a reality. The region and Europe (by means of ERDF grants) contributed to funding the project, both for construction and for soil remediation. When construction was finished, the Newton SME Park was inaugurated on 14 February 2014. Its 5 540 m² in single-storey workshops divided over two buildings provides room for 16 workshops that are adaptable from 250 m² to 500 m² each. This project corresponds to several specific objectives, because it encourages economic stakeholders already present in the area to remain


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Newton SME Park


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Industrial wasteland before the Paepsem development

in place, all while supporting plans to bring back activities that had previously migrated elsewhere. Through the businesses that take up residence there, the Newton SME Park aims to create jobs that correspond to the socioeconomic profile of those living in the priority intervention zone. Furthermore, the ERDF funding granted to the project also aims to create low-skilled employment in the areas receiving support. The Newton SME Park should in time allow 220 new jobs to be created.

Lastly, it should be noted that a significant degree of environmental performance was attained, with the goal being to reduce the project's carbon footprint, save energy, reduce the environmental impact and make it a good aesthetic fit within its environment. In this way the area's economic activity can receive a boost, while respecting and improving the quality of life in the neighbourhood. This type of example therefore proves that a contaminated parcel of land can be turned into an opportunity for the installation and development of new projects that have a positive impact on the region. The contaminated-soil policy implemented and defended by Brussels Environment is therefore essential to obtaining sustainable development that takes into account all of the environmental, social and economic factors that drive the Brussels Capital Region.

Further readings

http://ec.europa.eu/regional_policy/en/funding/erdf/
http://www.citydev.brussels/FR/main.asp
http://www.environnement.brussels/thematiques/sols-0

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Entrance of Newton SME Park


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Buildings of Newton SME Park

Brownfields

2. Belgium: from one euro to the most expensive remediation case in Flanders ever

LOCATION	Bekaert, Dendermonde and Zeebrugge, Belgium
POLLUTANT	Heavy metals, ar, oil, PAH, BTEX, cyanides and asbestos
SOURCE	Industrial and military sites, storage, transhipment and coke factory
GENERAL CLEAN UP OBJECTIVES	Reduce groundwater and soil contamination
REMEDIATION ACTIONS	Legal instruments, sale for one symbolic euro
SITE/END USE	On site thermal and biological soil remediation
SOCIAL-LEGAL ISSUES	On site thermal and biological soil remediation
KEY LEARNING/ EXPERIENCE TO SHARE	Protocol agreement providing solutions to ensure the start up of soil investigation and remediation

Author's profile

Eddy Van Dyck Head of Department OVAM Graduate as (hydro)geologist at the University of Ghent in 1979. Worked 1979-1987 as research assistant at the Chair for Engineering Geology and Hydrogeology of the University of Ghent on: groundwater production and groundwater contamination and vulnerability maps. Employed at OVAM, since 1987, initially as geologist and now as Head of Department (director). He is member of the Management Committee of OVAM.

Johan Ceenaeme staff advisor soil remediation policy and expert for policy and legislation on soil and sediment contamination at OVAM. He has an educational background as agricultural and environmental remediation engineer. In 1991, he worked as environmental editor on environmental policy. From 1995 to 2000 he joined OVAM, first as responsible of soil investigations and later as head of the service. In 2009 he became acting administrative judge for the Council of environmental enforcement. Nowadays he works as policy coordinator and advisor for the two soil departments of the OVAM.

Tim Caers project manager and policy officer at OVAM (Public Waste Agency of Flanders). Graduated in 2002 as a bio-engineer, specialised environmental technology and soil conservation. He started his career as a case officer in soil investigation at the OVAM, the competent authority for waste, material and soil management in Flanders, Belgium. Tim's currently main focus is unlocking redevelopment of brownfields and blackfields by developing customised solutions for the soil contamination on a project and policy level.

Author's profile

Youri Mertens, project manager at OVAM, graduated in 1988 as chemical engineer. He started as nucleaire technologie professor at the Industriële Hogeschool Hasselt. In 1991 he joined OVAM, the competent authority for waste, material and soil management in Flanders, Belgium as a case officer in soil remediation. He stood at the cradle of Flemish soil remediation policy and started up some of the first soil remediation actions by the Flemish authority. Youri's currently main focus is unlocking redevelopment of contaminated sites by developing customised solutions for the soil contamination on a project level.

An Eijkelenburg, project manager and policy officer at OVAM, graduated in 2001 as engineer-architect and in 2003 as a master in water resources management. In 2001, she started as a researcher at the Katholieke Universiteit Leuven. Between 2005-2010 she worked in the Belgian development cooperation as an expert in water. She joined OVAM in 2010 supporting internal analysis and studies. Since 2015, she focus on redevelopment of brownfields and blackfields by developing customised solutions for the soil contamination, seeking opportunities to integrate sustainable development and the circular economy in pilot projects.

Katleen Jansen, case officer at OVAM, graduated in 1995 as a bio-engineer, specialised soil science. As a researcher at the Department of Applied Geology at the University of Hasselt (Belgium) she worked on questions of soil and groundwater contamination from 1995 until 1997. Since 1997 she works as a case officer for OVAM, the competent authority for waste, material and soil management in Flanders, Belgium. Katleen has experience in complex land contamination issues and she is an expert in company-specific agreements.

Bavo Peeters, works as an international policy officer for OVAM and acts as its representative in the EU expert group on soil protection and in the Common Forum on Contaminated Land.

From one euro to the most expensive remediation case in Flanders ever, Belgium

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Although the Flemish soil remediation policy features very strict and enforceable investigation and remediation obligations, it also offers room for flexibility and margin for negotiation when necessary. In this regard we describe two flexible instruments: the company-specific agreement which allows better planning and scheduling of soil investigations and remediations in line with the company's priorities and possibilities; and the acquisition of contaminated blackfields for one symbolic euro from bankrupt companies according to the protocol agreement between OVAM and the Flemish Bar Council. Finally, we also briefly describe the clean-up of the Carcoke site, which still is the most expensive remediation in Flanders ever.

Keywords: *agreements, bankruptcy, Belgium, Carcoke, contamination, Flanders, instruments, investigation, OVAM, redevelopment, remediation, soil.*

Introduction

Flanders is a small region of about 13 500 km^2 with 6.5 million inhabitants in the northern part of Belgium. Thanks to its strategic position in western Europe, trade and industry brought prosperity and welfare to this densely populated area, but sometimes with severe environmental consequences. In the 1980s, new waste legislation was used to tackle soil contamination problems. It soon became clear that large-scale soil contamination caused decades ago needed different legal approaches than those used to deal with a small illegal waste dump. So, in 1995, the Soil Remediation Decree was adopted, which contained a number of new legal instruments to encourage soil investigation and remediation.

- 'New' soil contamination asks for a stricter approach than 'historical' soil contamination: anybody not paying enough attention to pollution prevention after 1995 would have to bear the remediation costs, while on the other hand enough flexibility was guaranteed to treat the old problems of the past in a reasonable way;
- In many countries it proved difficult to force a party (e.g. a company) to pay for soil investigation and remediation. By linking the information on soil quality (mandatory soil certificate) and the obligation to investigate sites with potentially contaminating risk activities to the transfer of land, the owner of risk-entailing land became responsible for the soil investigation and remediation, or otherwise he could not sell his property. This way new owners were legally protected and soil quality has become an important element


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Bekaert site, industrial site.

of real estate prices in Flanders.

- A distinction was made between the obligation to remediate and the liability. Discussions on liability always end up in court, may take years and cost a lot of money to be paid for lawyers. When a law clearly states who has the obligation to remediate a contaminated site, it is useless to go to court.
- All investigations have to be carried out by soil remediation experts who are certified by the government. This creates a basic quality level and facilitates OVAM's (Public Waste Agency of Flanders) duty to control and evaluate investigation and remediation reports. When the soil remediation experts underperform and their quality of work is poor, the government can cancel the certification.

The problem

Talilor-made soil management for companies: company-specific agreements.

Although since 1995 more than 37 000 exploratory soil investigations have been carried out and more than 4 600 soil remediations have been started, some companies still struggle with legal compliance because they own a lot of land with potentially contaminating risk activities. All these sites should be investigated and could require soil remediation, resulting in high costs in a very short time frame. Strict enforcement of these investigation and remediation obligations by OVAM could lead to financial difficulties or even bankruptcy, which is not a solution because the land would then remain contaminated.

> “**Soil Remediation Decree** *was adopted, which contained a number of new legal instruments to encourage soil investigation and remediation.*”

The solution

Companies owning a lot of sites with risk activities can negotiate a company-specific agreement with OVAM to better spread and plan their soil investigations and remediations in time according to a priority list, without prejudice to the provisions of the Soil Decree. Priority criteria can be, for example, the human, ecological and spreading risk of the contamination, or planned construction and infrastructure works. Each year OVAM evaluates the priority list and the progress in consultation with the company. A company-specific agreement makes soil investigation and remediation obligations manageable and financially viable for the company, while OVAM gets clear commitments bound to a strict time frame signed by the CEO. In past years, OVAM closed agreements with Umicore, Electrabel, the Manufactured Gas Plant sites, Bekaert, the national railway company NMBS, Tessenderlo Chemie, the Flemish public transport company De Lijn, Belgian Defense, the Roads and Traffic Agency and the Port of Antwerp.

The study cases

The case of Bekaert

Bekaert owns several industrial sites with potentially contaminating risk activities in Flanders. Soil investigation and remediation operations on these sites are mostly complex. To plan and schedule all these efforts and costs in line with the company’s priorities and possibilities, a company-specific agreement between OVAM and Bekaert was signed in 2000 covering a period of 10 years. Before the signing of the agreement, the severity of the different contaminations was first evaluated. Severely contaminated locations and sites subject to reconversion plans needed to be addressed first.

With the recent signing of a new agreement, additional locations were added to the schedule and strict timings were imposed on the execution of the descriptive soil investigations (within 4 years after the signing of the agreement), the preparation of soil remediation projects (within 6 years) and the start of the remediation (within 10 years).

Case: Belgian defense

Many Belgian Defense sites are contaminated by the storage and transport of fuels and products used for the maintenance of weapons. Also incidents, activities of foreign armies during and after the two world wars and military training exercises (fire, demining, shooting, etc.) have left their marks. Belgian Defense owns several sites of more than 100 ha where the surface of the risk installation is often extremely small in comparison to the total area of the site. Nevertheless, due to the risk activities the execution of exploratory soil investigations on all these sites is legally obligated but organisationally and budgetary unfeasible. Therefore, OVAM and Belgian Defense signed a first agreement which stated that all military sites with potentially contaminating risk activities first had to be mapped, and that the execution of the exploratory soil investigations could be spread over a reasonable period of time. A cost estimate to address the pollution was asked to assess the required budgets. In 2012 a second agreement was signed which scheduled the execution of all descriptive soil examinations on the military sites. A third agreement on the remediation planning will soon be negotiated.

Acquisition of contaminated sites from bankrupt companies

One of the key instruments of the Flemish soil remediation policy is the soil certificate. Whenever land is transferred in Flanders the seller is obligated to consult the Land Information Register, which is managed by OVAM, and has to hand over a mandatory soil certificate to the buyer. This document provides the buyer information on


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Industrial site in Scheldefuel in Dendermonde.

> *“A company-specific agreement makes* **soil** *investigation and remediation obligations manageable and financially viable for the company”*

the soil quality of the land that he plans to buy. On sites with (former) potentially contaminating risk activities, a soil investigation has to be carried out before the land can be transferred to the next owner. If soil contamination is detected for which further actions are required, the transfer of the land cannot take place before certain conditions are met:

- a soil remediation project has to be prepared;
- a financial guarantee has to be deposited;
- an engagement that the remediation will be carried out has to be signed.

The situation becomes more complicated when a company that performed risk activities is declared bankrupt. In that case the bankruptcy court will appoint an insolvency administrator to settle the bankruptcy, who will liquidate all assets and seek the maximum reimbursement of the company’s debts. When the bankrupt company performed risk activities, an exploratory soil investigation is needed and, if the site is contaminated, the land can only be transferred when the conditions of the Flemish soil legislation are met (cf. the three conditions cited above). Since bankrupt companies have limited financial resources, meeting these legal conditions is extremely difficult. In particular, in cases where the remediation costs outweigh the value of the land, settling the bankruptcy becomes impossible. Such sites mostly end up as abandoned blackfields. OVAM is well aware of these difficulties, and in order to unlock these unmarketable blackfields it concluded a protocol agreement with the Flemish Bar Council in 2007, which was updated in 2009 and expanded in 2016, to create instruments for the support of insolvency administrators confronted with contaminated real estate. The protocol agreement provides solutions to ensure that all necessary actions can be taken to start up soil investigation and remediation and to avoid unmanaged soil contamination and abandoned sites in the very densely populated region of Flanders.

> **“The soil certificate** *provides the buyer information on the soil quality of the land. On sites with (former) potentially contaminating risk activities, a soil investigation has to be carried out.”*

The main provisions of the agreement are:

- a procedure for the conducting and prefunding of soil investigations by OVAM on sites owned by bankrupt companies;
- the possibility to transfer unmarketable contaminated land from bankrupt companies to OVAM for one symbolic euro. In these cases OVAM takes over the obligation to remediate the site.

Prefunding soil investigations

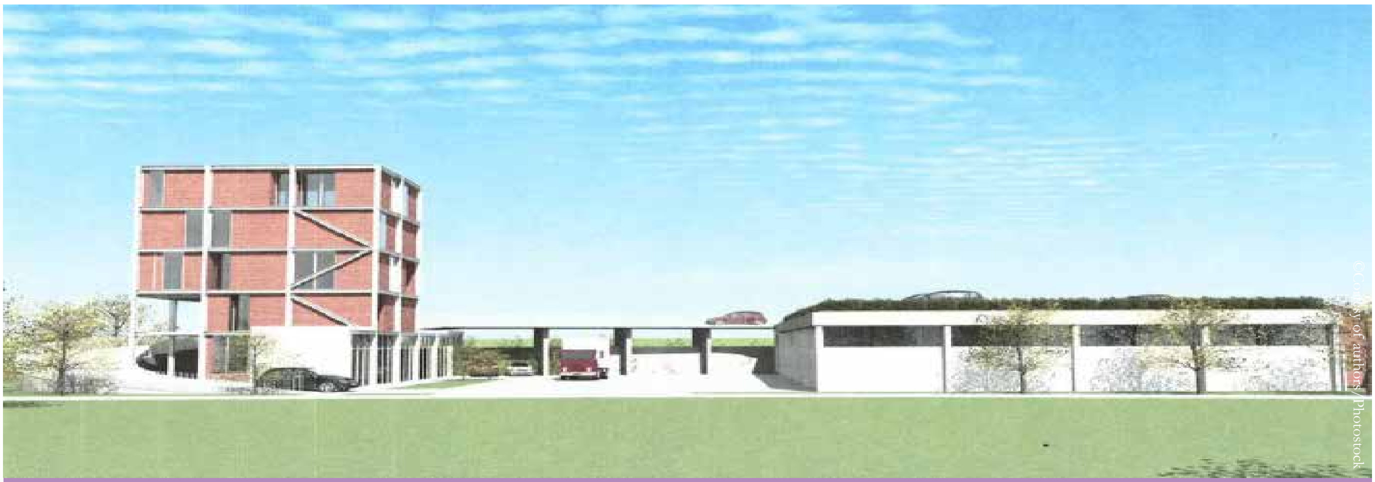
When an insolvency administrator wants to sell land with potentially contaminating risk activities, he has to conduct an exploratory and possibly also a descriptive soil investigation. Preferably, he will use the remaining assets of the bankrupt company to finance the cost of these investigations. If the resources are insufficient he can request that creditors or an interested buyer prefund the soil investigations. If none of these parties are able or willing to do this, the protocol agreement states that the insolvency administrator can ask OVAM to prefund the soil investigations. Some guarantees were incorporated in the protocol agreement to ensure that the prefunded costs are paid back to OVAM as soon as the land is sold, but in some cases the revenue generated from the sale will be insufficient to reimburse the costs. This is a calculated financial risk that OVAM is willing to take to ensure that contaminated sites don't become abandoned blackfields.

> “**OVAM** *pays one symbolic euro for the land, but finances and carries out the soil investigation, the soil remediation and all other expenses related to the land.*”

Sale for one symbolic euro

Sometimes the estimated remediation cost exceeds the value of the land, which means that the revenue of the sale of the property is insufficient to finance the remediation. In that case an insolvency administrator has the possibility to sell the contaminated land to OVAM for one symbolic euro. In order not to disturb the free market it is required that certain conditions be met before OVAM can buy contaminated land from a bankrupt company.

1. The estimated remediation costs must exceed the value of the (uncontaminated) land.
2. The insolvency administrator has to prove that no brownfield developer, real estate company or other possible buyer is interested in purchasing the land. This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Simulated scenario of the area after the reclamaition works, Scheldefuel in Dendermonde.

indicates that there is a market failure and that the site can be considered as a blackfield.

OVAM pays one symbolic euro for the land, but finances and carries out the soil investigation, the soil remediation and all other expenses related to the land. Since 2009 OVAM has acquired 13 sites from bankrupt companies. From a purely financial point of view, the balance of these acquisitions is negative for OVAM and thus for the taxpayer. However, the bigger picture is that OVAM can at least recover part of the remediation costs by reselling the remediated site. The alternative would be worse: if the site becomes an abandoned blackfield, according to the ex officio procedure, OVAM would sooner or later have to remediate the site because of the risks of the contamination. In that case, OVAM would try to recover the remediation costs from the polluter in court, but since that company has gone bankrupt OVAM would not stand a chance. Although the financial balance is negative, there are some interesting opportunities when buying a site that has to be remediated.

- As owner and manager of the property, OVAM can take all necessary decisions to enable a more thorough remediation, such as a (partial) demolition of the buildings.
- Innovative (green) techniques can be tested.
- By selling the land at the right time and under certain contractual terms and conditions, the remediation can be better integrated into the redevelopment of the site. This results in a greener and more sustainable remediation, which sometimes is less expensive.
- By negotiating certain terms and conditions with the buyer of the remediated site, other ambitions of OVAM regarding the circular economy or sustainable building can be realised.

Case: Scheldefuel in Dendermonde

In Dendermonde, on the banks of the river Scheldt, an installation for the storage and transshipment of oil was in operation until 1999. The site has a surface area of 9.30 ha. In the late 1990s soil investigations identified very severe soil and groundwater contamination with oil and aromatic hydrocarbons, which had spread to a nearby ditch and some neighbouring gardens

In 2001 the operating company went bankrupt, and an insolvency administrator was appointed to settle the bankruptcy. In order to refund the creditors the insolvency administrator tried to sell the land. At that time, however, the estimated remediation cost was 5.5 M €, while the approximate value of the site was only 190 000 € (not taking the contamination into account). Obviously there were no interested buyers. The insolvency administrator had no financial means at his disposal to remediate the contamination. Moreover, since remediation was not in the interest of the creditors, he didn't even have authority to conduct the remediation. There was no solution and the site degraded to a totally abandoned and neglected blackfield. When the protocol agreement between OVAM and the Flemish Bar Council came into force, a new opportunity arose. In 2011 OVAM bought the terrain for one symbolic euro. After more than 10 years the insolvency administrator was finally able to close the bankruptcy. On top of the one euro OVAM paid all selling and transaction costs and a limited fee for the insolvency administrator. The creditors agreed with the settlement as they acknowledged that there was no other way out of this deadlock. After the purchase, OVAM immediately demolished the building, enabling a more effective and cheaper remediation, and started the remediation of the site in 2013. At the same time, a call for buyers was launched. The selling price was not the only thing taken into account to evaluate the offers; the possibility to integrate remediation with construction activities, the sustainability of the redevelopment project and the integration in its surroundings were also considered.

Among the three proposals that OVAM received, the project put forward by the intermunicipal association DDS was evaluated as being the most valuable, so the site was sold to them. The plan is to develop an area for starting entrepreneurs and microenterprises, as this target group has difficulties finding an affordable location for their business. The strong points of the proposal were the involvement and support of the city of Dendermonde and the innovative

Signing a company-specific agreement makes soil remediation manageable.

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solutions offered to the starting entrepreneurs. The building will be constructed very consciously, with respect for the principles of sustainability (including material sustainability), and will be adaptable to changing use(rs). The contrast between the 'before' picture and the proposal by DDS shows how an instrument such as the acquisition of land for one symbolic euro can turn hopelessly abandoned and polluted sites into positive catalysts for the entire Flemish society.

Carcoke: turning a brownfield into a port

The former coke factory Carcoke was active in Zeebrugge from 1910 until 1996. During this period its buildings, soil and groundwater were severely contaminated with tar, oil, PAH, BTEX, cyanides, metals and asbestos. In 1996 Carcoke was liquidated, leaving behind one of the worst brownfield sites Flanders had ever seen. Due to this legacy and its related high costs no one was interested in buying the site. The liquidator reached an agreement with the three Belgian regions, which all had similar contaminated Carcoke factories on their territory. In Flanders OVAM received the ownership of the site in Zeebrugge, together with financial compensation from the liquidated company to finance the clean-up. In 2002 OVAM started the remediation operation in close cooperation with environmental consultants and contractors. OVAM started with the selective demolition of the old coke factory, the buildings and installations. Solid preparation ensured that waste was reduced to a minimum and building materials were recovered and recycled to a maximum. Along the way a lot of challenges were dealt with, like dynamiting chimneys or handling asbestos and bombs from the two world wars. Where possible, innovative and sustainable solutions were implemented, for example on-site thermal and biological soil remediation, use of a tractor with an airtight cabin and purifying equipment or using local solar panels and a windmill to produce green energy for the site offices and the water treatment installation. These experiences were later exploited and implemented in remediation projects all over Flanders.

Some key figures:

- > 6 000 t of hazardous waste was removed;
- > 70 000 t of building material and 15 000 t of fireproof stone was recovered and recycled;
- > 10 500 t of asbestos material was removed;
- > 20 km of pipes were cleaned;
- > 400 000 t of contaminated soil was recovered;
- > 3 km of waterways were dredged;
- > 45 000 l of contaminated groundwater was cleaned per hour.

The demolition and remediation of the Carcoke site has cost about 55 B €, which makes it the most expensive remediation in Flanders. Thanks to the extensive integration of remediation and redevelopment, 12 ha of strategic and well-located harbour area will soon be available for new economic activities.

Further reading

- Soil Remediation Decree: Flemish Decree of 22 February 1995 on Soil Remediation
- Soil Decree: Flemish Decree of 27 October 2006 on Soil Remediation and Soil Protection
- New soil contamination: soil contamination which originated after 28 October 1995
- Historical soil contamination: soil contamination which originated before 28 October 1995.

Relevant websites

http://www.ovam.be

Brownfields

3. Restoration of Penttilänranta area, Joensuu. Finland methods in national programs

LOCATION	Joensuu, Finland
POLLUTANT	Heavy metals: Arsenic, Copper and Chrome. Furans and dioxins, oil compunds creosote and PAHs
SOURCE	Industrial and military sites, storage, transhipment and coke factory
GENERAL CLEAN UP OBJECTIVES	Industrial activities
REMEDIATION ACTIONS	Reduce river and soil contamination
SITE/END USE	New small boat harbour, new apartments buildings, residential and new industrial sites
SOCIAL-LEGAL ISSUES	The City Council of Joensuu bought the area for one Euro and committed to take responsability for retoration of the area
KEY LEARNING/ EXPERIENCE TO SHARE	Restoration activities carried out under severe winter conditions, -30 °C

Author's profile

Vesa Isokauppila acts as a works manager and project manager in the field of sludge handling, waste water treatment and environmental technology. Isokauppila has solid experience in waterway remediation, both industrial and municipal sludge handling and industrial waste water treatment

Restoration of Penttilänranta area, Joensuu. Finland methods in national programs

Vesa Isokauppila, *Sito Rakennuttajat Oy Tuulikuja 2 FI-02100 Espoo, Finland,* vesa.isokauppila@sito.fi

In 2008 the city of Joensuu purchased an old sawmill area located next to the city centre by the river Pielisjoki. The size of the Penttilänranta area is about 40 ha. Before the purchase the site saw industrial activity over a period of about 100 years. Thus the soil and river sediments were quite contaminated, containing for example a lot of heavy metals and dioxins. The area was turned into a new high-quality residential area with about 3 000 inhabitants and new industrial sites.

Keywords: *area development, contaminated sediments, contaminated soil, dredging, Finland, Geotubes, industry, landfill, restoration, sludge dewatering.*

Introduction

Joensuu is the second largest city in eastern Finland, with about 76 000 inhabitants, of whom about 53 000 live in the main city area. It was founded by Czar Nicholas I of Russia in 1848, and has grown to become the regional capital of North Karelia. During the 19th century Joensuu was a city of manufacturing and commerce. Starting in 1860 local sawmills started to grow and prosper as the city received commercial rights and restrictions against industrial activities were lifted. The population has grown steadily, and with changing age structure, university, etc. the city is expected to have a need for more apartments in the future.

The Penttilä area started to develop during the late 19th century when a new sawmill was built. After some fires and other hard times a major decision was made after the First World War when it was decided to close other sawmills in the area and to centralise all this activity in Penttilä. After this the sawmill area became an important part of the city and the sawmill itself was at that time the biggest sawmill in the Nordic countries. Company also employed several hundreds of workers thus playing a big part of the economy, development and growth of the city.

The study case

The area consisted of a sawmill and impregnation area, landfill area, workers' apartments and a log pond used to store the logs in Pielisjoki, via which the lumber material was mainly delivered. Finally, after more than 100 years of activity the sawmill finally reached the end of its working life in 1988, when competition made its operation unprofitable. The area was considered to be of historically significant value and was considered to be protected. However, this discussion ended when the sawmill was once again destroyed by fire in 1996.
The decision to carry out this major development

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Penttilänranta area during its past industrial activity.

> **“The restoration** *of Penttilänranta project was one of the biggest ever done in Finland with a total budget of 21.2 M €.”*

project was made in 2000 by the city council of Joensuu. The city bought the area for the price of 1 € and thus committed to take responsibility for the restoration of the area. Project Penttilänranta was carried out with a target of best possible outcome because of the area's central position next to river Pielisjoki and the centre of city of Joensuu. Thus it was possible to carry out such extensive restoration by offering new quality living and office spaces close to the city centre. The city itself welcomed the possibility to cover the costs of land-repair and investment with the profits from the real estate deals. The restoration project was calculated to be the most expensive contaminated-area development project in Finland outside the capital region. Sito Rakennuttajat Oy was the project management consultant responsible for the restoration of the contaminated soil and sediments at Penttilänranta.

The problem

Key figures

- Total surface area: approx. 40 ha.
- Contaminated sawmill area: approx. 26 ha.
- Old log basin: approximately 3 ha.
- Old landfill: approx. 7 ha.
- Contaminated soil: 280 000 m^3.
- Contaminated sediment: 35 000 m^3.

Main sources of contamination in different areas

- KY-5, used to prevent wood turning blue, contained dioxins and furans.
- The soil in two impregnation areas contained heavy metals, arsenic, copper, chrome, etc.
- The log pond sediment was contaminated with heavy metals, dioxins and furans, PAH and oil compounds.
- The old landfill was heavily contaminated with

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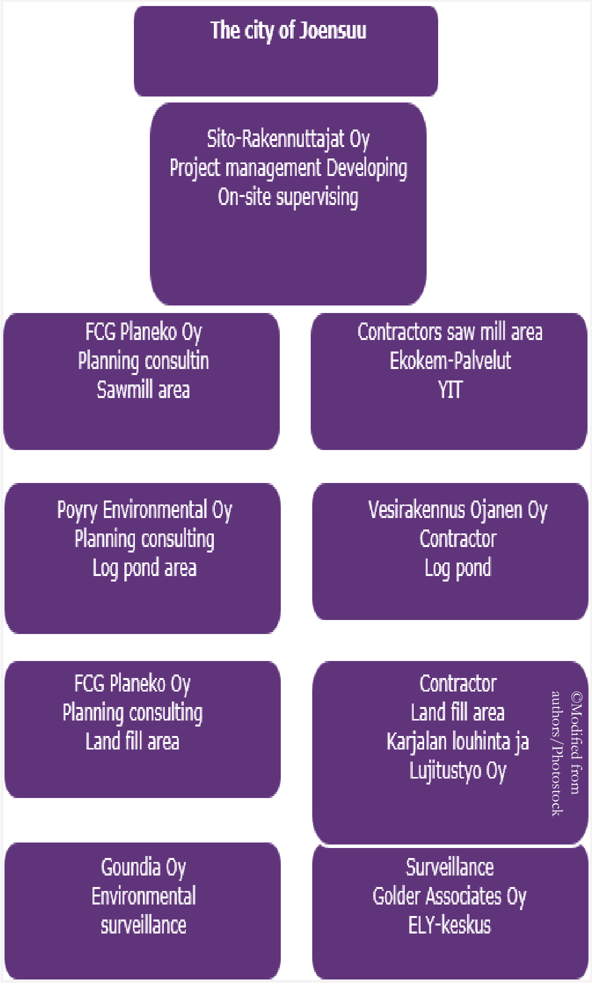
Aerial wiew of Penttilänranta area on the course of restoration works.

heavy metals, dioxins and furans and PAH compounds.

Restoration phases

Both the soil and the sediments in the area were heavily contaminated, mainly because of wood impregnation substances such as creosote. The Penttilänranta area was divided into three parts based on the earlier and future uses. An old log pond with a size of 3 ha and containing contaminated sediments was suction dredged for future use as a boat harbour. Geotubes® were used for sediment sludge handling and dewatering. An old landfill with a size of 7 ha was restored to a landscape hill and industrial plots with encapsulation. The 26 ha area that had acted as sawmill and impregnation area was turned into a residential area and offices.

The restoration project was carried out observing the responsibilities of the environmental projects regarding quality. There were regulations from five different environmental licenses that were monitored to be followed throughout the



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Restoration area in Penttilänranta, division based on the future land use.

> “The savings made by recycling the large portion of contaminated masses were the main reason for achieving the economic success of the restoration project.”

project. All together about 1 million tonnes of sediments contaminated and clean soils were moved. About 95% of the contaminated masses were sent for recycling. The remediation took place in 2009-2011 and was partly carried out in the harsh winter conditions of eastern Finland, with temperatures below -30 °C. This restoration project was one of the biggest ever in Finland, with a total budget 21.2 M €.

This was, however, a significant underspend, despite the larger amounts of contaminated soil and, especially, sediment than had been predicted. The savings made by recycling the large portion of contaminated masses were the main reason for achieving the economic success of the restoration project.

> “In the end there will be about 1 000-1 500 apartments with a capacity of 3 000 inhabitants.”

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Future residential use after remediation.

The conclusions

Current situation

The aim of the project was reached and the Penttilänranta area has now been restored for further use, including about 400 M € in expected investments during the 2010 -2040 period. The expenses of the city of Joensuu were calculated to be about 35 M €, consisting of the restoration and new infrastructure, including for example a new bicycle and pedestrian traffic bridge connecting the old city centre to Penttilänranta and a small boat harbour. With this new area the city of Joensuu has made it possible for the city centre to grow within its most beautiful surroundings. The first new apartment buildings were completed in 2013. In the end there will be about 1 000 -1 500 apartments with a capacity of 3 000 inhabitants. The continuing development of the area is also expected to keep on creating various direct and indirect positive impacts on local employment levels.

Further readings

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http://www.sito.fi/en/
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The soil putridness at the sawmill area compared to the 2007 PIMA-regulation

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Spatial distribution of heavy metal contaminants in Penttilänranta.

Brownfields

4. Securing a polluted site by removing and treating the source of pollution, in the town centre of Pont-à-Mousson, France

LOCATION	Pont-à-Mousson, Lorraine region, France
POLLUTANT	Chlorinated solvents, mainly perchloroethylene
SOURCE	Former plastic plate and tube machining factory
GENERAL CLEAN UP OBJECTIVES	Securing the site by removing and soil treatment
REMEDIATION ACTIONS	Tent containment, soil excavation, air and water treatment by activated carbon, reuse of treated material, soil liming
SITE/END USE	Possibly parking and square construction
SOCIAL-LEGAL ISSUES	Land reclamation
KEY LEARNING/ EXPERIENCE TO SHARE	Story of a successful site remediation in a town centre

Author's profile

Benjamin Roqueplan Project manager — Brownfield and Contaminated Sites Department — Sustainable Cities and Territories Directorate — ADEME.

Securing a polluted site by removing and treating the source of pollution, in the town centre of Pont-à-Mousson, France

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Located in the town centre of Pont-à-Mousson, a brownfield was used as informal parking area for years. Following the discovery of pollution by chlorinated solvents and given its orphan contaminated-site status, the brownfield has been secured thanks to ADEME's action. The land reclamation project is now finished, and the municipality is currently assessing several reuse options.

Keywords: *activated carbon, brownfield, chlorinated solvents, cofferdam, environmental monitoring, land planning, orphan contaminated site, perchloroethylene, reuse, remediation, soil excavation, tent containment, urban context, vapours.*

Introduction

The study case

The site to be restored is located in the centre of Pont-à-Mousson, near the most-visited tourist site in the Lorraine region. It corresponds to a former electricity tube machining factory called 'SUTE', active until 1972. It was acquired by the municipality in 2003 with a view to building a central kitchen as an annex to the nearby high school. However, pollution of the groundwater table and the subsoil was found during the demolition works.

The construction project being frozen, the site became an informal parking area over the years.


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General overview of the site.

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Excavation works under the confined tent.

> “**Pollution**
> *of the groundwater table and the subsoil was found during the demolition works.*”

The problem

The main constraints

This site remediation faced four main constraints. Firstly, the site is located in an urban area: within the town centre, located 10 m from dwellings, close to middle and high schools and near the most-visited tourist site in the region, the so called Abbaye des Prémontrés, classified as cultural heritage building. Secondly, hazardous substances were located in the saturated zone. Thirdly, the excavation work planned for the land reclamation had to be performed during the school summer holidays. Finally, the remediation work had to be carried out on a particularly confined site (8 500 m^2).

The strategy

The depollution steps

A cofferdam with secant piles of 1 320 m^2 was initially set up. Afterwards, a containment tent of 2 250 m^2 was installed and depressurised by a 80 000 m^3/h extraction unit in order to treat the ambient air with activated carbon. In parallel, the groundwater table was lowered inside the cofferdam and the water was treated with activated carbon as well. The polluted materials were covered by soil excavation and the use of slide rail shoring. Excavation to a depth of 2-6 m and the release of buried materials followed. The soil within the depressurised tent was screened and limed. The excavations were backfilled, with full on-site reuse of the treated material (100%). At the end, the site was restored by reshaping the

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Soil excavation and the use of slide rail shoring.

subsoil. Environmental monitoring was carried out for the entire remediation works period and after.

The results

Thanks to financial help from the French state and the technical help of the French Environment and Energy Management Agency (ADEME), this land reclamation project in the centre of Pont-à-Mousson succeeded. ADEME assisted the municipality in several fields, including diagnosis steps, provision of information to officials and residents and specification drafting, but also after the remediation works, with site monitoring being carried out over several years. The land reclamation project is now finished, and the municipality is assessing several reuse options, including a formal parking area and a green space.

Further readings

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Relevant websites

http://basol.developpement-durable.gouv.fr/fiche.php?index_sp=54.0102

http://basol.developpement-durable.gouv.fr/ Recherche > Lieu > Request like: 'Site = Sute'

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http://www.ville-pont-a-mousson.fr/fr/information/65715/depollution-terrain-ancienne-sute

http://www.ville-pont-a-mousson.fr/ Vie quotidienne > Grands Projets > Dépollution du terrain de l'ancienne SUTE

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The confined tent.

Brownfields

5. Remediation technologies of contaminated soils, developed in Andalusia, Spain

LOCATION	Andalusia, Spain
POLLUTANT	Hydrocarbons: PAH (mostly pyrene), TPH (mostly benzo)
SOURCE	Cleaning and degassing tanks and leak of hydrocarbons from tanks
GENERAL CLEAN UP OBJECTIVES	Reduce groundwater and soil contamination
REMEDIATION ACTIONS	Biological treatment in biopiles and thermal desorption with a mobile plant installed in situ
SITE/END USE	Artificial surface
SOCIAL-LEGAL ISSUES	Land reclamation
KEY LEARNING/ EXPERIENCE TO SHARE	New implementation of biological treatment in biopiles tecniques and thermaldesorption.

Author's profile

Reyes García Falantes, graduated as industrial engineer. by University of Seville (Spain). Since 2003, she works providing technical assistance to the Regional Governance of the Environment on contaminated soil. She has extensive experience in the study of contaminated sites and subsequent decontamination, collaborating also in the development of technical documents and regional regulations on contaminated soils.

Remediation technologies of contaminated soils, developed in Andalusia, Spain

Reyes García Falantes, *Environment Assesstment Technician, Water and Enviromental Agency — Junta de Andalusia. c/Johan Gutenberg s/n Isla de la Cartuja, Sevilla, Spain,* rgarciaf@agenciamedioambienteyagua.es

The present report describes two actions of remediation made in Andalusia in order to achieve the remediation of soils contaminated by hydrocarbons in industrial sites, employing two different techniques.
The first site developed the activity of cleaning and degassing tanks over 37 years. A prior study estimated a volume of 27 000 m^3 of soil affected by TPH (Total Petroleum Hydrocarbons), which eventually amounted to 29 000 m^3 of soil treated by thermal desorption with a mobile plant installed at the site.
The second site suffered the consequences of a leak of hydrocarbons from tanks located on an attached parcel of land, determining a volume of 24 928 m^3 of contaminated soil. A reduction in TPH concentration was achieved through biological treatment with biopiles.

Keywords: *Hydrocarbons; thermal desorption; biopiles.*

Introduction

Remediation by thermal desorption from soils contaminated by hydrocarbons

Description of the site

The site is located in an area reclaimed by the dredging of the seabed in the Bay of Cadiz. The activity began in 1969, focusing on cleaning and degassing of tanks coming from oil tankers trucks, with tanks for the storage of the oily water. The contribution of oil has been decreasing since the 1980s, and oily waters come mainly from tanker trucks.
Later on, a concrete raft was constructed in order to deposit the solid waste coming from the cellars and oil tanks.
In addition, the plant had two lagoons for the settling of sludge contained within the waters.

The problem

Investigation study

The work aimed at finding out the status of the soils and groundwater was developed in several phases. The first studied the deposit area, the raft of sludge, the reception area and the old waste area. After that, the decanting lagoons were studied.
A total of 38 soil-sampling points (six deep drilling, 24 pits and eight light drilling) with the installation of six piezometers were located. Finally, 35 soil samples, six water samples and four sludge samples were taken. The parameters analysed were: TPH, PAH, EOX and metals (As, Cd, Cr, Cu, Hg, ni, Pb and Zn).
The results of the studies determined a condition generalised by TPH and various PAH compounds in former waste storage areas, storage of hydrocarbon deposits nearby and in the land located between the pond of sludge , and the entry area of polluted water. In total it was determined that there was a volume of

Aerial view of the plant before the remediation works.

> “The investigation study determined that in totat there was a volume of 27 000 m^3 of contaminated soil, reaching concentrations of 100 000 mg/kg TPH at some points.”

27 000 m^3 of contaminated soil, reaching concentrations of 100 000 mg/kg TPH at some points. Unacceptable risks due to the presence of TPH (Total Petroleum Hydrocarbons), As and benzo(a)pyrene were detected in lagoon 2.

The strategy

Remediation

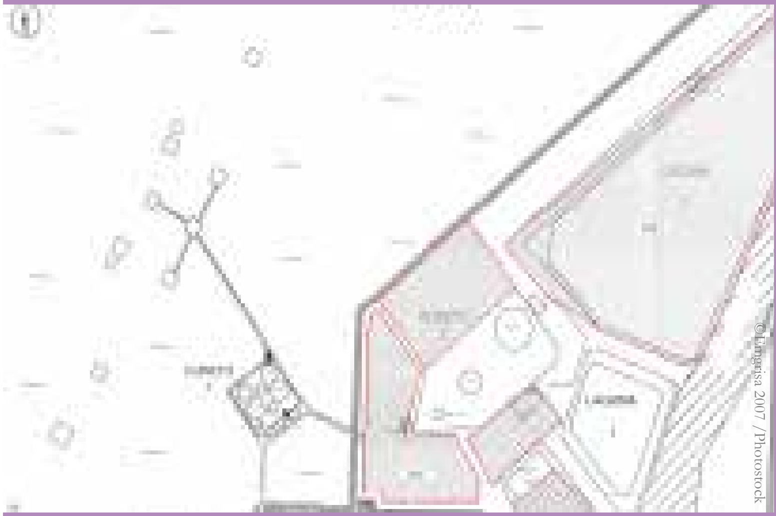
The remediation of the soil was addressed using two different strategies. The risks generated by direct exposure to contaminated soil in lagoon 2 were eliminated through the interposition of barriers that prevented contact. It was filled with a clean, previously analysed material 2 m thick. The lagoon was previously partially emptied by constructing dykes that allowed the transfer of the water while filling the emptied areas. The second part of the treatment strategy was based on decreasing the concentrations of organic compounds in soils using thermal desorption in mobile plant. This technique involves the application of heat to the excavated soil to evaporate and oxidise the pollutants. The warming occurs in two phases, the first by indirect contact with hot gases in a rotary kiln, reaching a temperature of 110°C, and the second by direct contact with a flame, arriving at the optimal temperature of 450°C. After that, the soil is cooled down. Evaporation and combustion gases go through a bag filter prior to its entry into the thermal oxidation furnace.

After 29 000 m^3 of soil treatment, the analysis returned results below the level of 50 mg/Kg TPH at most points, with the exception of some samples that exceeded that value, the highest concentration being 480 mg/kg. However, after conducting a risk analysis, the absence of an unacceptable risk caused by these levels of pollutants was found. Despite this, in areas where the target levels of decontamination were not achieved, the affected soil was removed, transported and managed in a landfill.

Remediation through biopiles of soils contaminated by hydrocarbons

Description of the site

Within the framework of the management entrustment agreement between the General Administration of the State (Ministry of Environment) and the Company for the Management of Industrial Waste (Emgrisa), related to the investigation of contaminated soils under state owned (Decision of 25 July 2006, published in the Official Gazette BOE of Thursday 10 August 2006), the study of two sites located in the Port of Seville was undertaken. Initially the study focused on a site with an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Contaminated area

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Stages of filling of lagoon 2 by the interposition of dykes

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Aerial view of the study plots

area of 35 227 m^2. In later phases of the work, the study area was expanded to an adjoining plot, reaching a total area of about 50 090 m^2. Although these plots had not been known to be used for anthropic activities, soil and groundwater were affected by the existing activities on an adjoining site intended for the storage of large deposits of petroleum products.

Investigation study

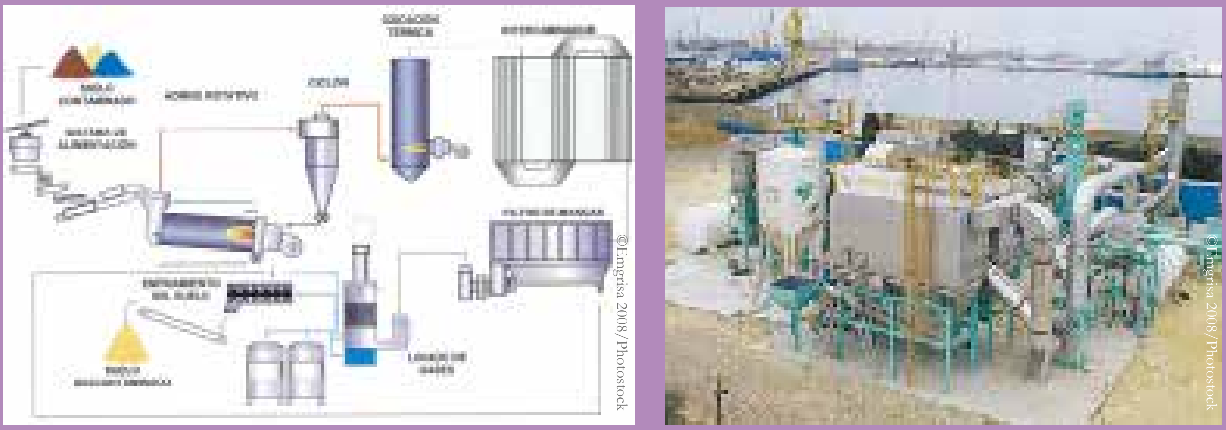
Sampling was conducted in two phases. As there are no facilities on the site, the sampling was carried out in a systematic way, with seven pits and 10 probes in the first plot that covered the whole of the area, and another seven pits and three probes in the adjoining plot. All probes were installed as piezometers for the sampling of groundwater. A total of 34 soil samples at different depths and 10 samples of groundwater were taken in the first plot. The sampling was completed in the adjoining plot with two samples of soil and three water samples. The parameters analysed were TPH, PAH, BTEX and heavy metals in the initial sampling and TPH, PAH and BTEX in the large adjoining plot. The condition in the soil was detected by the presence of TPH in 30% of the samples, reaching a maximum value of 7 900 mg/kg.

In general, the condition was present at a deep level, and it was not detected at the surface level. In four of the analysed samples, Pb and Zn were detected in two of them. PAH and BTEX were not detected above the NGR (Generic levels of reference). In relation to water, in eight of the 13 samples the results indicated the presence of TPH with a maximum value of 240 000 µg/l. Two samples exceed the level of intervention of the Dutch rules for BTEX. Also, these values are exceeded for several PAHs in two water samples. In total, it was estimated that a soil volume of 24 928 m^3 was affected, as well as 1 413 m^3 of groundwater.

Remediation

For the treatment of soil, two biopiles were made at the same time, each with a biological treatment capacity of 18 000 t, over a period of 5 months. The biopiles were located in an area of 5 300 m^2, conditioned and waterproofed with high-density polyethylene and geotextile blade. They are provided with the following functional units: internal irrigation, an internal system of collection and treatment of leachate external system, an internal system of gas extraction and external treatment of gases, an internal system of air injection and outdoor insulation in some periods of treatment. Waters were stabilised through a dual-phase extraction high vacuum system, with a total of eight pumping wells.

After the treatment period, 20 285 m^3 of soil (34 485 t) was finally decontaminated, reaching concentrations of 505 mg/kg TPH in the first biopile and 210 mg/kg in the second one, both of them being below the objective, set at 1 400 mg/kg, given the use of the site. The treated land was move back to fill the holes.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Thermal desorption treatment

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Biopile diagram

Brownfields

6. Sustainable remediation: building the London 2012 Olympic park, United Kingdom

LOCATION	London, UK.
POLLUTANT	Organic: Benzene, toluene, ethylbenzene, xylenes, Polycyclic Aromatic, PAH, TPH, chlorinated solvents. Inorganic: Metals, cyanides
SOURCE	Historical land uses: chemical works, railway sidings, land fill, vehicle breakers yards. Leaking of PAH from tanks and site activities
GENERAL CLEAN UP OBJECTIVES	Improve soil and groundwater quality to meet site specific assessment criteria protective of future users and the environment, including design and implementation, bulk earthworks, infrastructure
REMEDIATION ACTIONS	Ex situ soil remediation: primary screening, crushing, soil washing, bioremediation, chemical stabilisation, geotechnical stabilisation, complex sorting. Groundwater: hydraulic containment, chemical treatment, in-ground barriers
SITE/END USE	Mixed-use residential development, landscape and public realm, stadia/venues, commercial, Queen Elizabeth Olympic Park (QEOP)
SOCIAL-LEGAL ISSUES	Land regeneration
KEY LEARNING/ EXPERIENCE TO SHARE	Innovative and robust risk assessment, combined with on-site soil treatment and re-use of site won materials are likely to provide both the most sustainable and the most cost effective approach to large-scale remediation schemes

Author's profile

Nick Ketchell, is a Chartered Environmental Manager (C.WEM), Chartered Scientist (C.Sci) and Chartered Environmentalist (C.Env) with 13 years experience in environmental assessment and Brownfield regeneration. He played a key role in the development of the Queen Elizabeth Olympic Park (QEOP), first as Remediation Supervisor within the Atkins Enabling Works team from 2006, followed by a secondment to the Olympic Delivery Authority's Delivery Partner. His involvement continued post Games as Remediation Manager working with the current land owner, the London Legacy Development Corporation. Ten years on, Nick has maintained his involvement in the QEOP via a consulting role with LLDC, as well as providing remediation focussed Technical Lead roles for several other major infrastructure projects within Atkins' portfolio. He strongly believes that the sustainable remediation approach adopted during the Enabling Works should be the norm for remediation schemes and strives to impose these high standards on other sites wherever possible.

Sustainable remediation: building the London 2012 Olympic Park, United Kingdom

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The creation of the Queen Elizabeth Olympic Park (QEOP) set a challenge to remediate a large, derelict site with a long industrial heritage close to central London. This paper tells the geo-environmental story of the Enabling Works project, which was responsible for the design and implementation of the earthworks and remediation package. Site teams embraced a sustainable remediation approach, which focused on innovative risk assessment, the treatment and re-use of site won materials to minimise off-site disposal of soils to landfill. In doing so, they demonstrated that full and robust risk assessment with the most appropiate re-use targets can also provide the most cost effective solution.

Keywords: *bioremediation, brownfield, development, groundwater, groundwater treatment, London, London 2012, olympics, regeneration, remediation, soil treatment, soil washing, stabilisation.*

Introduction

When London won the right to host the 2012 Olympic and Paralympic Games, it provided a catalyst to regenerate a former industrial area covering approximately 250 ha in Stratford, East London. The Olympic Delivery Authority (ODA) was established to manage the creation of the Olympic Park, which later became the Queen Elizabeth Olympic Park (QEOP). This process started with the Enabling Works project, which provided the development platform upon which the London 2012 Olympic Games and its associated venues and infrastructure would sit, but also to establish the basis for one of Europe's biggest urban parks as part of the Games' legacy. The Enabling Works scope therefore included demolition and site clearance, soil and groundwater remediation design and implementation, bulk earthworks, and infrastructure such as utilities, temporary and permanent bridges and roads.

This case study focuses on the geotechnical and geoenvironmental aspects of the Enabling Works, whilst considering the sustainable approach to the remediation works upon which the redevelopment of the Olympic Park was based, the planning regime that operated and details of the key quantities. Further information on the other aspects of the Enabling Works, and on-going site development post Enabling Works can be found in the Further Reading section.

Site history

The site had a historical legacy of mixed industrial land use dating back over 150 years, much of which had the potential to generate contamination in soil and groundwater. In addition, owing to the location of the site in the Lower Lea Valley, significant importation of fill material had been carried out over several phases to reclaim the original marsh land, largely during the mid to late period of the Industrial Revolution. Further land raise was generated by the addition of demolition


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Industrial area on the Queen Elizabeth Olympic Park (QEOP) taken during the early 20th century.

> ***“The remediation works** in Olympic Park were based on geotechnical and geo-environmental aspects and sustainable approach.”*

material from the clearance of damaged buildings in central and eastern London during World War II, as well as licensed and unlicensed landfill activities during the nineteenth and twentieth centuries. The area was also known to have been in economic decline since the 1970s.

The ODA took possession of the site in 2007 following completion of land assembly by the London Development Agency (LDA), which included the successful relocation of existing businesses and residents on the site. Land uses at that time included offices and warehouses, car breakers, chemical works, food processing facilities, concrete plants, bus depots, railway sidings and a small area of residential properties, amongst many more. In addition, derelict areas and some surface waters were contaminated with extensive fly-tipped waste including several thousand illegally dumped tyres (go on see picture of waste tyres in and adacent to surface waters).

Geology

The geological profile of the site was key to developing the remediation strategy and understanding the hydrogeological regime of the site. Two groundwater bodies are present in the form of a shallow groundwater table within the River Terrace Deposits, separated from a deeper groundwater table in the Chalk and Thanet Sand by the Lambeth Group.

Typical geological conditions were as follows:

- Made ground – site wide and varies in thickness 1-2 m to over 15 m
- Alluvium – 1-3 m thick consisting of soft silty clay
- River Terrace Deposits, around 3-5 m thick deposits of sands and gravels
- Lambeth Group deposits, generally around 20-30 m thick, made up of interbedded clays, silts and sands


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Aquatics site Enabling Works early.


©Courtesy of authors/Photostock

Aquatics site Enabling Works later.


©Courtesy of authors/Photostock

Enabling works aerial.


©Courtesy of authors/Photostock

On-site contamination.

- Thanet Sand, 10-20 m thickness of very dense, very silty fine sand
- Chalk, thickness >150 m.

The strategy

Remediation strategy

The two fundamental principles of the remediation strategy were to protect future human occupiers of the site (human health) against potential risks from contamination once construction was complete, and to ensure that no unacceptable risks remained to environmental receptors (surface water features and the Chalk aquifer).

Quantitative assessment of the risks posed by contaminants to these receptors was undertaken for the whole site, which identified where contamination was present at unacceptable concentrations below the earthworks formation level in identified 'hotspot' areas. These materials were then excavated where necessary and replaced with alternative materials that complied with derived site specific re-use criteria.

The main method for the protection of human health was to establish a 'separation layer', a thickness of suitable quality material at surface based on the proposed use of the site, to isolate occupants from any residual below-ground contamination. Proposed uses were set by the most conservative land use identified in the Olympic and Legacy masterplans, ensuring that areas intended for residential use post-Olympic Games would be remediated to this standard, even if a less stringent land use was proposed during the Games phase.


©Courtesy of authors/Photostock

Soil treatment plant, also known as "soil hospital"

> **"Site works** *focused on the treatment and re-use of site won materials to minimise off-site disposal of soils to landfill."*

Programme was clearly a significant driver for the completion of the Enabling Works as the remediated development platforms unlocked the next phases of venue and infrastructure development. However, sustainability was also high on the ODA's agenda; the Sustainable Development Strategy for the Enabling Works set above industry standards for the re-use or recycling of demolition, site clearance and soil arisings.

With this in mind, the over-arching objective of the Enabling Works was to maximise the re-use of site derived soils via on-site treatment to reduce contaminant loading, whilst minimising the volume of soil leaving site for off-site disposal. This was achieved using the processes identified earlier, including; detailed quantitative risk assessment to derive appropriate remediation target values and re-use criteria, soil profiling (such as the use of separation layer materials), extensive use of on-site treatment technologies to render site won soils suitable for re-use on the site, and close liaison with waste regulators to ensure appropriate licenses were in place to allow materials to be re-used.

Implementation

The site was naturally split in to northern and southern sections by an existing railway line. Separate contractors were therefore commissioned to complete remediation works in these two separate areas. In addition, the site was divided into a series of construction zones for the control and implementation of the remediation works, based on geographical boundaries such as the network of surface water features that crossed the site.

Waste tyres in and adjacent to surface waters.

Earthworks for the main Olympic Stadium

Groundwater treatment.works

The remediation works included:

- Site investigation, demolition and site clearance.
- Design and implementation of bulk earthworks.
- Soil treatment.
- Groundwater treatment.

Site investigation and clearance

Initial site investigation commenced in late 2006, where access allowed, in advance of the site clearance and demolition works. This comprised combined geotechnical and environmental investigation to delineate the chemical and physical properties of the soil and groundwater beneath the site. By July 2007 the ODA had taken possession of more than 450 land packages within the QEOP, which allowed site clearance and investigation works to run in parallel wherever space allowed.

The principles of the site investigation were established early on with the planning decisions team to ensure that the information provided would be appropriate and sufficient to support the design and implementation works. Following the initial desk study and site investigation design phase, over 3 500 exploratory locations comprising a combination of boreholes, trial pits and windows samples were undertaken across the site at approximately 25 m centres.

The demolition methodology and process was developed which took account of health and safety, sustainability, programme constraints, budget, storage space, and lack of existing buildings designed for deconstruction. The ODA's target for 90% re-use or recycling of arising materials was exceeded with a final figure of 98.5%. On-site processing included approximately 445 000 tonnes of concrete, brick and masonry turned into aggregates, which saved over 20 000 lorry movements and significantly reduced impact on the local community, as well as CO_2 emissions and other environmental factors. Specific achievements of these works included:

- Maximising the reuse of materials from the over 200 demolished buildings, bridges and roads.
- Dismantling of eight steel-framed buildings for re-use elsewhere.

- 12 roof trusses reclaimed for re-use.
- 500 t of yellow stock bricks were reclaimed.
- 1.3 million m^2 site clearance undertaken, including reclamation of items such as granite sets, cobbles and railway track for reuse on the Olympic Park or off-site.

Design and bulk earthworks

The findings of the site investigation were used to inform the Earthworks Design and the Site Specific Remediation Strategies (SSRSs), which were produced for each construction zone, as well as providing geotechnical data for venue and infrastructure designers. The SSRSs provided a detailed remediation design with associated chemical compliance criteria to identify 'hotspots' of soil and groundwater contamination that were present beneath the site in line with the prevailing guidance (Defra; 2004).

The design and implementation documentation, in the form of a Remediation Method Statement (RMS) produced by the earthworks and remediation contractor, fell in line with the site specific planning conditions for the works. A dedicated Planning Authority was established for the site as part of the London Olympic Games and Paralympic Games Act 2006, which bought together regulators from the local authorities involved in the games as well as various specialist third parties. This enabled on-going regulatory involvement with the works and prevented delays occurring in the planning process. In addition, the Environment Agency (EA) was involved in the remediation design and implementation from the outset, providing a dedicated, site-based, co-located team to work closely with the designers and contractors. Monthly coordination meetings were undertaken with all client, regulators, consultants and contractors to ensure attendees were kept informed of progress and issues that required early resolution.

The bulk earthworks design was focused on maximising material re-use on-site. As such, only material that was geotechnically and/or chemically unsuitable, and which could not be rendered or treated suitable for re-use, was disposed off-site to landfill. This was combined with a complete re-profiling of the site to enable the Games and Legacy phase masterplans, but was also designed to provide an earthworks cut and fill balance. To that end, approximately 2.2 million m^3 of cut and over 2 million m^3 of fill materials were managed in the bulk earthworks operations, with over 80% of the soil arisings re-used in the works. This phase of the site development also sought to reduce potential below-ground constraints on future development by removing hard obstructions present on-site to 2 m below the proposed construction platform level.

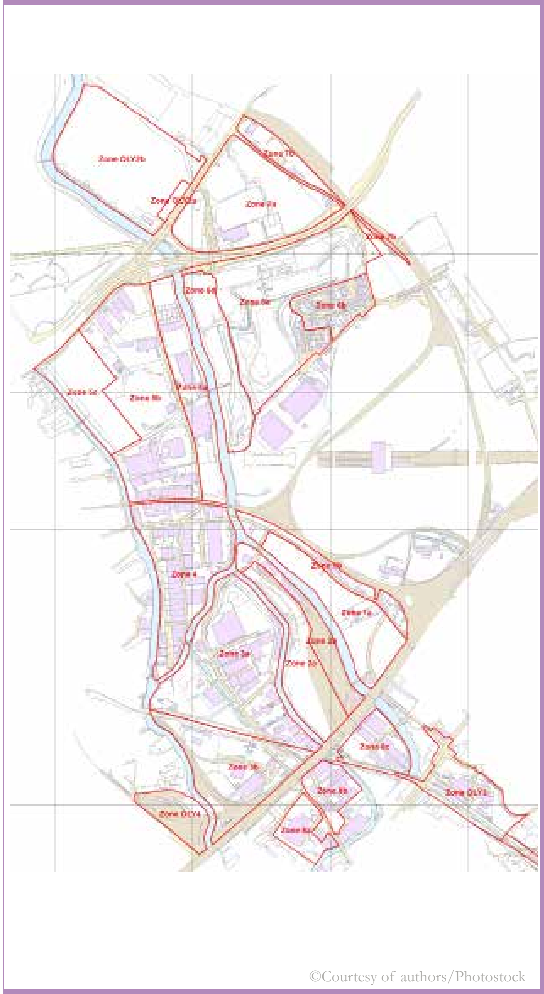
Separation layer

The SSRSs also sought to balance the protection of future site users with maximising the re-use of materials on-site, which led to the use of a 'clean' cover system, which was installed across the QEOP. On other schemes, this cover system would be in excess of 1 m thickness, however, work by the Building Research Establishment (BRE; 2004) confirmed that 600 mm of soil cover was the optimal thickness required for a cover layer given the proposed uses across the Olympic Park.

Based on the BRE guidance, it was decided that the Human Health Separation Layer (separation layer) utilised on the Olympic Park should be no less than 0.6 m thick and more typically 0.8 m to allow a 0.2 m construction tolerance. This separation layer provided a barrier to prevent future site occupants from coming into direct physical contact with either the underlying general fill materials or existing undisturbed ground. It was demarcated from the underlying General Fill or existing undisturbed ground by the presence of a brightly coloured geotextile or geogrid, which was known as the Marker Layer.

The presence of the separation layer allowed less conservative chemical criteria to be utilised for the General Fill, which formed the bulk of the soil to be re-used on-site. As a result, a greater proportion of either site won treated soils or directly excavated soils could be re-used below the Marker Layer. The design profile is illustrated in the soil profile graph. The separation layer was constructed in two stages. The first stage was installed by the Enabling Works contractor and the second stage during

> **"Separation layer** *allowed less conservative chemical criteria to be utilised for the General Fill, which formed the bulk of the soil to be re-used on-site."*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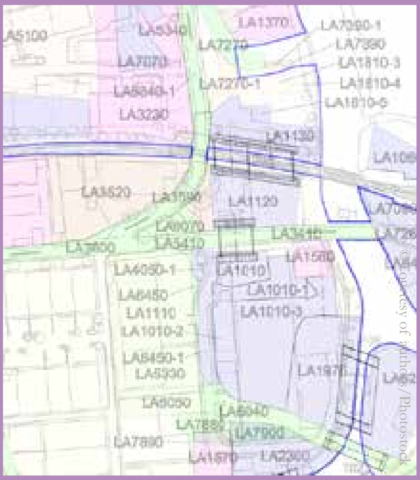
Construction zones.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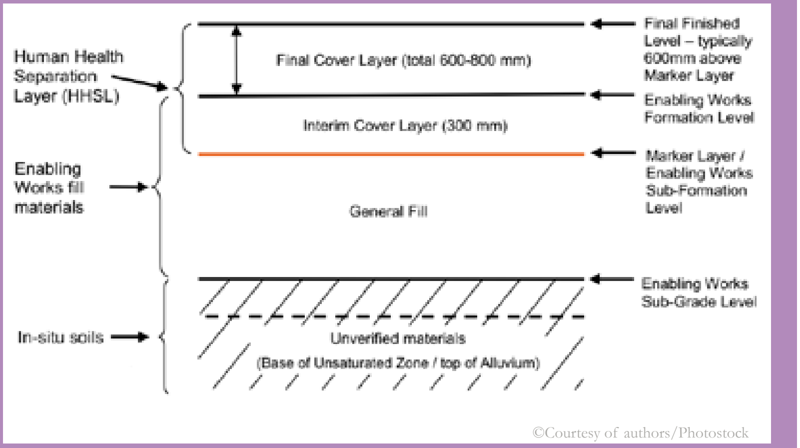
Multiple handovers/land packages



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Typical soil profile.

follow-on works by the venues, structures and public realm contractors. This was considered to be an effective use of the final finishes.

Generally, made ground from the on-site earthworks was not of sufficient chemical quality, even after treatment, to be used in the separation layer. The materials that were used therefore included:

- Thanet Sand derived from tunneling works beneath the site to take the power lines that formerly crossed the site underground (Twine et al., 2011).
- Crushed hard materials derived from the demolition works.
- Imported virgin quarried materials.

Soil treatment

The most common approach used to remediate sites prior to the Enabling Works was to identify and excavate all contaminated materials, export these from site for disposal to landfill and replace them with imported clean soil. As a result of the potential quantum of lorry movements and the associated sustainability implications, as well as the likely impact on landfill capacity from such a large earthworks scheme, this traditional process was the option of last resort during the QEOP development.

The ODA adopted an on-site treatment approach to maximise the quantity of excavated material that could be rendered suitable for use as fill. This provided a much more sustainable solution and as a result of the steady supply of feed stocks and the demand for fill materials as works progressed, it was also the most cost effective. It also ensured usable products were readily available for use in establishing the development platform, minimising the amount of both virgin and recycled aggregate materials that would need to be imported.

All excavated materials from the bulk earthworks operations were in the first instance sampled and tested using an on-site testing laboratory to classify them for direct re-use elsewhere on the site, disposal or treatment as appropriate. Sub-grade level sampling and testing confirmed the suitability of soils to remain in situ and, if required, further excavation was carried out. Approximately 80% of the material to be remediated on-site was made ground, which varied considerably in soil and contaminant types and required a wide range of treatment technologies.

Those selected for use on-site included:

- Primary screening.
- Crushing.
- Soil washing.
- Bioremediation.
- Chemical stabilisation.
- Geotechnical stabilisation.
- Complex sorting.

Soils classified as requiring treatment were transported to one of two on-site treatment centres, known as ‘soil hospitals’ where materials would be assessed and allocated to one or more treatment chains. Soil hospital operations commenced with a single soil-washing plant in July 2007, but as more of the site became available for development, these facilities expanded to match demand.

Soil washing

Soil washing is a physico-chemical process that uses water and additives to separate input materials in to different particle sizes. This helps to remove a wide range of contaminants including organics such as total petroleum and polyaromatic hydrocarbons and inorganics such as heavy metals and cyanides from the larger grained materials with the majority of the contaminants sorbing to the fine grained silt and clay particles. Soil washing plant on the QEOP generated four distinct output materials:

- Sands, >2 mm diameter, generally around 40% of output materials.
- Gravels, <50 mm diameter, generally 40-50 % of output materials.
- Filter cake, fine silts and clays (generally 15-18%).
- Coarse organic matter, ash and coke materials (generally 2-5%).

Sands and gravels were able to be re-blended following treatment to produce engineering fill with defined chemical and geotechnical specifications (Highways Agency: 1998) that could be re-used on the QEOP. Filter cake and other by-products were removed from site to appropriately licensed landfill facilities. At the peak of the earthworks programme, five soil washing plants were in operation, treating up to 10 000 m^3 soil arisings per week, with a total of over 700 000 m^3 treated over the duration of the Enabling Works.

Soil washing worked very well for granular made ground soils, but as the proportion of fine grained material in the input materials increased, this technology became less cost effective, as a greater volume of filter cake would be produced requiring off-site disposal. Finer grained soils were therefore scheduled for soil stabilisation or bioremediation, depending on their contaminant profiles.

Chemical/geotechnical stabilisation

Fine grained soils with leachable contaminants (heavy metals and PAHs in particular) were chemically stabilised using proprietary and specialised reagents to immobilise contaminants and bind them into the soil matrix. This was carried out ex-situ in a pugmill in a dedicated area within the soil hospital. Achieving regulatory approvals for the technology required significant negotiations with regulator and landowner, with aggressive leachate tests used to assess the long term suitability of the treatment methods, and demonstrate that contaminants would not re-mobilise at a later date. Soils that had been chemically stabilised maintained their physical properties, which meant that treated materials still behaved like soils and not monolithic blocks. Approximately 50 000 m^3 of soil were processed using this technique.

Material strength properties for materials such as river silts and soft alluvium were enhanced using geotechnical stabilisation with lime using a Wirtgen soil rig or a mixing Trommel. Up to 210 000 m^3 of made ground soils were geotechnically stabilised, as well as 157 000 m^3 of Thanet Sand arisings from the power lines undergrounding project, which were predominantly used as permanent separation layer fill materials as noted earlier.

Bioremediation

Soft alluvium or cohesive materials with principally hydrocarbon (organic) contaminants were placed in specially designed bioremediation beds, with conditions closely managed to maximise the activity of indigenous micro-organisms. These used contaminants as a feed stock, which resulted in the degradation of organic contaminants via metabolisation, converting them to innocuous end-products. Temperature was controlled by running hot/cold water through pipes embedded in the biopile with hot water returning back to the heating system to be reheated and recirculated. Soil hospital contractors were also able to control the degradation of contaminants by adding nutrients (C:N:P) at a ratio of 100:10:1, and managing moisture and oxygen contents.

This technique was used to treat a relatively small volume of material, as a result of the nature of the arisings generated during the earthworks but also because the biopiles required a large surface area and each batch took 6 to 8 weeks to process at a time when space and time were at a premium. Approximately 30 000 m^3 of soil were bioremediated over a period of 19 months and successfully reused as general fill.

Complex sorting

The materials excavated from the nineteenth and twentieth century landfill depositories in the northern part of the site required sorting prior to any other treatment to render them suitable for re-use. Soils were initially sorted via vibratory screening to separate soil from general landfill materials. The soil was treated using electromagnets to remove metal fragments and then processed using a manual picking zone for final removal of deleterious items. The finer soil fraction was typically reused directly on-site or scheduled for secondary treatment within the soil hospital, with the coarser fraction re-processed via crushing or screening. Approximately 82 000 m^3 of material were treated using this process.

Direct re-use

In addition to the extensive use of treatment technologies on the site, approximately 880 000 m^3 were directly re-used on-site without the need for further treatment. This material was either generated as part of the site re-profiling and did not require treatment, or exceeded remedial targets in a sensitive area of the site and were available to be reused in less sensitive areas with higher re-use criteria.

Programme management

The performance of the two Enabling Works contractors was constantly monitored with contractual weekly targets set in terms of cut, fill and treatment volumes. If targets were not achieved, the project management team worked to identify potential problems and assist the contractors to bring work back on programme. This was achieved by, for example, providing more plant or extending working hours. The bulk earthworks programme was also maintained throughout the winter months, involving careful stock-piling to keep excavated soil dry, with occasional lime stabilisation to enable wet material to be re-used, to maintain the cut-and-fill balance. In total, over 1.4 million m^3 materials were treated using the methods described above to allow re-use within the scheme.

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Soil treatment plant, also known as “soil hospital”

> **“The project** *also demonstrates the benefits of developing remediation technologies to maximise on-site soil treatment.”*

Groundwater treatment

The industrial heritage of the site also resulted in dissolved phase contamination and the presence of free phase hydrocarbon products in groundwater, particularly within the shallow river terrace deposits aquifer. Three main techniques were utilised during the Enabling Works to address this contamination:

- Hydraulic containment.
- Chemical treatment.
- In-ground barriers.

Containment

Following excavations to provide the bowl for the Olympic Stadium, there was a requirement for the excavation of a further 200 000 m^3 of soils for the protection of controlled waters. However, given the programme and cost constraints involved with such an operation, alternative options were considered. A hydraulic capture system provided the most flexible solution particularly given that construction could commence during the installation of the system. A network of abstraction boreholes was therefore installed in the River Terrace Deposits around the perimeter of the Olympic Stadium site, with pumping rates tested to provide a local reversal of groundwater flow direction, thereby preventing migration of contaminants beyond the site boundary. A purpose built treatment plant was also constructed, with the majority of the effluent being discharged to sewer. The development platform for the Olympic Stadium was handed over to the venue contractor, with the hydraulic containment system in place, 10 months ahead of schedule in April 2008.

A similar network was installed to the south of the Olympic Stadium although, due to the organic nature of the contaminants, the treatment included stripping towers, skimming tanks and activated carbon filters (Groundwater treatment picture).

Chemical treatment

Gross hydrocarbon contamination was identified in two areas on the site, which required a combination of earthworks and groundwater treatment. BTEX and TPH contamination was encountered in the river terrace deposits to the south of the Aquatics Centre, and a combination of chlorinated ethenes and ethanes, TPH and PAH were encountered to the south of the Olympic Stadium. Made ground soils and contaminated gravels were excavated in both locations to reduce the mass loading of contaminants in the aquifer, with arisings scheduled for soil washing at the soil hospital.

At the Aquatics site, a proprietary oxygen release substrate was injected in to the groundwater to create an oxygen-rich environment within the aquifer to encourage naturally occurring aerobic microbes to break down contaminants into inert by-products. Chemical oxidation was utilised to the south of the Olympic Stadium, with potassium permanganate and Fenton's reagent (iron-catalysed hydrogen peroxide) injected in to the aquifer via a network of 110 injection boreholes individually linked to a batching area. This resulted in long-term reductions in certain key organic contaminants by 90-99%.

In each case, the injection was specifically tailored to the concentration and type of contaminant present. In addition, where free products in the form of non-aqueous phase-separated liquids were present, their removal by skimming of lighter and heavier products from the surface of the aquifer and the top of the underlying strata respectively was undertaken.

In-ground b33399arriers

In an area adjacent to the main river in the northern part of the QEOP, destructive treatment of dissolved phase contamination was not viable. A sheet-pile wall was therefore installed to cut off the flow of contaminated perched water between the made ground and the river. This was designed in such a way that any increase in the level of the contaminated perched water behind the wall was collected and pumped to a treatment plant where it was treated and discharged to foul sewer. The nature of the remediation in the unsaturated made ground prevented any further leaching of contaminants into the perched water and the treatment system was able to be decommissioned post Games.

Validation and regulatory approval

The final part of the remediation process was the production of validation reports. These followed the requirements of the planning conditions for the site and provided the formal basis for the contractors and project management team to satisfy the planning authority that the remediation had been completed and the requirements set out in the SSRS and RMS documentation had been achieved. Planning conditions relating to ground contamination and its subsequent remediation were subsequently discharged.

The ODA regularly consulted with a number of expert regulators and stakeholders. These included the Environment Agency (EA), Canal and River Trust, environmental health officers from the London Boroughs of Newham, Waltham Forest, Hackney and Tower Hamlets, and independent and specialist technical and legal consultants acting on behalf of the planning authority.

Follow–on works

Following the phased completion of the Enabling Works project, development platforms were handed over to follow-on contractors to commence the 'Big Build' construction phase to create the venues and infrastructure for the Games. However, given the nature of these works with up to 60 Principal Contractors working concurrently across the QEOP, it was recognised that the site would be split down into much smaller land parcels (PTP split map). As a consequence of this subdivision of the site, Principal Contractors would have neither the space nor the capability to stockpile or treat soils, and verify that they were compliant with re-use criteria. The soil hospital was therefore centralised within the scheme and tasked with managing the excavation arisings, stockpiling, testing and blending of soils to produce earthworks materials with defined chemical and geotechnical specifications (Highways Agency: 1998) that could be re-used on the QEOP.

In combination with the soil hospital, the Permit to Proceed (PtP) protocol was developed in order to protect the remediation works that had already been constructed. The PtP team was established to support and engage with the main infrastructure and venue contractors to ensure that all previously installed site remediation measures were incorporated and maintained within the subsequent project works, including cut off walls, groundwater treatment networks and the hard and soft cover systems detailed earlier.

Conclusions

The Enabling Works was the first major project on the QEOP and was vital in establishing high standards for protecting health, safety and the environment, maximising quality and sustainability and achieving programme targets, which could be taken forwards as an example during follow-on works. It also provided an industry leading example of collaboration between the ODA, their delivery partner, the contractors and the Atkins design and project management teams. With a great amount of respect, trust and co-operation between these parties, contractors were able to receive clear instructions as and when required, who would then take immediate action, with over 9 000 instructions issued throughout the works.

The Enabling Works project started in October 2006 and was substantially completed, on programme, in September 2009, whereas best practice at the time indicated that such a large-scale remediation scheme would typically take 10 to 15 years to complete. It has enabled the delivery of an Olympic Park that is safe for use, meets the prevailing legislation and planning conditions and satisfies the requirements set by both the Olympic and Legacy use masterplans.

The project also demonstrates the benefits of developing remediation technologies to maximise on-site soil treatment, thereby minimising the requirement to transport contaminated material to landfill and reduce the subsequent volume of imported clean fill material. It also confirmed that high levels of material treatment and re-use do not just provide the most sustainable approach, but can also be the most cost-effective.

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Games final phase.

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Brownfields

6. Cava Pirata: technology train to address a complex contamination

LOCATION	Mantova, Italy.
POLLUTANT	Benzene, toluene, xylene and aromatic amines
SOURCE	Illegal dumping
GENERAL CLEAN UP OBJECTIVES	Reduce soil and groundwater contamination
REMEDIATION ACTIONS	Intervention techniques, bioremediation, soil vapour extraction (SVE) and air sparging (AS)
SITE/END USE	Natural area
SOCIAL-LEGAL ISSUES	Land reclamation and complex contamination
KEY LEARNING/ EXPERIENCE TO SHARE	Materials that could interfere with the selected techniques, they should be managed separately

Author's profile

Alessandro Teani, is Ambienthesis's technical director. He has been working for 15 years in remediation of contaminated sites, decommissioning of disused industrial areas and environmental plant construction.

Marco Falconi, is a contaminated-site expert working for ISPRA (Italian EPA) on the sites of national priority list. He teaches in several universities in Italy and abroad on characterisation, risk assessment and remediation technologies.

Cava Pirata: technology train to address a complex contamination

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The case of Cava Pirata in Castiglione delle Stiviere (MN) involves the application of multiple and synergic technologies. The intervention is characterised by high environmental sustainability, in addition to the achievement of remediation objectives within a reasonable time. The targeted design of interventions has allowed the identification of intervention techniques, bioremediation, soil vapour extraction (SVE) and air sparging (AS) who have proven optimal as technology train for the treatment of soils of this site.

Keywords: *technology train, air sparging, soil vapour extraction, bioremediation, biopile, sustainability, BTEX (Benzene, Toluene, Ethylbenzene, and Xylenes).*

Introduction

The objective of the intervention was to achieve the site remediation of all the matrixes involved: bioremediation (biopile) for soils, soil vapour extraction for soil gases, air sparging for groundwater.
The technology consisted of injecting pressurised air into the groundwater, the gaseous flow allowing the stripping of contaminants, which are transported in the vapour phase into the unsaturated zone. The system consists of one or more injection points and a compressed air injection system at sufficient pressure to overcome the hydrostatic load. The intervention of air sparging (AS) was associated with a soil vapour extraction (SVE) system for the recovery of the stripped contaminants from groundwater that have migrated into the unsaturated zone and also for stripping contaminants already present in the soil.
Air sparging (AS) provides direct intervention on the source of contamination, as opposed to pump-and-treat (P&T) implementation, which would have provided only a barrier to downgradient contaminant migration.
The SVE-AS system allowed the treatment of aquifers contaminated by volatile organic substances, reaching the remediation targets.

On the basis of past experience, the grain size is crucial to the success of this kind of treatment. This system showed a faster deadline and lower costs compared to an intervention with P&T.

The problem

Contaminants of concern and concentration

The contamination had been caused by previous unidentified activities of illegal dumping (picture waste present on-site mixed with contaminated soil) and is characterised mainly by mono-ring hydrocarbons such as benzene, toluene, xylene and aromatic amines


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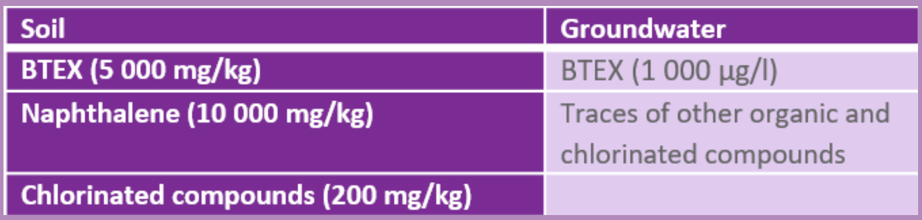
Waste present on-site mixed with contaminated soil

> **“The contamination** *had been caused by previous unidentified activities of illegal dumping.”*



Soil	Groundwater
BTEX (5 000 mg/kg)	BTEX (1 000 µg/l)
Naphthalene (10 000 mg/kg)	Traces of other organic and chlorinated compounds
Chlorinated compounds (200 mg/kg)	

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Concentrations in soil and groundwater

(aniline) in soil and groundwater. Some of the contaminants were in the vapour phase.
The contamination of the site-specific data is summarised in the table above in terms of maximum concentrations found in soil and in groundwater.
Following a careful examination of the specific site characteristics, including the type of contamination to be treated, the lithology and the depth to groundwater, interventions characterised by low environmental impact and high economic sustainability have been proposed. On-site treatment has been implemented, partly in situ (SVE) and partly ex situ (biopile) in the soil, with two wells collecting groundwater, then treated with a scrubber and a granulated active carbon (GAC) system.

The strategy

Operations

After the fencing off of the yard, a concrete platform was prepared and boxes were built (picture yard at early stage of the process). After the installation of all the systems, soil treatment started. The area most contaminated was excavated after the installation of a provisional tensile structure (volume of about 20 000 m^3), with the objective of limiting dust volatilisation. Furthermore, as an additional control measure, an active depression system was set up for the collection of any vapour coming from the soil. The excavated soil was placed in various provisional tensile structures (approximately


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Yard at early stage of the process

18 000 m^3), also confined with an active depression system, in which six static biopiles were set up, for a total of about 8 000 t of soil.

The bioremediation process was improved through the supply of air (picture of air supply to bioplies) and enhanced though the inoculation of specific bacterial strains. The whole process was constantly monitored for some parameters, such as the O_2/CO_2 ratio, CH_4, humidity and RedOx condition (picture of bioremediation parameters). The area of intermediate contamination was treated with a combination of SVE and AS (picture of SVE well and two AS wells).

The SVE system consisted of 15 wells equipped with control systems, all connected to a single extraction system (picture of SVE extraction system) with high flux and then to the pollutant abatement system, which for this area was a catalytic oxidiser. The SVE system was enhanced by an AS system consisting of nine wells with discontinuous insufflations of atmospheric air into the groundwater table, which both helped SVE to strip volatile contaminants and helped microorganism activity, creating aerobic conditions in the radius of influence (ROI).

The area of low contamination was subjected to a low-flux SVE treatment without AS (picture SVE well). The SVE system consisted of 15 wells equipped with control systems, all connected to a single extraction system and to the pollutant abatement system, which for this area was adsorption on granulated activated carbon (GAC) that treated both the vapour and the liquid phases (picture granulated activated carbon system). Prior to the installation of all the systems, a P&T system was installed downgradient, in order to prevent any contamination plume from the site during the operations.

The global extraction rate was optimised at 72 m^3/h and the groundwater quality was monitored monthly.

Management of unexpected issues

During excavation, some anthropogenic waste that was untreatable in biopile were found (less than 100 t). They were disposed of off site in a nearby landfill for non-hazardous waste. During excavation, in a small volume of soil, contamination from heavy hydrocarbons (long linear chain) was unexpectedly discovered. It was necessary to proceed with the treatments by developing dynamic aeration cycles (picture of dynamic aeration cycle using a bucket excavator) for the purpose of achieving the objective within the scheduled time frame.

The results

At the end of the intervention, which lasted for 2 years, they achieved all the remediation targets, even solving unforeseen contamination (heavy hydrocarbons) and waste. The site was returned to the contracting authority as a result of the environmental restoration of the whole area, with


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Excavation of most contaminated soil

> “The bioremediation *process was improved through the supply of air and enhanced though the inoculation of specific bacterial strains.*”


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Air supply to biopiles


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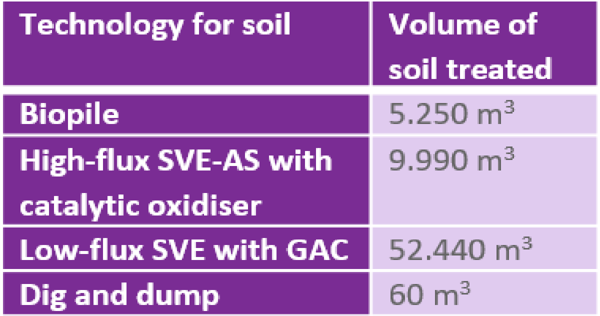
Monitoring of bioremediation parameters

the placement of many tree species (picture of trees planted in the area as final cover page 121). The control authorities monitored all the activities though several reports that were produced for each step of the project, ensuring the full traceability of the data (volume treated, monitoring data). Ultimately, the volumes of



Technology for soil	Volume of soil treated
Biopile	5.250 m^3
High-flux SVE-AS with catalytic oxidiser	9.990 m^3
Low-flux SVE with GAC	52.440 m^3
Dig and dump	60 m^3

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Soil volume treated divided among technologies used


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Dynamic aeration cycle using a bucket excavator

SVE well (with manometer) and two AS wells

SVE extraction system

SVE well

Granulated activated carbon system

soil treated with the individual technologies are illustrated as summarised below.

The conclucions

Bioremediation using biopile techniques has proved immediately effective for the removal of aromatic contaminants. The kinetics of the process is sufficiently rapid and the achievement of remediation objectives happened quickly for BTEX.

The fact of using the SVE systems allowed the remediation objetives to be fullfilled in situ. There were no significant rebound effects, therefore the project reached its target on schedule.

The groundwater table, constantly monitored, was not affected by the plume correlated to the implemented processes. During the operation of the SVE-AS system it was necessary to activate the P&T system, within a narrow time frame. Collected and treated quantities are estimated at a few thousand cubic metres.

The interventions were characterised by high environmental and economic sustainability, minimising the handling and disposal to landfill, limiting the impact on viability and saving costs in comparison with other techniques that could be costly or not effective at solving the problems. A key finding is that if there are some materials that could interfere with the selected techniques, they should be managed separately, and good characterisation is the key to differentiating areas where enhancements (that can be


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Waste present on-site mixed with contaminated soil

> ***"The interventions** were characterised by high environmental and economic sustainability in comparison with other techniques."*

costly and/or energy consuming) are needed from others where they are not needed.

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LANDFILL

LANDFILL

1. **Hungary: remediation of cave homes in Budafok**
2. **Poland: the decommissioned Piekary Slaskie Zinc and Lead ore smelting plant.**

Landfill remediation

1. Remediation of cave homes in Budafok, Hungary

LOCATION	Budapest, Hungary.
POLLUTANT	Solid gas paste, liquid phase leachat, dilute sludge
SOURCE	Gas factory, illegal landfill dumping
GENERAL CLEAN UP OBJECTIVES	Reduce soil and groundwater contamination
REMEDIATION ACTIONS	Pumping of leachate, dilute sludge, waste discharge of the disposals, cleaning of wells using alpine technics, deep yards' rock surface cleaning using dry and wet methods
SITE/END USE	Recreation and residential space
SOCIAL-LEGAL ISSUES	Land reclamation and human exposure to contaminants
KEY LEARNING/ EXPERIENCE TO SHARE	Further technologies had to be used to remediate wells, establishment of monitoring wells, water flow measurement with cleaning of the well

Author’s profile

Miklós Hollósy, he is a consultant at the Herman Otto Institute. He received a Ph.D. in Chemical Engineering at the Technical University of Budapest. From 1982 he works on hazardous waste management and remediation technologies as an environmental expert for different companies. He has significant laboratory practice, experience in controlling and proficiency in implementation of projects. He has published about 20 papers to journals and conference proceedings.

András Béres, is the director of the Directorate for Environmental Protection and Nature Conservation at the Herman Otto Institute. He graduated as agricultural engineer at the Faculty of Agricultural Engineering of the Agricultural University of Gödöllő. He acquired a German-Hungarian vocational training qualification. He is PhD in technical science by the School of Agricultural University of Gödöllő in 1998. Previously, he did lecturing, worked as accredited in environmental analytical laboratories and conducted management executives taks and in R&D activities. Currently he acts as manager of all environmental related projects at the Herman Otto and he is assistant professor at the Szent István University.

Norbert Baross is an environmental expert at the Herman Ottó Institute Nonprofit Ltd with a post gradual master in Environmental Engineering in 2010 at Szent István University. He started his work as an engineer assistant at the National Institute for Environment. For three years he conducted surface water management tasks for the Budapest Regional Branch. In 2014, he joined the environmental remediation workgroup. He has considerable experience with GIS programs. He used to attend training courses and conferences regularly. He has participated in a numberof international projects and also in publication of professional articles.

Lorant Riesz, is the deputy director of the Directorate for Environmental Protection and Nature Conservation at the Herman Otto Institute. He graduated as an environmental engineer and started his professional work in the National Institute for Environment in 2013. One of his main tasks is the coordination of the remediation of contaminated sites related projects, managing preparatory work of decision making, providing data service and reporting for the Ministry of Agriculture. He also carries out the remediation tasks under governmental responsibility.

Remediation of cave homes in Budafok, Hungary

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In the framework of the National Environmental Protection and Remediation Programme 1996-1997 as the responsibility of the State, in the area of cave homes in Budafok, XXII. District, Budapest remediation has been implemented, which was necessary due to the pollution by disposal of gas cleaning paste. There were four supposed sources in Budatétény, two more in Budafok on cca. 8654 m^2. The hazardous materials have been found in two different phases. The amount of previously disposed of harvested solid gas paste was 77 344 t, of liquid phase leachate was 559 t, and of dilute sludge was 3000 t. The real estates on the remediated area are built-up, inhabited or non-built-up with weekend houses and gardens, or industrial estates or public areas and roads with public utilities. The target of the technical intervention was the thorough decontamination of the area.

Keywords: *cave house, disposal, gas paste, hazardous waste, leachate, metallurgy, mine, recovery, recultivation, remediation, utilization.*

Introduction

In the 1950's economic crisis was going around, so that a lot of workers, who moved to Budapest due to the job opportunities there, looked for shelters in the desolate limestone mine area and settled in there. A flat sometimes make up only 15-20 m^2, moreover there were sometimes 3-4 families living together in a bigger flat amongst saddening conditions.

The XXII district was established as a union of Budafok, Budatétény and Nagytétény in 1950, which's first decision was to cease the mentioned cave flats. The families living in the cellar flats had been provided other ones, so that they moved away, and then the quick shutdown of the cellar ones had been started. It was thought that the cheapest way of disposal was to close the area and fill the caves.

The filling works finished in 1966-1967, while exploited gas cleaning paste and slag was being used, which stem from the Óbudai Gas Factory. Putting and closing the paste in the mine holes seemed to be an obvious solution, because it was not regarded as environmental pollution, since the effects were unknown and yet no legal rules about the requirements of disposal of had been introduced that time.

The problem

Decades after disposal of it turned out that it had serious environmental polluting impact.
In the framework of the National Environmental Protection and Remediation Programme (OKKP) 1996-1997 as the responsibility of the State, the plan to remediate the area had been accepted. Between 1999 and 2001 the fact-finding phase of remediation took place. After the open public procurement process started in the framework of the OKKP had been finished, the tender to implement the technical intervention phase of remediation was won by TERSZOL Environmental


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Excavation works on-site.

> *"According to the framework of the National Environmental Protection and Remediation Programme 1996-1997 the illegal landfills with building on them need to be remediated."*

Protection and Building Industrial Ltd. There were four supposed sources in Budatétény, two more in Budafok on cca. 8 654 m^2. The hazardous materials have been found in two different phases. The amount of previously disposed of harvested solid gas paste was 77 344 t, of liquid phase leachate was 270 m^3, and of dilute sludge was 3 000 t.

The real estates on the remediated area are built-up, inhabited or non built-up with weekend houses and gardens, or industrial estates or public areas and roads with public utilities. The target of the technical intervention was the thorough decontamination of the area.

The strategy

Preparation

TERSZOL began the technical intervention phase works according to the environmental implementation plan accepted by the administration on 1 August 2004. Afterwards the original state of environment was assessed, which covered real estates, buildings, facilities, public utilities and green surfaces, geodetic measurements, measurement points for sinking, assessment of original state of environmental elements and trial period of waste utilization.

The preparation tasks of the area has been finished by the isolation of potential polluters from the direct environment, the implementation of public utilities, mobile and necessarily fixed technological facilities, the cut down of trees, shrubs, vegetation, the demolition of buildings and the construction of inner, temporary transportation roads.

Technological intervention phase

Remediation of potential polluters includes the following steps:

- Pumping of leachate, dilute sludge, gathering in the waste body according to ADR requirements, public road transportation, treatment with water recycling, transportation of dry matter content to process and for further usage.
- Waste discharge of the disposals of and the cellars beneath, aka cave homes in the first phase by exploitation, transferring


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Cleaning works on-site.

> “**The** *stakeholders returned a healthier* **environment** *ready to be used as recreational or green space.*”

to landfills with 15% of manual power, 15% of small machines and 70% of big machines.

- After the exploitation the cellar walls, rocks were dry and wet cleaned by machines and manually
- The cleaning of wells found in deep yards was carried out with machines and alpine technics, what was followed by the cleaning of well walls manually and with machines, and of the well bottom, and finally of the water and slop by pumping. The next steps were the water flow measurement, the sampling and the laboratory examinations.
- The deep yards' rock surface was cleaned by machines, small machines, manually, dry and wet methods. It was followed by labelling as clean by the Authority based on accredited sampling, final control and assessment.

After the transportation ruled by ADR the gas paste were given away to BÉM Ltd. to recycle according to the implementation plan. The leachate and the dilute sludge were treated at the TERSZOL's plant in Szolnok to recycle the water for further usage, furthermore the dry content with the gas paste in it was material recycled at BÉM Ltd.

The former Ministry for Environmental Protection and Water Affairs had managed to buy two real estates being on illegal landfills with buildings on them, both had been demolished by mutual agreement with the contractor. The remediation of the other 12 inhabited estates were more complicated. The residents of 5 houses had to move away, their buildings had to be conserved, and the waste had to be kept there unmovably by the so called jet-grouting technology, putting the houses' basement on rocks, building walls to incorporate the hazardous waste, strengthening the houses and water drainage system was built there. Under the building, the remaining waste is isolated with technical protection. In case of the other houses unique solutions were carried out. During the remediation process one of the houses had to be strengthened immediately, since it came up that the 5-flat house was standing upon two crashed in cellar floors, and only a false vaulting held it.

The TERSZOL wrote a process report in each month according to the requirements, which were sent to the Inspectorate, the National Public Health and Medical Officer Service, the municipality, the Hungarian Central Directorate for Water & Environment, the Research Institute for Environment and Water Ltd, the Green Future Association and the principal. During the intervention the building log and the implementation document were daily refreshed on-site and at the processing plants, as well as all the necessary documents related to the transportation of waste and hazardous waste.

The soil, the groundwater, level of sinking, the noise, the air quality, the gas paste, the dilute sludge, the leachate, the vegetation, the quality and quantity control of newcoming soil were monitored by accredited companies, what is more isotopic compactness examinations were executed.

Further tasks

The active phase of remediation showed that there were more contaminated areas and further cellar flats, where significant extra amount of polluter and dilute sludge were found unpredictably. That meant that extra work had to be done, as the area had to be extended (6 802 m^2 added to it), bigger amount of pollutants had to be treated, and more flats had to be remediated.
After the public procurement process, on 21 February 2005 the extra works was ordered in a complementary contract. The TERSZOL sent the results and assessment of polluter searching to the Inspectorate and the principal. Based on these, further technologies had to be used (to remediate wells, establishment of monitoring wells, water flow measurement with cleaning of the well etc.). Finally, much more soil and waste was exploited.

The conclusions

The technical intervention began in June of 2004 and all the remediaton and recultivation tasks on the regarded estates mentioned in administrative decrees, works contracts have been finished by TERSZOL in time, before 28 June 2007.

The Inspectorate labelled the real estates as clean before the beginning of recultivation. During the technical intervention 77 344 t of gas paste, 559 t of leachate, 3 000 t of dilute sludge was exploited, packaged and transferred according to the ADR requirements. After the technical interventions the stakeholders got back a clean, healthy environment which had been recultivated and got value added real estate for everyday usage.

Further readings

Relevant websites

www. terszol.hu

Landfill remediation

2. The decommissioned Piekary Slaskie Zinc and Lead ore smelting plant, Poland

LOCATION	Piekary Slaskie, Poland
POLLUTANT	Zinc, Lead, Cadmium, Arsenic
SOURCE	Zinc and Lead smelting
GENERAL CLEAN UP OBJECTIVES	Revegetate smelter wasteland, reduce dispersion of pollutants
REMEDIATION ACTIONS	Top layer amendment with biosolids and by-product limestone, phytostabilisation
SITE/END USE	Revegetated wasteland/ecological site
SOCIAL-LEGAL ISSUES	Land reclamation, human health risk
KEY LEARNING/ EXPERIENCE TO SHARE	Knowledge on effectiveness and long-term performance of the applied phytostabilisation approach

Author's profile

Dr Grzegorz Siebielec. is a research scientist at Institute of Soil Science and Plant Cultivation (IUNG) – State Research Institute in Pulawy, Poland. He received a Ph.D. in agronomy in 2001. Current Head of Soil Science Erosion and Land Protection at IUNG. His main research interests are soil contamination and remediation, land use change, soil quality, soil sealing, waste management. He participated in ten international projects, including 5, 6 and 7FP, and coordinated work packages in two of them (CANTOGETHER and URBAN-SMS). Coordinated national monitoring of soil quality for Ministry of Environment. Currently a national representative for soil issues in EIONET, Common Forum on Contaminated Lands and Global Soil Partnership. He has published more than 110 contributions to scientific journals, chapters and conference proceedings.

Prof. Tomasz Stuczynski. has been involved for over 30 years in research on soil protection, including: testing of soil contamination, development of metods for land reclamation and land use change modelling. In the 90's he lead the Silesia project, developing low cost remediation/revegetation methods, contributing also to a number of EU funded R&D projects, such as SENSOR dealing with sustainability assessment, LUMOCAP working on assessment and modelling of policy impacts on land use change. He led an assessment of CAP Rural Development Plan impacts on soils and waters in Poland. He also contributed to the development of draught monitoring systems for agriculture land in Poland. He managed several large projects financed by government agencies to establish monitoring schemes, indicators, databases and systems needed for the assessment of CAP. Working at SGS he developed and managed an accredited testing laboraotry specializing in monitoring of soil and water polution, noise monitoring, stack emission analysis, food testing, site and risk assesmment.

The decommissioned Piekary Slaskie Zinc and Lead ore smelting plant, Poland

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Prof. Tomasz Stuczynski, Department of Soil Science Erosion and Land Protection, Institute of Soil Science and Plant Cultivation-State Research Institute in Pulawy, Poland, ts@iung.pulawy.pl

The study case presents the decommissioned Zinc and Lead ore smelting plant located in Piekary Slaskie, Poland. The wasteland had wastes from two different smelting processes — Welz and Doerschel. Both wastes contained extremely high loads of Zinc (up to 128 g kg^{-1}), Lead (up to 40.6 g kg^{-1}), Cadmium (up to 3.46 g kg^{-1}) and Arsenic (0.76 g kg^{-1}). The pilot reclamation of smelter waste sites was performed within the framework of the Silesia project. The project was a joint effort by local government, industry and national or international research institutions and agencies: the US Environmental Protection Agency (USEPA), the Centre for Research and Control of the Environment (OBIKS), Virginia Polytechnic Institute, USDA-ARS in Beltsville and the Institute of Soil Science and Plant Cultivation (IUNG). The main objective of the Silesia project was the development of guidelines for the effective and safe use of bio-solids for the reclamation of degraded lands and waste sites.

Keywords: *smelter waste sites, Silesia project, biol-solids, Zinc and Lead decommissioned.*

Introduction

The demonstration was established at the decommissioned Zinc and Lead ore smelting plant located in Piekary Slaskie, Poland. The wasteland had wastes from two different smelting processes — Welz and Doerschel. Both wastes contained extremely high loads of Zinc (up to 128 g kg^{-1}), Lead (up to 40.6 g kg^{-1}), Cadmium (up to 3.46 g kg^{-1}) and Arsenic (0.76 g kg^{-1}). The pilot reclamation of smelter waste sites was performed within the framework of the Silesia project. The project was a joint effort by local government, industry and national or international research institutions and agencies: the US Environmental Protection Agency (USEPA), the Centre for Research and Control of the Environment (OBIKS), Virginia Polytechnic Institute, USDA-ARS in Beltsville and the Institute of Soil Science and Plant Cultivation (IUNG). The main objective of the Silesia project was the development of guidelines for the effective and safe use of biosolids for the reclamation of degraded lands and waste sites.

The problem

In the 1990s metal waste sites in the Silesia region were known to contain more than 87 million tonnes of waste. The deposited wastes, containing several per cent zinc and lead, had become a hazard to humans and the environment through leaching and wind erosion (picture above on page 137 of barren smelter wasterland in Piekary before the reclamaton). It must be noted that smelter or mining wastelands are dispersed within the mosaic of various land uses in the region: settlements, arable lands, hobby gardens, parks. This creates a range of various pathways for negative impact from the wastelands, which

Barren smelter wasteland in Piekary during the 90's before the reclamation.

> **"The pilot reclamation** *of smelter waste sites was performed within the framework of the Silesia project and it was a joint effort between local government, industry, national/international research institutions and agencies."*

are generally barren and susceptible to dispersion of pollutants. Spontaneous vegetation processes are very slow and inefficient in terms of reducing health and environmental risks. Therefore it was evident that a simple and cost effective solution for stabilizing these sites was needed and aimed at establishing permanent vegetative cover on the waste piles to reduce leaching or erosion of toxic elements, as well as to keep metallic fugitive dust from being dispersed. Difficulties in revegetation of these sites are related to a combination of many variables limiting plant ability to grow, including harsh physical conditions, lack of water retention, Zinc phytoxicity and deficiency of nutrients.

The strategy

Method

Due to shortage of valuable soil material for top-soiling, an alternative method was needed for the site remediation. The implemented integrated approach involved application of two types of wastes – biosolids and by-product lime for revegetation of the toxic wastelands, selection of resistant grass species and long-term monitoring of the reclamation performance. Two experimental sites were reclaimed in mid- 90's in Piekary covering almost 1 ha. The reclamation treatments for Site I took place in summer 1994. The top layer of Welz waste was treated by application of municipal biosolids at the rate 300 dry Mg ha^{-1} (dry matter basis) combined with the incorporation of lime in an oxide and carbonate form at the rate of 1.5 and 30 Mg, respectively. The incorporation of materials used for stabilization was done by a chisel plow to a depth of 15 to 20 cm. Different approach was applied for the more toxic Doerschel part of the Site I in a subsequent season (1995). It involved the use of a 30 cm byproduct lime cap which was lined over the top of the waste surface. This capping was followed by incorporation of biosolids at a rate of 300 Mg ha^{-1} (dry matter basis). The by-product lime was obtained from the sedimentation pond of a ground water treatment facility where calcium hydroxide was used to precipitate metals from water. Biosolids were obtained from the municipal waste water treatment process. The fields were then seeded with following mixture of grasses: *Festuca rubra* L. cv. Atra, *Poa pratensis* L. cv. Alicja, *Festuca arundinacea* Schreb. cv. SZD, and *Festuca ovina* L. cv. Sima. These approaches

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Remediation works on-site - 1995.

> “The deposited wastes, *Zinc and Lead, had become a hazard to humans and the environment through leaching and wind erosion.*”

resulted in establishing plant cover (picture above page 138: reclaimed site in 1995).

The Site II was the experimental field established in 1997 for testing effectiveness of biosolids/lime rates (6 combinations) and grass species/cultvars (23 cultivars) in revegetation of the wastelands. The 23 grass cultivars represented the following species: *Festuca rubra*, *Poa pratensis*, *Festuca arundinacea*, *Festuca ovina*, *Festulolium*, *Agrostis alba*, *Lolium perenne*, *Agrostis canina*, *Agrostis capillaris*,

	Impact pathway	Status before the remediation	Remediation effect
1	Soil to groundwater	Leaching of mobile metals (Pb, Cd, Zn)	Leaching stopped due to water retention by incorporated biosolids and plant cover. Water soluble metals drastically reduced
2	Soil to plants	Limited, surface is rather barren. Metal uptake by spontaneously growing plantsv	Some uptake by plants introduced during remediation but below phytotoxicity level
3	Soil to animals	Waste ingestion by wild animals	Waste ingestion by wild animals reduced, Fauna diversity highly improved
4	Soil to microorganisms	Very low activity of microbes	Microbial activity recovered
5	Soil to humans	Contaminated waste material dispersed through wind erosion	Erosion reduced after establishing plant cover
6	Plants to animals	No plant cover before remediation	Possible some transfer of metals to wild animals but limited bioavailability
7	Animals to humans	No close linkage, not investigated	No close linkage, not investigated
8	Water to humans	Transfer of metals through groundwater	Leaching of TE to groundwater reduced or stopped
9	Plants to humans	Not relevant, no production for food. Some impact of waste erosion on arable lands around. Not investigated	Not relevant, no production for food. Likely lower impact of erosion on arable land around but not investigated

Effect of the wasteland reclamation on pollutant linkages

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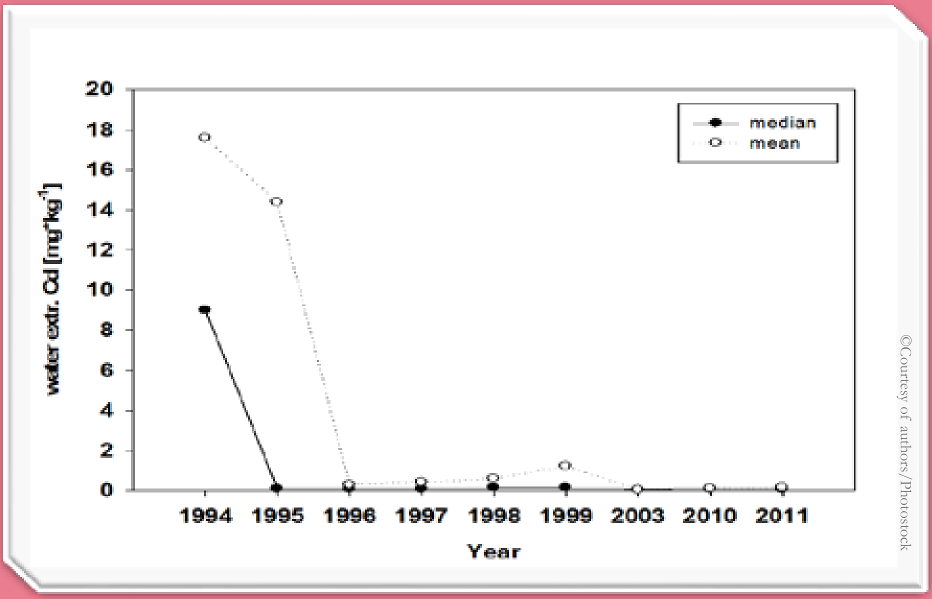


Long-term changes in Cadmium (Cd) water solubility after reclamation of slags by application of biosolids and lime performed in 1995 (Piekary Site I). Year 1994 represents initial status - before the reclamation.

Dactylis polygama, *Deschampsia caespitosa*, *Puccinella distans*, tested in separate plots. Site II treatment involved the following six combinations of amendment rates: municipal biosolids (B) low (150 Mg ha^{-1}) and high rate (300 Mg ha^{-1}) and by-product lime (BL) low (100 Mg ha^{-1}) and high rate (200 Mg ha^{-1}): low B; high B; low B + low BL; high B + low BL; low B + high BL; high B + high BL.

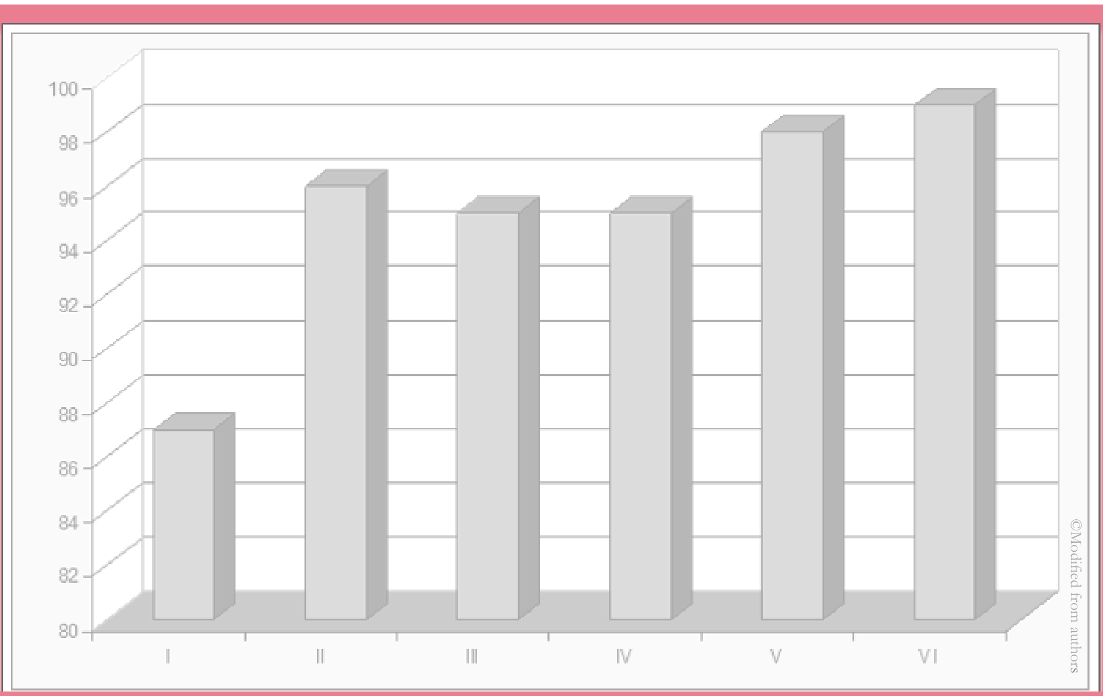
The conclusions

Effects

At both sites the biosolids combined with lime developed conditions suitable for grass growth and enabled establishment of permanent plant cover which drastically reduced wind and run-off driven dispersion of metals. Assessment of metal solubility in subsequent years showed substantial decreases of Zinc, Cadmium and Lead solubility as measured by water extractions. This was an effect of pH shift due to dissolution of applied limestone and accelerated adsorption and occlusion of metals in the presence of organic matter and iron oxides. The important question was raised after the plant had been established at the sites regarding safety of the proposed remediation methodology to food chain. Subsequent feeding trial revealed that potentially toxic metals such as Lead and Cadmium were not excessively transferred to muscles of cattle fed with hay harvested at the site. The animals also did not show any visible symptoms of health disorder. Obviously, such a reclaimed site would not be acceptable for permanent grazing due to risk of cattle exposure to direct soil ingestion. However, it is evident from the studies that plant cover of the reclaimed Zn -, Cd -, and Pb - contaminated site do not pose any identified risk for wildlife.

Effects of the applied remediation on most significant pathways of negative impact of the wasteland are presented in the Table page 138 - effect of the wasteland reclamation on pollutant linkages, as based on the conceptual model exercised in GREENLAND project.

Generally the reclamation limits the pollutant dispersion into the environment and reduces the related risk to human health. On the other hand the tested approach did not induce any recognized secondary risks.



Average plant coverage (%) as response to the stabilization treatment at Piekary Site II recorded in 2012 (15 years after the treatment). Plots I-VI correspond to low B; high B; low B + low BL; high B + low BL; low B + high BL; high B + high BL, respectively (B-biosolids, BL-byproduct lime). No plants grown at untreated control area.

Monitoring

The sites were regularly sampled in a regular grid in subsequent years (1995–1999) under the SILESIA project. Then the sites were resampled in 2003 and in 2010-2014 under 7FP GREENLAND project. Samples were taken from 0 to 15 cm depth. The samples were analyzed for labile metals in the soils, plant metals, microbial activity, pH, carbon, salinity.

The analysis proved permanent reduction of metal mobility as indicated by water or neutral salt extractions (graph above page 138 on long-term changes in Cadmium). Measurements of enzyme activities in reclaimed top layer produced similar levels to that of arable soils from the region, both 4-5 and 15 years after remediation. This proves that the applied reclamation methods effectively establish fully functioning ecosystems and nutrient cycling that support plant growth.

Long-term observations of both Site I and Site II revealed that combinations of high rates of biosolids and lime established permanent plant cover (go on see bar graph above page 140 showing average plant coverae).

In 2012-2014 we did extensive research of Site II biodiversity, including appearance of original and spontaneous plant species and diversity of some mesofauna. The most persistent, among original grass species, were *Poa pratensis*, *Agrostis capillaris* and *Festuca ovina*. These species covered the largest area of the field 17 years after remediation among all grasses. Most of the area was covered by spontaneous vegetation - *Calmagrostis epigejos*, *Hypochoeris radicata*, *Melandrium album*, *Artemisia vulgaris*, *Daucus carota* and *Solidago gigantean.* High number of fauna representing Gastropoda, Myriapoda and Collembola was observed for plots treated with biosolids and by-product lime.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Site I in 2011. Untreated control area on the left.


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Site II in 2014.

> *“Long-term observations of both Site I and Site II revealed that combinations of high rates of biosolids and lime established permanent plant cover .”*

Current status and the conclusion

In accordance to the original aim of the implement approach, the plant cover is not managed and it is left to spontaneous changes in vegetation. Regardless the weather conditions, each year high plant biomass and coverage is produced at the site, preventing erosion of toxic waste and leaching of pollutants.

Long-term observations prove that permanent plant cover has been established, consisting with initial grasses and spontaneous species (pctures Site I and Site iI).

Summarizing, the most important strengths of the method are:

- reduction of labile metal (Cd, Zn, Pb) pools in the waste top layer
- plant cover reducing leaching and wind erosion
- microbial activity and site biodiversity recovered
- low cost of the remediation.

Further readings

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NETWORKING

NETWORKING

1. Italy: Reconnet, the Italian network on management and remediation of contaminated sites

Networking

1. Reconnet: the Italian network on management and remediation of contaminated sites

LOCATION	Italy
POLLUTANT	Non specified
SOURCE	Landfill
GENERAL CLEAN UP OBJECTIVES	Reduce soil and groundwater contamination
REMEDIATION ACTIONS	Development of new managements tools
SITE/END USE	Non specified
SOCIAL-LEGAL ISSUES	Land reclamation, human health risk
KEY LEARNING/ EXPERIENCE TO SHARE	Risk-net software became the official Reconnet software for risk assessment

Author's profile

Renato Baciocchi has been Associate Professor of Environmental Engineering at the University of Rome Tor Vergata since 2014. He received a PhD in chemical engineering from the Politecnico di Milano in 1995 and worked as a process engineer before starting his academic career at the end of 1998. His main research interests focus on the remediation and management of contaminated sites and on the carbonation of minerals and industrial residues, with his most recent works focusing on innovative approaches for in situ chemical oxidation, vapour intrusion modelling and brownfield regeneration. He has published more than 200 contributions to international journals and conference proceedings, with about 75 papers published in peer review journals. He is the coordinator of the Reconnet network.

Iason Verginelli has been a postdoctoral research associate at the University of Rome Tor Vergata since 2012. He received a PhD in environmental engineering in 2012 from the University of Tor Vergata (awarded with the Italian national prizes 'Remtech 2012' and 'GITISA 2013'). Dr Verginelli has project experience in human health risk assessment and characterisation and remediation of contaminated sites. He is the author and developer of the Risk-net tool, one of the most widely used software programmes at the Italian national scale for the evaluation of soil and groundwater remediation sites. He participated as a trainer in different classes on risk-assessment for second-level professional master's programmes and for professional courses of environmental control agencies. He has published more than 50 contributions to international journals and conference proceedings, with 20 papers published in peer review journals.

Igor Villani is a civil servant at ARPAE Emilia Romagna (the Environmental Agency for the Emilia Romagna region). He has two masters in environmental managing and environmental risk assessment from the University of Ferrara. His main activities focus on institutional control of the remediation process and management of contaminated sites and on the development of new strategies for land management and risk management. He has contributed to the drafting of national environmental guidelines and he is part of the scientific committees of national environmental congresses. He holds university lectures and specialised courses. He has published more than 30 contributions to journals and conference proceedings. He is the secretary of the Reconnet network.

Reconnet: the Italian network on management and remediation of contaminated sites

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The Italian network for the management and remediation of contaminated sites (Reconnet), established in 2010 on the basis of an agreement promoted by the University of Rome Tor Vergata, is the main multistakeholder network operating in Italy in the field of contaminated sites, counting around 60 members among universities, scientific institutes, research centres, consultants, regional environmental agencies, trade associations and large private companies. This paper presents the activities carried out by the working groups operating within the network and the main results obtained so far. These include the human health risk assessment software Risk-net, the White Paper on sustainable remediation and the document discussing the management of contamination events in landfill areas. These activities, together with the many dissemination events organised by the network, assign to Reconnet an increasingly important role in promoting the stakeholders' engagement in the management of contaminated sites.

Keywords: *contaminated sites, ecological risk assessment, human health risk assessment, landfill, persistent organic pollutants, phyto-technologies, remediation, stakeholders' engagement, sustainability, vapour intrusion.*

Introduction

The current pace of remediation activities in Italy is limited by the lack of effective stakeholder engagement in the definition of the remediation pathway, while contrasts often arise between problem owners and regulators. The involvement of universities and research institutes by problem owners and consultants is often motivated by the need for getting support in administrative or legal controversies, rather than for introducing innovative approaches and solutions. Thus, contaminated sites are a sort of lost opportunity for the development of new management tools, new technologies and new approaches for the requalification of brownfield sites. The establishment of a drive belt, connecting problem owners and consultants, regulators and scientific institutes, universities and research centres, could have the potential to accelerate the clean-up of contaminated sites, thus fostering the growth of the remediation market and making it a relevant part of the green economy, as is the case in other industrialised countries. The generation of this drive belt is the main goal of the Italian network on the management and remediation of contaminated sites (Reconnet), which was established in 2010 and now includes members representing the different stakeholders involved in contaminated sites issues. This paper will provide an overview of the network, discussing its goals, how it is organised and the main results (products, tools and dissemination activities) achieved so far.

Set-up, goals and members of Reconnet

As already outlined above, Reconnet was established in 2010 on the basis of an agreement promoted by the University of Rome Tor Vergata and signed by INAIL (National Institute for Insurance against Accidents at Work), ISPRA (Italian National Institute for Environmental Protection and Research), Sapienza University

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The Reconnet network.

of Rome, the University of Eastern Piedmont and ARPALazio (Regional Environmental Protection Agency). Currently, the Reconnet network has around 60 members, including universities, scientific institutes, research centres, consultants, regional environmental agencies, trade associations and large private companies. The logos of the members of the network are shown in page 150. The network aims at providing a contribution to solve the main technical and regulatory open issues on the management and remediation of contaminated sites. Namely, Reconnet has the following goals: encouraging collaboration and promoting exchange of data and information between research centres, regulators, private companies and consultants; transferring and spreading information through databases, websites and other e-media types; organising conference and seminars; identifying the main topics requiring theoretical and technological investigation. The network activities are steered by the assembly — composed of the representatives of the six members who signed the original agreement — following the suggestions of the general assembly — composed of the representatives of all members. As it will be discussed in more detail later in the paper, the activities of the network are carried out by working groups dealing with specific issues. The decision on setting up specific working groups and the final approval of their products (tools, documents, White Papers, etc.) is taken by the network assembly.

Working groups

The network is currently organised into the following thematic working groups: ecological risk assessment; phytoremediation; regeneration of contaminated sites and urban planning; persistent organic pollutants; vapour intrusion; sustainable remediation (SuRF Italy). The main products developed so far within Reconnet include: the Risk-net software, which has become the national reference tool for carrying out risk assessment for contaminated sites; the Leach8 software, useful for carrying out risk assessment for landfills; the White Paper on sustainable remediation; the document with warning levels for landfill monitoring; the benchmark for risk assessment software. This section provides an overview of the activities performed so far and to be still carried out by the different working groups.

Working group on the Sustainable Remediation Forum: SuRF Italy

This working group, led by Claudio Albano (CH2M) and Paola di Toppa (ISPRA), stems from an initiative carried out by a group of experts

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Logos of the Reconnet members (as of 30 June 2016).

operating at national and international level in the field of contaminated-site remediation and familiar with the issue of sustainability. In 2012 this group started to elaborate on the opportunity of working together in order to disseminate the practice of sustainable remediation among the stakeholders involved and to promote a kind of initiative similar to the ones already started in other countries and international contexts. At the beginning of 2013 this group officially launched the Italian branch of the Sustainable Remediation Forum (SuRF Italy), which started its activities as a working group of the Reconnet network. The goal of this working group is to establish a permanent national discussion forum among the stakeholders involved in the management and remediation of contaminated sites, for the definition and application of sustainable approaches and practice. The first step of SuRF Italy was to provide a definition of sustainable remediation as 'the process of management and remediation of a contaminated site, aimed at identifying the best solution, that maximises the benefits achievable through its implementation from an environmental, economic and social point of view, through a decision pathway shared with the stakeholders involved.' The SuRF Italy working group has already issued its first product, the White Paper on sustainable remediation, available for download from the Reconnet website. This document first provides an overview of the different initiatives already ongoing at international level on sustainable remediation; then, it summarises the legislative framework on remediation of contaminated sites in Italy and the current situation of the remediation market; finally, it discusses the fundamental principles of sustainable remediation and its scope of application and lists the main activities needed to apply sustainability concepts to the remediation of contaminated sites in Italy. The appendix to the White Paper includes around 10 case studies of sustainable remediation, some of which refer to applications in Italy. Currently, a second document on the operating criteria for sustainable remediation in Italy is in preparation, which will represent a sort of guideline to be applied, on a voluntary

basis, by the stakeholders involved, in order to drive the remediation process following the best practice of sustainable remediation.
Finally, it is worth mentioning the contribution of SuRF Italy in organising the 2014 edition of the International Conference on Sustainable Remediation in Ferrara, and also in supporting and promoting the latest edition held in Montreal (Canada) in April 2016 by the active participation of some members of the working group to the scientific committee of this conference.

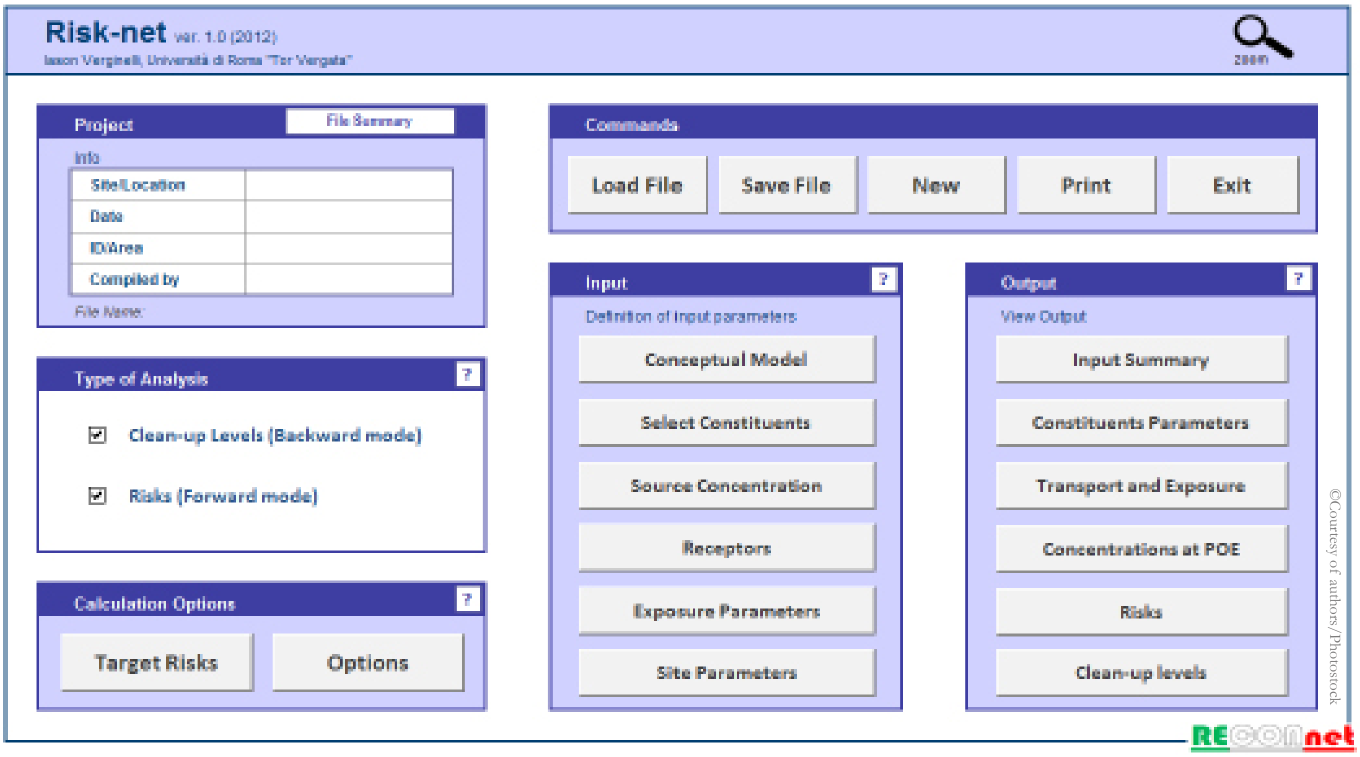
Working group on interaction between landfills and remediation

This working group deals with the critical issues related to the interaction between landfill management and remediation of impacted soil and groundwater. The group, led by Igor Villani (ARPAE) and Andrea Forni (Professional Engineering Society of Bologna), has already issued a document titled *Determinazione e gestione dei livelli di guardia per il monitoraggio delle discariche — Relazioni con i siti contaminati* (‘Definition and management of guard levels for monitoring of landfills — Relationship with contaminated sites’), available for download from the Reconnet’s website.

The document deals with the thin borderline between the impact of a landfill plant on the environment linked to its normal operation on one side and the pollution event on the other. The study deals with emissions into the atmosphere or into groundwater from landfills, describing the methods to be employed for their monitoring and then discussing the main issue of interest, that is how to identify a significant modification of the quality of the environmental matrices, and particularly its correlation with the activities carried out in the landfill.
Proper management strategies have also been developed that can be integrated into the Environmental Integrated Authorisation (EIA) with the aim of minimising the potential for emerging conflicts between authorisation and remediation procedures. A case study, proposed by the Abruzzo regional environmental agency, is also provided in annex to the proposed management strategy.
The methodology introduced and discussed in the document provides the fundamental framework for setting up a decision support system for the management of significant events that can be correlated to leachate and/or gas dispersion from the landfill.
As far as the impacts on groundwater quality are concerned, the proposed methodology relies on the definition of screening levels for a limited set of contaminants (typically three) selected by taking into consideration their mobility in the unsaturated/saturated zone and considering their significant presence in the leachate produced in the landfill. The latter factor is considered to be particularly relevant in order to avoid tracing back to the landfill contamination those plumes deriving from external sources and to wrongly activate useless remediation procedures for the landfill, with costs to be borne by the company in charge of the landfill management but also indirectly by the regulator.
As far as the impacts on air are concerned, the document provides useful indications for the determination and identification of proper screening values for both air and soil gas.

Working group on vapour intrusion

The working group on vapour intrusion, led by Simona Berardi (INAIL) and Iason Verginelli (University of Rome Tor Vergata), first prepared a survey that was shared with the different members of the Reconnet network on the ‘Criteria and methods adopted for the analysis of soil gas’. The results of this survey highlighted the main issues that will be addressed by the Reconnet WG. In particular, the working group on vapour intrusion is preparing a technical document that will address the following critical aspects: the procedure to be used for the inclusion of soil-gas data in risk assessments; the definition of risk-based soil-gas screening levels; the criteria to be used to evaluate the contribution to the overall volatilisation from subsurface as a result of contamination in both soil and groundwater; the analytical models to be used for a more realistic assessment of the vapour-intrusion pathway; the exposure and site-specific parameters to be used for the risk assessment procedure.



☑ Clean-up Levels (Backward mode)

☑ Risks (Forward mode)

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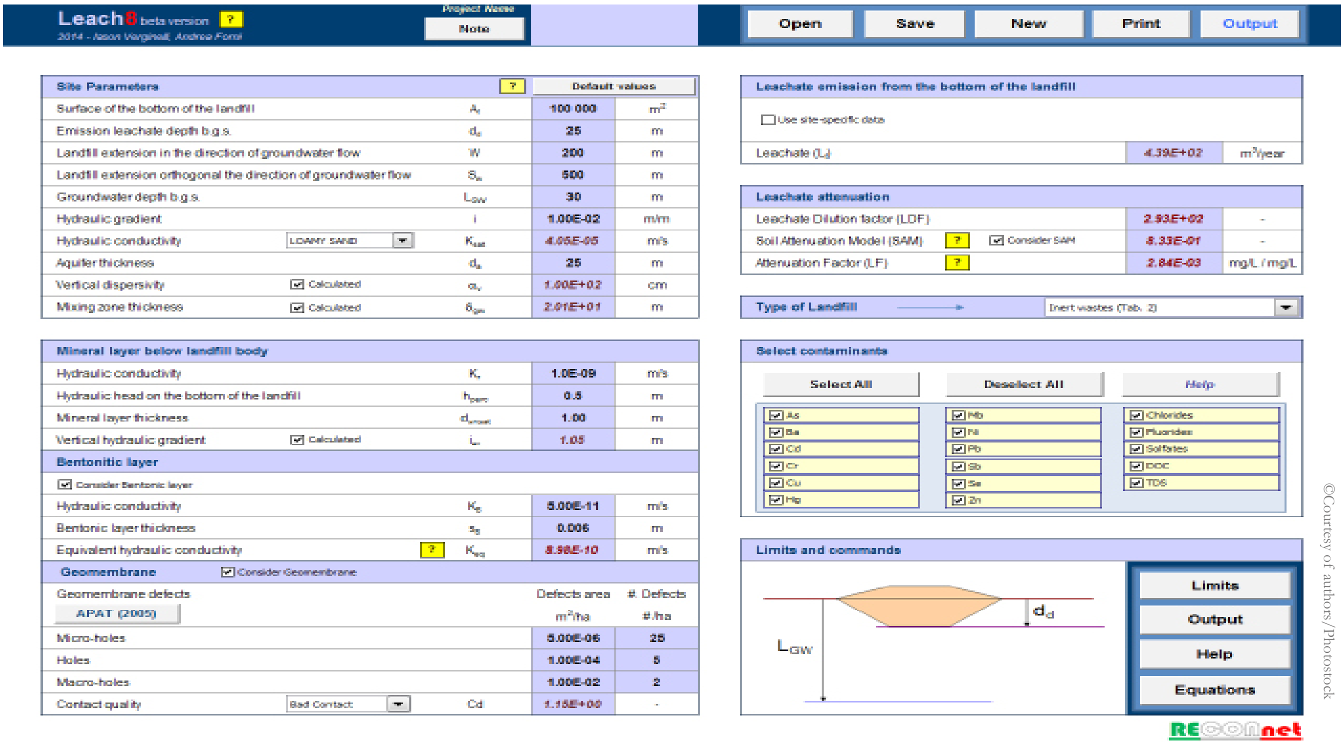
Main screen of Risk-net.

Working group on environmental risk assessment

The working group on ecological risk assessment (ERA), led by Guia Agostini and Renato Baciocchi (University of Rome Tor Vergata), aims at the definition of criteria and approaches for the application of this procedure in the Italian context, making reference to international approaches. A first document, currently being finalised, reports a critical analysis of the main ERA procedures adopted at international level. All the analysed procedures are based on a tiered approach, characterised by levels of increasing complexity. This results in an increase in site-specific data needed when moving to higher tiers in place of more conservative assumptions typically used in lower tiers. Based on the outcomes of this first document and considering that the human health risk assessment procedure, used in the Italian legislation to set the clean-up goals for soil, is based on the RBCA-ASTM approach, it was decided to follow the Eco_RBCA standard (ASTM E2205/E2205M 2002 — reapproved in 2009) as reference for an ERA procedure in Italy. It is expected to produce four documents, which will detail the data to be collected and the approach to be used for each of the four tiers provided for by the Eco-RBCA approach: scoping; Tier I with the definition of ecological screening levels; Tier II, with the definition of a site-specific modelling approach; Tier III with the identification of appropriate experimental methods for assessing the ecological quality of the potentially affected environmental matrices.

Working group on phyto-technologies for the remediation of contaminated sites

This working group, led by Andrea Sconocchia (ARPA Umbria), was formed with the idea of creating a scientific reference pole for the application of phyto-technologies for the remediation of contaminated sites. Although there is an increasing interest in this approach at both national and international level, there are still many critical issues hindering its application, which include technical and regulatory aspects, the solution to which requires the availability of a reference point at national level, currently missing. The working group will investigate in detail the main technical and regulatory obstacles to a full deployment of phyto-technologies for the remediation of contaminated sites and will propose solutions to overcome these



Site Parameters				
Surface of the bottom of the landfill		A_f	100 000	m^2
Emission leachate depth b.g.s.		d_e	25	m
Landfill extension in the direction of groundwater flow		W	200	m
Landfill extension orthogonal the direction of groundwater flow		S_w	500	m
Groundwater depth b.g.s.		L_{GW}	30	m
Hydraulic gradient		i	1.00E-02	m/m
Hydraulic conductivity	LOAMY SAND	K_{sat}	4.05E-05	m/s
Aquifer thickness		d_a	25	m
Vertical dispersivity	☑ Calculated	α_v	1.00E+02	cm
Mixing zone thickness	☑ Calculated	δ_{gw}	2.01E+01	m

Mineral layer below landfill body				
Hydraulic conductivity		K_l	1.0E-09	m/s
Hydraulic head on the bottom of the landfill		h_{perc}	0.5	m
Mineral layer thickness		$d_{mineral}$	1.00	m
Vertical hydraulic gradient	☑ Calculated	i_v	1.05	m
Bentonitic layer				
☑ Consider Bentonic layer				
Hydraulic conductivity		K_B	5.00E-11	m/s
Bentonic layer thickness		s_B	0.006	m
Equivalent hydraulic conductivity	?	K_{eq}	8.98E-10	m/s
Geomembrane	☑ Consider Geomembrane			
Geomembrane defects			Defects area	# Defects
APAT (2005)			m^2/ha	#/ha
Micro-holes			5.00E-06	25
Holes			1.00E-04	5
Macro-holes			1.00E-02	2
Contact quality	Bad Contact	Cd	1.15E+00	-

Leachate emission from the bottom of the landfill		
☐ Use site-specific data		
Leachate (L_d)	4.39E+02	m^3/year

Leachate attenuation			
Leachate Dilution factor (LDF)		2.93E+02	-
Soil Attenuation Model (SAM)	? ☑ Consider SAM	5.33E-01	-
Attenuation Factor (LF)	?	2.84E-03	mg/L / mg/L

Type of Landfill → Inert wastes (Tab. 2)

Select contaminants

☑ As
☑ Ba
☑ Cd
☑ Cr
☑ Cu
☑ Hg
☑ Mo
☑ Ni
☑ Pb
☑ Sb
☑ Se
☑ Zn
☑ Chlorides
☑ Fluorides
☑ Solfates
☑ DOC
☑ TDS

Main screen of Leach8.

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problems. The starting point for this activity will consist in the systematic collection and classification of the experience gained at national level on the application of phyto-technologies. Namely, the working group will deal with the following issues: study of the legislative framework regulating remediation processes based on phytoremediation; application and technical issues with specific reference to the use of vegetable species for the characterisation and monitoring of contaminated sites and for their remediation; comparative assessment of tools available for evaluating the sustainability of phyto-technologies with respect to other clean-up options; valorisation of obtained products and by-products also relying on green chemistry techniques (i.e. phytomining). The results obtained so far have been collected in a first report on Phytoremediation techniques in the cleanup of contaminated sites (Sconocchia et al., 2017).

Working group on contaminated sites and land management

This working group, led by Igor Villani (ARPAE) and Jean Pierre Davit (Golder), aims at examining the main problems linked to the relationship between the management of contaminated sites and land management, with specific reference to the issues of brownfield regeneration and soil consumption. In Italy, the main elements that form the basis of actual land management practice are the protection and restoration of the environment, but the tools available are often not sufficiently evolved to meet the needs. The goal of the working group is to identify and characterise the main problems and to develop new strategies, and eventually proper tools, supporting land management for the regeneration of contaminated sites. The main problem to be tackled consists in the lack of any link between the legislation on urban planning and that on the protection of the environment. Whenever a building project takes place together with a remediation project, each of the procedures (the building permit and the clean-up permit) is usually managed and proceeds independently following its own time frame. Anyhow, this kind of administrative separation between the two processes does not correspond to an operative separation, as the two processes strongly affect each other, thus generating delays and cost increases that may become detrimental to the successful completion of the financial plans. This situation, which may ultimately lead to the interruption of the site requalification process, is a deterrent for private investors, thus negatively affecting the evolution of the remediation market and the opportunities for the requalification of contaminated sites. The working group is currently looking for new pathways to achieve an evolution and modernisation of the approaches for urban planning and land management in sites undergoing remediation. This will be achieved introducing new concepts, such as those of adaptive reuse and adaptive remediation, while also relying on risk management as an effective tool to reconcile the protection of the environment with the needs of a growing (post-)industrial society.

The strategy

Tools developed within Reconnet

The Risk-net software for risk assessment at contaminated sites

The Risk-net software has been developed within the Reconnet network by Iason Verginelli (University of Rome Tor Vergata). The tool is based on the ISPRA (Italian National Institute for Environmental Protection and Research) guidelines for risk analysis application at contaminated sites that were developed following the ASTM RBCA (Risk-Based Corrective Action) standard approach. The software allows the application of the risk assessment procedure in both forward and backward mode, thus evaluating the risk or the clean-up levels for a contaminated site, respectively. The software uses a simple and user-friendly graphical interface through which the user can define the different input parameters. To accelerate the compiling process, according to the conceptual model of the site defined by the user, only the data actually used in the calculation are required. Some controls also allow management of the presence of conceptual and numerical errors. The results are returned in terms of risk (for human health and groundwater resource protection) and clean-up levels. Intermediate outputs are also displayed, allowing the user to evaluate more critically the obtained results. The key features of Risk-net include the following.

- Risk-based clean-up level calculations: Risk-net completes all calculations required for Tier 1 and Tier 2 RBCA evaluations, including risk-based exposure limits and attenuation factor derived from simple fate and transport models.
- Fate and transport models: validated analytical models for air, groundwater and soil exposure pathways, including all models used in the ISPRA (2008) standard.
- Chemical and toxicological database: integrated toxicological and chemical parameter library preloaded (ISS-INAIL Database). The database is customisable by the user, including import features for management of external database.
- User-friendly interface: point-and-click graphical user interface with online help, unit conversion and load/save capability.

Risk-net can be downloaded for free from the website of the Reconnet network (http://www.reconnet.net). So far 3 000 users have downloaded this software, which has become in few years the reference tool for carrying out risk assessment at national level.

The Leach8 tool for risk assessment at landfill sites

The Leach8 tool has been developed within the Reconnet network by Iason Verginelli (University of Rome Tor Vergata) and Andrea Forni (Professional Engineering Society of Bologna). The tool is based on the ISPRA Italian guidelines for risk analysis application at landfill sites. Namely, the tool can be used for the estimation of maximum allowable leachate concentrations for groundwater resource protection at inert, non-hazardous or hazardous waste landfills. These screening levels are calculated by Leach8 based on the acceptable concentration levels in groundwater set by the Italian legislation and based on the leaching factor calculated by the tool from the site-specific parameters defined by the user. Leach8 can be downloaded for free from the website of the Reconnet network (http://www.reconnet.net).

Dissemination events

The Reconnet network has been active since 2010 in several dissemination activities. The main event co-organised by the network is the School on the Remediation of Contaminated Sites, now in its fourth edition, organised in Ravenna as part of the Fare i Conti con l'Ambiente event. In addition, Reconnet also organised a series of thematic courses on human health risk assessment and the Risk-net software and a series of national conferences at the INAIL headquarters in Rome. Reconnet has also set up partnerships with Remtech, the main national exhibition and conference on remediation of contaminates sites in Italy, and ATIA-ISWA, the Italian chapter of the International Solid Waste Association, with the aim of developing joint dissemination activities. It has also pursued international activities in cooperation with CRC-Care, participating in the Australia-based CleanUp 2013 conference and has supported the organisation of the Sustrem conference series since 2014 through its working group on sustainable remediation.

The conclusion

The tenfold growth of the Reconnet network in only 6 years, from a small agreement between six members to a large network of 60 members, shows how strong was (and is) the need for the different stakeholders involved in the remediation of contaminated sites to find common ground for discussion on the many open critical issues which hinder the smooth development of remediation plans. Reconnet represents a virtual place where consultants, problem owners and regulators can even have harsh discussions on some topics, but always with the goal of finding a compromise to be translated in a technical document or a tool that has the potential to become an (un-)official reference for the management of contaminated sites. Reconnet represents an opportunity for the different stakeholders to disseminate their experience through the organisation of higher education and formation events. Reconnet represents an opportunity for innovators to spread their ideas, allowing the network to check and validate their new product or approach. In this way, the Risk-net software, developed within the University of Rome Tor Vergata, became the official Reconnet software for risk assessment, and in a very short time replaced all other HHRA tools used in Italy until few years ago. Reconnet has done much but has the potential to do more. Its limit is that all activities are carried out on a voluntary basis by its members. Its strength (the lack of financial interests) is also its weakness, as all members have a limited time slot to dedicate to the network. The past 6 years of Reconnet tell of a success story. The long term resilience of Reconnet will depend on its capacity to adapt to its new size and role, eventually by moving from its current status of network based on an agreement to the one of an association; but clearly any decision on the future form of Reconnet will have to consider the need to keep the original spirit of the network.

Further reading

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- Forni A., Villani I. et al. (2015), Determinazione e gestione dei livelli di guardia per il monitoraggio delle discariche — Relazioni con i siti contaminati. Available at: http://www.reconnet.net/Docs/Bonifiche_discariche_REV%200.pdf
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- Sconocchia et al. (2017), Tecniche di fitorimedio nella bonifica dei siti contaminati. Available at: http://www.reconnet.net/Docs/Tecniche%20di%20fitorimedio%20nella%20bonifica%20dei%20siti%20contaminati_RECONnet_2017.pdf.

Relevant websites

http://www.reconnet.net
http://www.surfitaly.it
http://www.remtechexpo.com
http://www.labelab.it/ravenna2016/

MINING SITES

MINING SITES

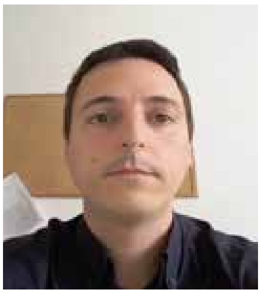
1. Italy: torrente Ritorto in Colline Metallifere (Tuscany); constructed wetlands for remediation of acid mine drainage

Mining sites

1. Torrente Ritorto in Colline Metallifere (Tuscany): constructed wet lands for remediation of acid mine drainage, Italy

LOCATION	Tuscany, Italy
POLLUTANT	Iron, Manganese
SOURCE	Former pyrite mine *Fontacinaldo*
GENERAL CLEAN UP OBJECTIVES	Reduce soil and groundwater contamination
REMEDIATION ACTIONS	Phytotreatment with aerobic/anaerobic lagoons
SITE/END USE	Natural areas
SOCIAL-LEGAL ISSUES	Land reclamation, human health risk
KEY LEARNING/ EXPERIENCE TO SHARE	Self-colonization of plant species both in the banks and in waters

Author's profile



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Torrente Ritorto in Colline Metallifere (Tuscany): constructed wetlands for remediation of acid mine drainage, Italy

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In lower Tuscany there is a high density of old mines. The waste tailings and the waters coming from those areas have a very low pH and are rich in metals (aka acid mine drainage), posing a hazard for receptors downgradient and a threat to water resources. In this case, Fontacinaldo Mine in Massa Marittima (GR), multiple wetlands have been put in place to alternate anaerobic/aerobic conditions, plus a sediment-deposit wetland with an overall residence time of waters suitable to treat contaminants of concern. The Ritorto creek got back good environmental quality that allowed some native species to settle on its banks and in the waters.

Keywords: *phytoremediation, acid mine drainage, metals, low pH, mine tailings, Iron, Manganese, aerobic condition, anaerobic condition, sedimentation.*

Introduction

The case study covers an area impacted by anthropogenic activities of the former Fontacinaldo pyrite mine located in the municipality of Massa Marittima (GR), in southern part of Tuscany. The area is approximately 2 km^2 and extends along the bed of the Ritorto creek. The reclamation project and environmental restoration was aimed at the environmental rehabilitation of the riverbed affected by mineral deposits piled along the banks of the Ritorto creek.

The problem

Contaminants of concern and concentration

The Ritorto creek showed a pH of 4.1, with an iron concentration of 7.5 mg/l in filtered samples and 56 mg/l in unfiltered samples. Also, manganese was detected in high concentrations in the waters of the creek, with a concentration of 1.75 mg/l in filtered samples and 11.9 mg/l in unfiltered samples.

The strategy

Remediation project

As the site is very difficult to reach, both the selection of the surface water treatment and sediment control should go for technologies with a low level of operation and maintenance (O&M), such as phytoremediation associated with mechanical filtration systems that can also contribute to the landscape upgrade of pyrite banks.

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Aerial view of the area in question. Blue arrows indicate where waste tailings piles are located.

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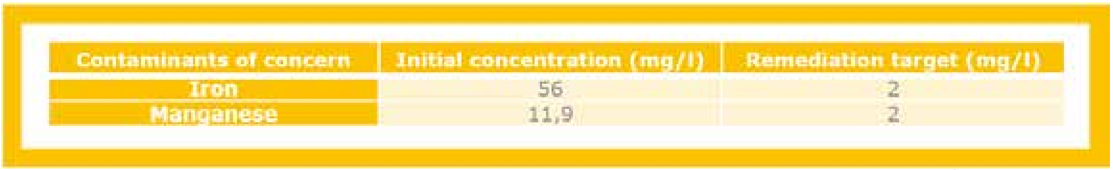
One of the many pyrite piles present in the area.



Contaminants of concern	Initial concentration (mg/l)	Remediation target (mg/l)
Iron	56	2
Manganese	11,9	2

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Contaminants of concern: concentration and remediation targets.

The treatment system is constituted of the following structures:

- Water intake of Ritorto creek.
- Sedimentation wetland.
- Three passive system wetlands with the aim of reduction of iron through anaerobic treatment.
- Four passive system wetlands with the aim of reduction of manganese through aerobic treatment.
- One terminal wetland, prior to the reintroduction of the water in the Ritorto creek.

For the correct sizing of the treatment the determination of the expected flow of the watercourse is crucial: the data collected showed that the Ritorto creek can pass from relatively high flow rates (maximum recorded flow rate: 1.05 m^3/s in case of significant rainfall and to close to zero (0 001 m^3/s) after a dry period.

Water intake

The intake structure is placed upstream of the phytoremediation wetlands and has the function of ensuring a maximum flow input to the plant system of 60 litres/minute.

The intake structure is made up of the following main stages:

1. Intake screen in the river bed.
2. Well with booster pump.
3. The sedimentation tank and the forebay.
4. Adduction pipes.

Anaerobic lagoons

At a structural level, the anaerobic lagoons are constituted of a treatment medium consisting of a thin, permeable layer of organic material placed above a bed of limestone. The combination of organic and limestone substrate allows for simultaneous removal of metals providing

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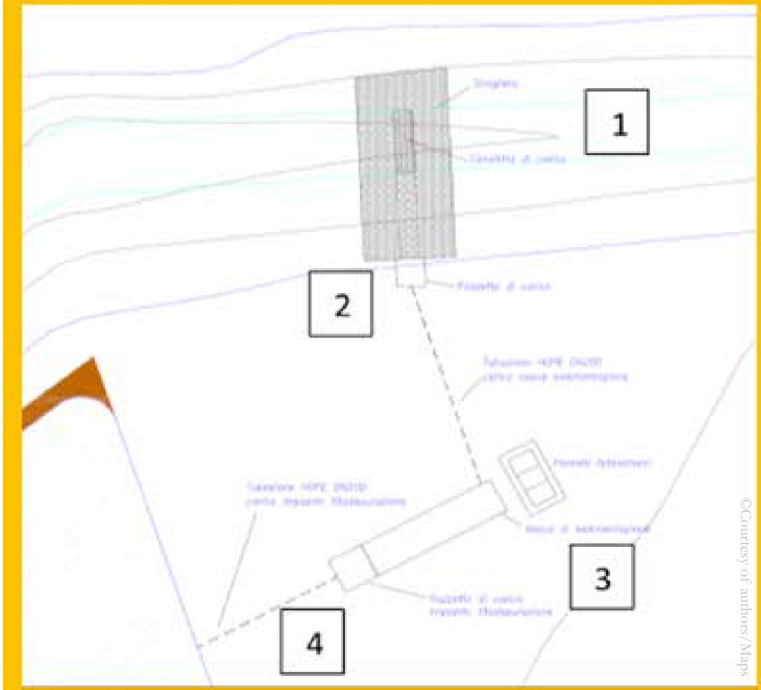
Ritorto creek: the presence of high concentration of Iron causes the reddish colouring of the waters

alkalinity in the waste water and thus reducing the initial acidity. Generally the anaerobic lagoons have depths of about 100 cm (30-60 cm of organic substrate, 15-30 cm of limestone), inside which the water flows in the horizontal direction with a hydraulic head of 5 cm. Anaerobic lagoons are then completed by the planting of plant species such as *Typha* and *Juncus* that have the task of stimulating the microbial processes.

As regards the type of organic substrate, ‘spent-mushroom litter‘ compost is usually used, mixed with limestone, although any other compound of an organic nature can be used. The medium is deposited in the preparation phase of the treatment system and never moved and/or reclaimed for the entire service life (estimated useful life of 15-20 years).

The table on page 166 (calculations anaerobic treatment system) shows the dimensioned calculations made for the definition of the treatment surface. The size criteria to be used is the one that makes reference to the Iron reduction, considering the precautionary concentration value of Iron and Manganese found in unfiltered water samples. It does not take into account Manganese, given the ineffectiveness of anaerobic lagoons in its removal. After the following calculations, assuming that the system should treat 10 grams of iron per square metre per day, three lagoons in a row were put in place, named A.1 (188 m^2), A.2 (165 m^2) and A.3 (128 m^2).



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Layout of the intake structure

> **“To reduce operation and maintenance** ***phytoremediation associated with mechanical filtration systems were selected as the best remediation techniques*** **”**

Aerobic lagoon

At a structural level, the aerobic lagoons are constituted of a treatment medium consisting of a layer of 0.60 m of compost within which water flows with a hydraulic head not exceeding 8 cm. Aerobic lagoons are usually completed by the planting of extensive flora root systems (i.e. *Phragmites*) that can stimulate the microbial processes and facilitate the transfer of oxygen to the deeper layers. The size criterion to be used is the one that makes reference to the precautionary concentration value of manganese found in unfiltered water samples. After the following calculations, assuming that the system should treat 0.5 grams of manganese per square meter per day, four lagoons in a row were put in place, named B.1 (278 m^2), B.2 (316 m^2), B.3 (713 m^2) and B.4 (750 m^2), with a depth of 1 m.

The effluent, before its reintroduction into the Ritorto creek, passes through a sedimentation lagoon to allow completion of the precipitation of heavy metals; it consists of a lagoon where the water surface is exposed to the atmosphere and to the action of floating plants such as macrophytes (i.e. duckweed, water hyacinth). Maintaining the dimensional criteria of the hydraulic retention time, bibliography data report a minimum retention time at least equal to 2.8 days (Skovran and Clouser, 1998) and, considering a flow rate of 60 litres/minute, the size was set at an area of 263 m^3 and a depth of 0.8 m (lagoon C).

Criteria for choice of plant species

The plant species selected for the various stages of the system have mainly an adjuvant function for the entire process, and should be able to grow and form an extensive root system in a water environment with critical chemical characteristics (low pH, presence of metals in high concentrations), be able to stimulate and support the microbial processes and, for aerobic lagoon, facilitate the transfer of oxygen to the deeper layers the filter bed. In this case, plants of the genus *Phragmites* were selected for

ANAEROBIC wetland				
pH	Acidity (grams/litre)	Flow rate (litre/day)	Acidity load (grams/grams)	Treatment surface (m^2)
4,1	0,000079433	86.400	6,862995948	10
Fe on filtered (grams/litre)		Flow rate (litre/day)	Iron load (grams/grams)	Treatment surface (m^2)
0,0075		86.400	648	65
Fe on non-filtered (grams/litre)		Flow rate (litre/day)	Iron load (grams/grams)	Treatment surface (m^2)
0,056		86.400	4838,4	484
Retention time (days)		Flow rate (litre/day)	Volume (m^3)	Treatment surface (m^2)
2,016		86.400	172,8	192

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Calculation for dimensioning the anaerobic treatment system

Treatment surface (m^2)	Porosity index	Porous volume in limestone	Porous volume in compost	Porous volume total	Retention time (days)
484	0,4	58,0608	116,1216	174,1824	2,016

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Dimensioning the porous volume in compost and limestone layers

Treatment surface (m^2)	Depth of the lagoons	Thickness of the limestone layer	Thickness of the compost layer	Retention time (days)
484	1 m	0,3 m	0,6 m	2,016

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Dimensioning the thickness of compost and limestone layers

aerobic lagoons, plants of the genus *Typha* were selected for anaerobic lagoons and aquatic plants such as floating macrophytes (i.e. duckweed, water hyacinth) were selected for sedimentation lagoons, with the aim of both improving the oxidation capacity of the water and fostering the environmental regeneration of the area.

Construction of the lagoons and following operations

Please go on see the pictures below where you will find all of the construction and operation phases, in chronological order.

The conclucions

Results and concluding remarks

Acid mine drainage is still a problem in many abandoned mine areas in Europe as the huge volume of mine waste tailings is a primary source for the release of heavy metals into both surface and ground waters. Occasionally, these areas are in impassable places where it is difficult to operate and even access, so a technology that can foster environmental quality without needing high O&M efforts is a priority. In this specific case of Fontacinaldo mine/Ritorto creek, a subsequent phytotreatment with anaerobic/aerobic lagoons, associated with a sedimentation lagoon, can be implemented as a stand-alone technology with a lifetime of 15-20 years. As a preliminary result after several months, nature returned to the creek downgradient through spontaneous plant growth both on the banks and in the waters.

Further reading

https://clu-in.org/download/studentpapers/costello_amd.pdf

https://clu-in.org/download/studentpapers/constructed_wetlands.pdf

Relevant websites

https://www.epa.gov/polluted-runoff-nonpoint-source-pollution/abandoned-mine-drainage
https://frtr.gov/matrix2/section4/4-43.html

AEROBIC wetland			
Mn on filtered (grams/litre)	Flow rate (litre/day)	Manganese load (grams/grams)	Treatment surface (m^2)
0,00175	86.400	151,2	302
Mn on filtered (grams/litre)	Flow rate (litre/day)	Manganese load (grams/grams)	Treatment surface (m^2)
0,0119	86.400	1028,16	2056

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Calculation for dimensioning the aerobic treatment system

Treatment surface (m^2)	Pore volume in compost	Thickness of the compost layer	Retention time (days)
2056,32	740,2752	0,6 m	8,568

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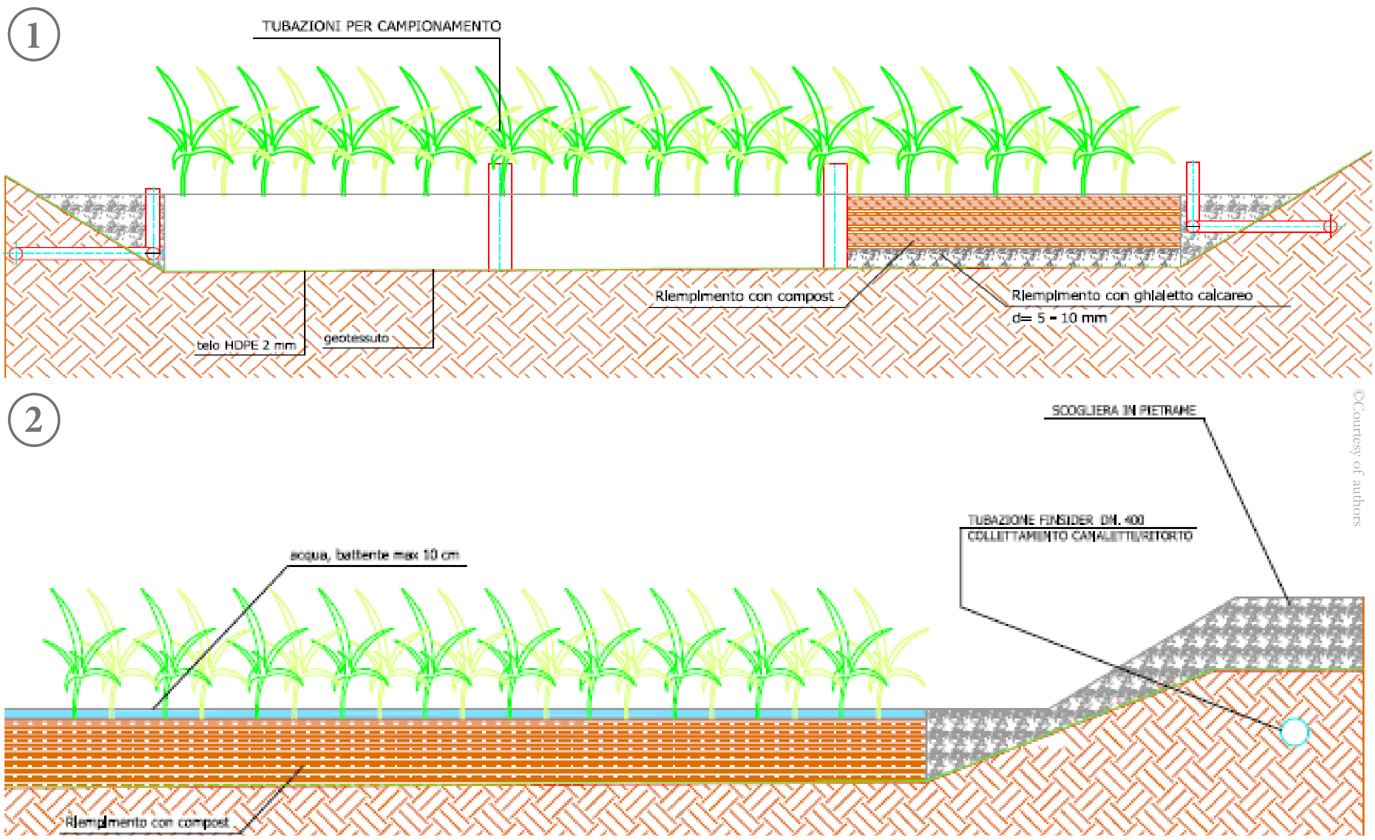
Dimensioning the thickness of compost and limestone layers



©Courtesy of authors

1. Anaerobic lagoon scheme. **2.** Aerobic lagoon scheme

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Excavation phase

©Courtesy of authors/Photostock

Waterproofing (HDPE)

©Courtesy of authors/Photostock

Preparation of limestone layer

©Courtesy of authors/Photostock

Preparation of compost layer

©Courtesy of authors/Photostock

End of construction

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Final layout (3. anaerobic, 4. aerobic, 1. sedimentation)

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Lagoon at the beginning of the operation

©Courtesy of authors/Photostock

Effects on the creek downstream

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Phyto-plant cover one year after the intervention.

RESEARCH

RESEARCH

1. France: site currently under treatment after liquidation, rehabilitation objectives under implementation, and R&D project of biostimulation treatments monitoring in real-time in Quincieux

2. Spain: success factors for brownfields redevelopment in Spain; a comparative analysis of three examples of brownfields with different status

3. Finland: utilisation of in situ techniques in remediation of oil-polluted sites in Finland

Research

1. Site currently under treatment after liquidation, rehabilitation objectives under implementation, and R&D project of biostimulation treatments monitoring in real-time in Quincieux, France

LOCATION	Quincieux (Rhône county, Auvergne-Rhône-Alpes region), France
POLLUTANT	Halogenated volatile organic compounds (HVOC)
SOURCE	Former metal office furniture manufacture
GENERAL CLEAN UP OBJECTIVES	Reduce soil and groundwater contamination
REMEDIATION ACTIONS	Pollutant extraction and in-situ oxidation treatment
SITE/END USE	Industrial or commercial
SOCIAL-LEGAL ISSUES	Land reclamation, human health risk
KEY LEARNING/ EXPERIENCE TO SHARE	Upgrade of a stepwise and still ongoing depollution process

Author's profile

Florian Philippon, Project Manager — Brownfield and Contaminated Sites Department — Sustainable Cities and Territories Directorate — ADEME.

Site currently under treatment after liquidation, rehabilitation objectives under implementation and R&D project of biostimulation treatments monitoring in real-time in Quincieux, France

Florian Philippon, French Environment and Energy Management Agency-ADEME, Direction villes et territoires durables (DVTD), Service friches urbaines et sites pollués (SFUSP), 20 avenue du Grésillé-BP 90406-49004 Angers Cedex 01, France
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Véronique Antoni, Ministry of Ecological and Solidarity Transition - MTES, Commissariat général au développement durable (CGDD), Service de la donnée et des études statistiques (SdeS) 5 route d'Olive -CS 16105-45061 Orléans Cedex 2, France
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A former metal-manufacturing site located in Quincieux showed abnormal hydrocarbon and HVOC concentrations in soil, water and air, assessed to be unsafe for the site's neighbours and a drinking water catchment. After the two first depollution steps, ADEME intervened as a matter of extreme urgency to ensure the clean-up steps. ADEME is also funding a R&D project coordinated by Enoveo (Environmental Bio-engineering consulting and analytical company), which aims to develop and implement an innovative tool in order to monitor the treatments by real-time biostimulation of the polluted aquifer.

Keywords: *aquiferous alluvium, brownfield, drinking water catchment, halogenated volatile organic compounds (HVOC), liquidation, orphan contaminated site, perchloroethylene (PCE), sparging, trichloroethylene (TCE), 1,1,1-Trichloroethane, urban context, venting, vinyl chloride, wells.*

Introduction

The case study

The so-called JEC site is located in Quincieux, in the Rhône county, upon aquiferous alluvium of the Saône river, made of sand, gravel and crushed stone. The groundwater water table directly below the site is at least 8 m deep. JEC Industries manufactured metal office furniture from cold-rolled sheets from the end of the 1950s on this site. After the company moved to another site in 2000, a soil survey showed concentrations of hydrocarbons and HVOCs, namely PCE. In addition, the water from the on-site well showed concentrations of HVOCs (PCE, TCE, vinyl chloride, 1,1,1-Trichloroethane). Potential beneficiaries from reclamation are the site's neighbours (residents, people depending on a nearby drinking water catchment). Following the company's liquidation in 2014, ongoing remediation work is being carried out by the French Environment and Energy Management Agency (ADEME).

The problem

The main constraints

This site remediation faced several constraints. First of all, about 60 private wells capturing the alluvial aquifer are located near the site,


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Processing unit of the effluents from the barrier sparging-venting barrier.

> ***“ADEME intervened as a matter of extreme urgency to ensure the clean-up of hydrocarbon and HVOC concentrations in soil, water and air.”***

reaching depths of between 20 m and 40 m. Secondly, agricultural wells were identified in the town of Quincieux for the irrigation of farming plots. Likewise, the groundwater flows towards a drinking water catchment (traces of HVOCs detected), the Saône river and the town of Quincieux. The risks incurred by the potential targets (site's neighbors: residents, people depending on a nearby drinking water catchment) lead to the implementation of a management plan. Furthermore, following company's liquidation in 2014, ongoing remediation work is being carried to ADEME. This French soil guide value, of the ‘sensitive use’ type in this case, relates to ‘residential with garden’, namely to garden watering, showers, toilets, swimming pools or even drinking water supplies. Moreover, three dwellings located downstream needed indoor air quality assessments.

The strategy

The depollution steps

Two different depollution steps followed. From February 2006 to October 2007, depollution of the underground water was undertaken. Some 390 kg of pollutants (primarily PCE) was extracted by well pumping, there was water treated by stripping (reducing concentrations by 95%) and injected back into the well. In addition, about 430 kg of HVOCs was destroyed by in situ oxidation treatment of the source area. But the clean-up operation did not achieve sustainable mitigation on the site boundary and outside. The volume of the impact source was estimated at about 100 m^3 (PCE concentrations at a depth of 0-6 m), but other sources of potential impact zones had not yet been investigated. Ultimately, this first clean-up operation significantly degraded the groundwater quality at the site and immediately outside the site, leading to an increase in the plume of pollution.

A second phase took place from 2010 to 2015. The source area was pre-treated by venting/sparging with 11 sparging wells and then treated by bio-anaerobic reduction. The on-site plume, accelerated by the pumping phase between 2006 and 2008, was treated by bio-anaerobic reduction downstream. A venting/sparging barrier, currently still in operation, was also installed downstream from the site boundary. Thereby, since 2010, the neighbourhood health risk linked with the inhalation of vapours from groundwater pollutants has been removed. The


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Soil coring to delineate the polluted areas 2.

> “ADEME results showed that the treatment has been carried out efficiently at a depth of between 0 and 7 m and has extracted more than 5 t of pollutants.”

migration of the PCE plume off site towards the drinking water catchment was also significantly limited and the impact of groundwater on the site was reduced with a reduction in HVOC concentrations of between 50 and 90%.

The conclusions

The results

Beginning 2014, a prefectural emergency decree imposed emergency control requirements and measures taken as a precaution by JEC Industries. Furthermore, ADEME intervened as a matter of extreme urgency to ensure the clean-up, namely to continue the treatment (sparging-venting), to monitor the underground water on a monthly basis, to evacuate and empty oil tanks and to undertake further investigations to delineate the volumes of the source area. The results of investigations conducted by ADEME in 2016 showed that the treatment has been carried out efficiently at a depth of between 0 and 7 m and has extracted more than 5 t of pollutants. Impacts observed off site are related to an area with high concentrations of HVOCs that has not previously been treated; this pollution is at a depth between 7 and 10 m. Several treatment options have been recommended, combining the excavation or thermal treatment of the soil located above the aquifer with an in situ biological treatment or zero valent Iron. Costs are estimated between 1 M € and 1.5 M €. This intermediate zone will soon be treated thanks to action by ADEME. Furthermore, ADEME is funding an R&D programme coordinated by Enoveo in order to implement a new tool to monitor the treatments by the real-time biostimulation of the polluted aquifer. The Remwatch project aims to validate in situ biosensors to monitor in real time the spreading and the persistence of the carbon substrate, for instance soybean oil, injected into the environment and its impact on biodegradation. This complementary study stands as a more cost and time saving approach than sampling/analysis studies. A summary of the main results will be available in the second half of 2017.

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In situ biosensors (Remwatch R&D project).

> **“The Remwatch** *project aims to validate in situ biosensors to monitor in real time the spreading and the persistence of the carbon substrate.”*

Further reading

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- Animation “The guide for private companies and local collectivities : issues related to contaminated sites and soils”: http://www.developpement-durable.gouv.fr/Animation-The-guide-for-private.html#ancrefilm

Relevant websites

http://basol.developpement-durable.gouv.fr/fiche.php?page=4&index_sp=69.0191
http://basol.developpement-durable.gouv.fr/

Recherche > Lieu > Request like: ‘Site = JEC’. Description, technical situation, impact characterisation, environment, monitoring, restrictions on use and planning measures and treatments already performed on the JEC site. https://www.ecologique-solidaire.gouv.fr/

Accueil > Politiques publiques / de A à Z > Risques technologiques > Installations classées pour l’environnement > Sites et sols pollués http://www.rhone.gouv.fr/

Accueil > Request like: ‘JEC’. Arrêté préfectoral de mise en demeure en date du 23 avril 2014.

Arrêté préfectoral en date du 17 janvier 2014 prescrivant des mesures d’urgence à la société JEC.

INDUSTRIE pour le site 26, Chemin de la Grande Charrière à QUINCIEUX.

Arrêté préfectoral en date du 29 octobre 2012 imposant des prescriptions complémentaires à la société JEC INDUSTRIE pour son ancien site 26, Chemin de la Grande Charrière à QUINCIEUX.

Research

2. Success factors for brownfields redevelopment in Spain: a comparative analysis of three examples of brownfields with different status.

LOCATION	Spain
POLLUTANT	Heavy metals, toxic and radioactive materials, coal.
SOURCE	Former brownfields and mining sites
GENERAL CLEAN UP OBJECTIVES	Identification of factors of success in the process of redevelopment
REMEDIATION ACTIONS	Non specified
SITE/END USE	Non specified
SOCIAL-LEGAL ISSUES	Land reclamation, lack of standards and legal framework
KEY LEARNING/ EXPERIENCE TO SHARE	Identification of an appropriated methodology including spatial planning adapted to brownfields redevelopment

Author's profile

Jesus Daniel González Carmena, is a recent graduate student in Land Management (AAU-CPH), living the last two years in Copenhagen all along his Master program. Born in Madrid, where he has achieved a Bachelor Degree in Land Surveying and Geo-Informatics at the Technical University of Madrid (UPM). Passionate about Territorial issues such as Spatial Planning and Urbanism with the focus in the redevelopment and recovery of negative contexts where the land plays a key role. All of this with a sustainable perspective plus the political and social approaches. GIS as the main tool of analysis of all the previous fields.

Success factors for brownfields redevelopment in Spain: a comparative analysis of three examples of brownfields with different status.

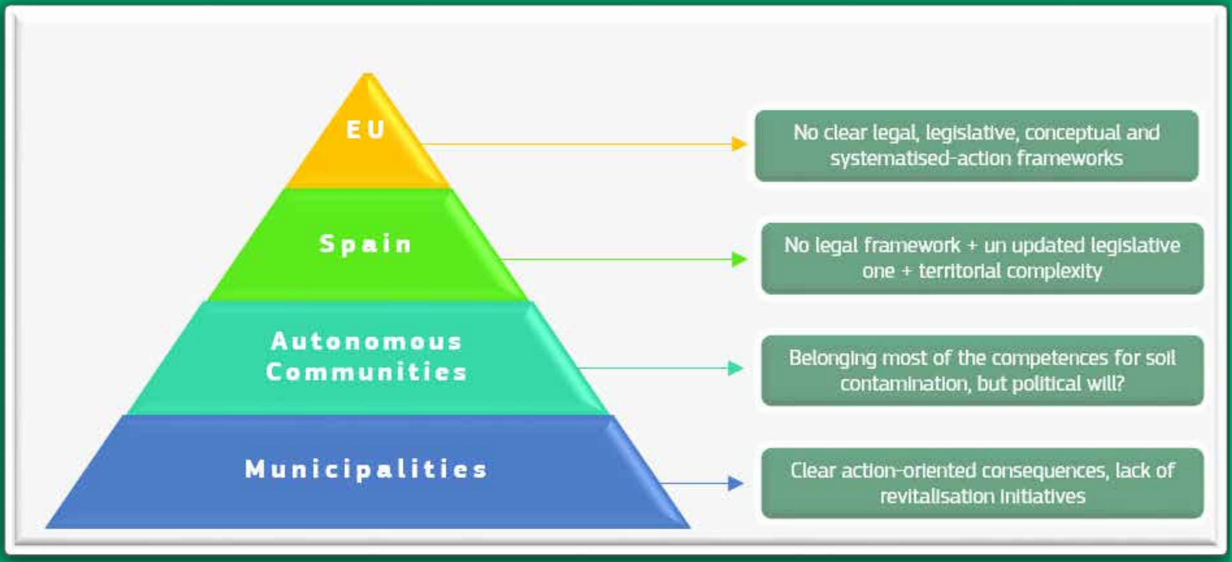
Jesus Daniel González Carmena, Vesterbrogade 138A, 2th, 1620 København K, Denmark, daniel.glezcarmena@gmail.com

The brownfields phenomenon has a clear aim in the creation of initiatives of revitalization and redevelopment for contaminated/abandoned/dere¬lict areas. Its heterogeneity in Europe has originated a complex conceptual framework with: an unclear scale of the phenomenon, a huge variety of interpretations, a lack of standards and finally the no existence of a specific and clear legal framework that would control, register and state a range of criteria and guidelines for cases all along the EU Members. This paper aims to state a mainly qualitative comparison between three cases of brownfields in Spain, looking for the identification of factors of success in the process of redevelopment of the affected areas. It focuses in four lines of analysis: the current general situation of the brownfields phenomenon in Spain, the explanation and justification of the figures of the factors of success, the possible convergences and divergences that may exist between brownfield cases with different status of redevelopment and finally how the potential findings can influence future perspectives of the phenomenon across the Spanish territory.

Keywords: *brownfields redevelopment, cultural & natural heritage, sustainable land management, factors of success, methodology of characterization, qualitative comparison, soil contamination.*

Introduction

Spain, presents a picture where there exist even more gaps related with the brownfields phenomenon, due partly to these European heterogeneities and partly to its own territorial, structural and political context. There is no use of the term 'brownfield' as such or specific regulations or mentions of the phenomenon itself. On the other hand, the soil contamination is present in the Spanish regulations, but with a no clear idea of the scale of the phenomenon, and this fact has created a range of negative consequences (lack of a legal framework, availability of information, action-oriented consequences, etc.). In addition, each region has mainly its own competences for management, cleaning up and recovery of the contaminated soils. With this context of uncertainty, the initiatives of revitalization of a brownfield in Spain are not very numerous and very complex, with long processes of negotiation between stakeholders, bureaucratic delays, lack of political will, urbanistic corruption, opposed interests, lack of concern regarding cultural and natural heritage, among others. As a consequence, the number of cases that have been successfully solved are very limited, so it is necessary to focus in those elements or factors that characterized successful cases of redevelopment and revitalization of a brownfield: the Factors of Success.
Brownfields scenarios are the direct result of causal actions: industrial activity nowadays abandoned, contamination of an area due



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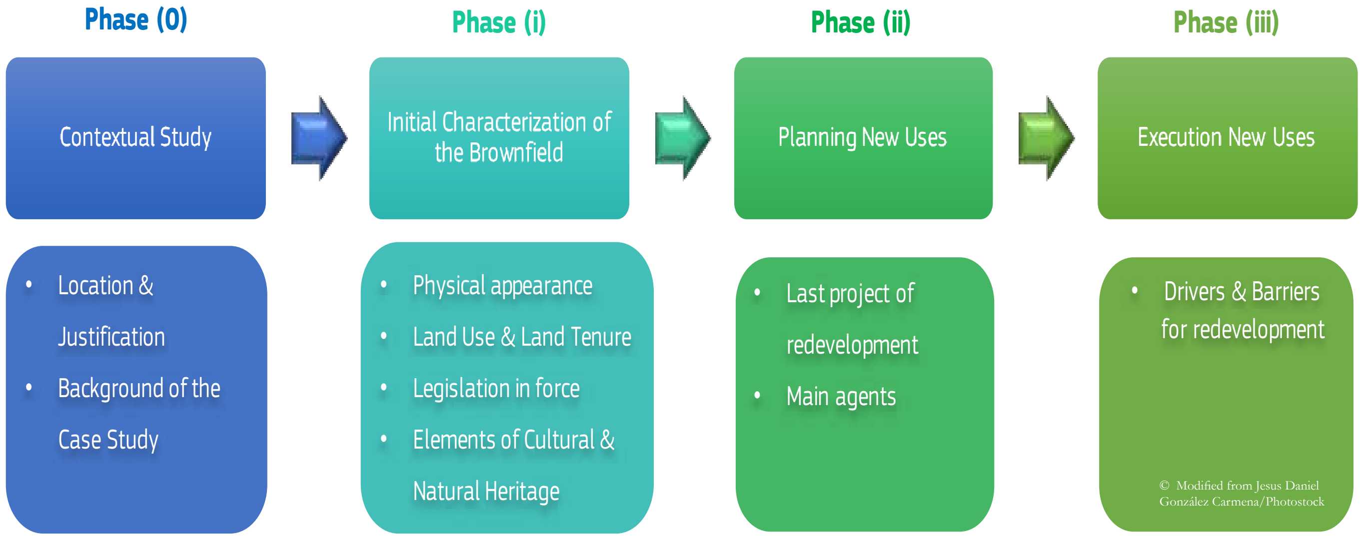
Possible outcome of the brownfields phenomenon in Spain.

to different reasons, underused areas due to social changes or derelict infrastructures as a result of shifts in the economic interests, among others. Consequently, their potential revitalization depends on a huge number of interconnected factors that might provoke a context of complexity and uncertainty when opposed interests exist. This project aims to compare the causal factors of three Case Studies with different status in terms of results across the Spanish territory. The chosen Case Studies have been selected as relevant positive and negative milestones keeping homogeneity in origin and context and heterogeneity in location and status:

- First the case study of the Bay of Portmán (CS1) shows how due to different conflicts and barriers, the contamination of a whole bay in the Mediterranean coast (being the worst case of heavy steel pollution in the history of the Mediterranean Sea), is still unresolved after 30 years of negotiations, projects refused and political shifts.
- Secondly, the case study of the Confluence of the Tinto and Odiel rivers (CS2) in the city of Huelva, exposes a case where there have been discharges of toxic residues from a chemical factory in one of the sides of the river, a few hundred meters from households, provoking the biggest dumping site of toxic and radioactive industrial residues of Europe, with a strong opposition from the local communities and an evident lack of political will from the local, regional and national Administrations. However, a project of redevelopment has been approved.
- Thirdly, the case of the Nalón Valley (CS3) is presented as an exemplary case of improvement in a context of large-scale pollution, resulting from over one hundred years of coal mining. The reclamation of the area had the support and commitment of the Administration and it stands as a good example of: keeping the territorial cohesion, developing an environmental restoration, maintaning the valorization of mining heritage and ensuring an adequate industrial transition.



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Distribution among the sequential phases of the selected factors.

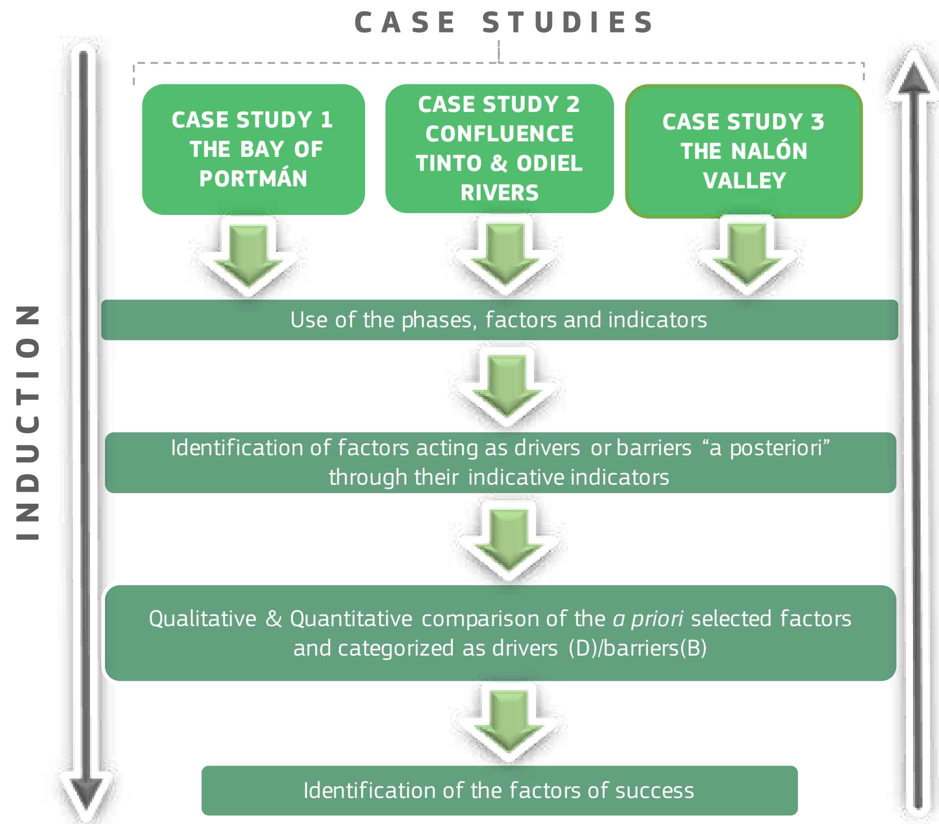
The problem

From the previous initial statements, the next figure summarizes the problem identification according to the existing evidences at a supra-national, national and regional levels, having direct impacts in the local one.

Conceptual framework

The Oxford dictionary defines 'factor' as "a circumstance, fact or influence that contributes to a result" (Oxford Dictionary). In the brownfield context, this term is understood as those different elements that characterize the site-level scenario, shaping its possibilities of recovery and redevelopment across time. These 'factors' for the successful redevelopment of brownfields are needed to overcome the existing barriers in that specific case, and as a result tackle the degradation of the area under study. But it is important to remember that "brownfields are placed and rooted in a certain geographical space and time, which is hierarchically and functionally structured" (Frantál et al., 2015), this means that brownfields should be analyzed not just according to site-specific attributes/factors, but also to other indirect and contextual elements that affected the current causal phenomenon, in short, projects and initiatives for brownfields redevelopment should be integrative (González Carmena, 2016). In the specialized literature, authors use the following notions for factors: drivers, determinants, criteria or site parameters (Frantál et al., 2015), tending to distinct between a two-folded categorization for the phenomenon under concern: drivers (Ramsden, 2010; Nicole, 2011; Clarinet, 2002; Cabernet, 2006) understanding them as key elements that are able, by themselves, to unblock a stuck case of brownfield and Barriers (Oliver et al., 2005; Jackson & Garb, 2002; Clarinet, 2002; Hollander et al., 2010; Cabernet, 2006; McCarthy, 2002) referred as those elements that are necessary to overcome for the increase of possibilities of an appropriate redevelopment. For the conceptualization of barriers and drivers in brownfields redevelopment, it is important to understand that these factors may vary from one country to another, even if according to Frantál et al. (2015) the ideas of complexity and multidimensionality on brownfields are common in different geographic areas. In this way, some of the main European agencies in charge of brownfields redevelopment declare the importance of this categorization of drivers and barriers, and their connection with success in brownfields (Nicole, 2011; Clarinet, 2002 and Cabernet, 2006).

In summary, this categorization and polarity



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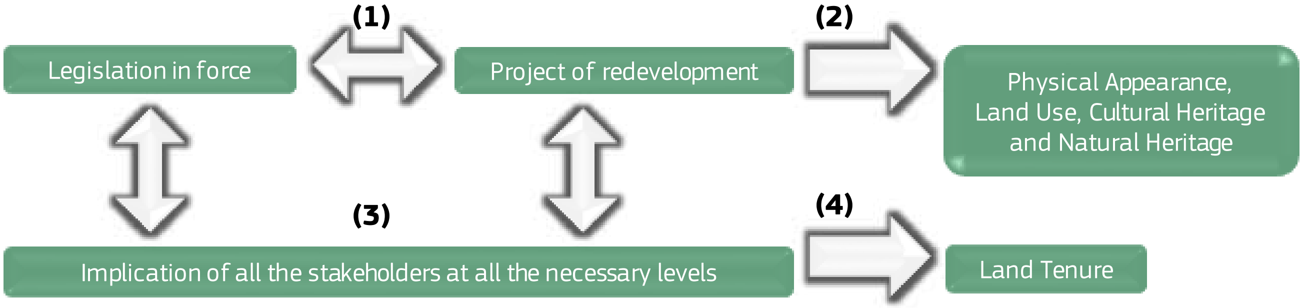
Logical flow of the identification of the factors of success.

is necessary, but it may dismiss the main objective when the existing frameworks are complex, with evident gaps and depending on the potential success in a vast range of interconnected elements, provoking, as a result, negative action-consequences. For this reason, this project embraces a more concrete and pragmatic approach, for local and site-level environments: the only focus on those factors, drivers, determinants or site parameters that are needed for a successful process of improvement and revitalization (partial or total). So the identification of these factors would set up the promotion of initiatives of implementation in the affected areas, varying the interests on a specific derelict area if its characteristic factors are favorable or not for a successful redevelopment.

Most of these factors can be expressed through a list of measurable indicators (qualitative and quantitative), giving in this way a specific weight or importance to the factor under concern. An indicator is defined in the Oxford Dictionary as "thing that indicates the state or level of something". In the brownfields phenomenon, those indicators such as size of the area, level of contamination, land ownership, use of the land, etc., are measurable characteristics, originated by causal contexts that describe qualitatively and quantitatively the existing conditions and elements that characterize a specific brownfield. So the establishment, combination and categorization between them, will state a list of factors that are necessary to target, set up and propose remediation and revitalization strategies of the brownfield under concern. Bacot & O'Dell (2006) insist in the importance of the standardization of indicators in the brownfields phenomenon. Likewise, the three Case Studies have been chosen in the same country, coming from a similar framework basis and being able to use common factors/attributes from similar indicators among the cases. In the specialized literature, different authors propose a list of factors and the subsequent indicators through different approaches; Bacot & O'Dell (2006), Wedding & Crawford-Brown (2007), Nijkamp



Interconnections between factors of success. © Modified from Jesus Daniel González Carmena/Photostock

et al. (2002). They presented approaches with a tendency to avoid site-scale approaches, developments very focused on the legislative level and without proposing direct action on the ground. Obviously, the identification of these indicators may differ from one author to another, depending their emphasis in the analysis.

Analytical framework

Regarding the analytical framework through which the factors of success are going to be identified across the three selected Case Studies, it is based on a land planning methodology stated by Gómez Orea (2007), merged with the context of recovery of degraded areas (Gómez Orea, 2004) and finally adapted and transposed to the phenomenon under concern (brownfields). This approach, so-called 'Ordenación Territorial' (OT methodology) is characterized by pursuing the development of Spatial Planning Plans, containing different sequential phases from where it is possible to state direct territorial characterization and analysis that might be useful for the corresponding identification of the representative factors and indicators of a specific brownfield. The use of this kind of literature and its transposition and adaptation to the brownfields phenomenon has been appropriate for different reasons: First, the compatibility between the methodology and the phenomenon under concern, with their subsequent common emphasis such as the time-line, integrative and multidisciplinary procedures, the importance of the endogenous perspective, the strategic character or the finalist aim, among others. Second, the need of an "a priori" non-exhaustive list of selected factors that will be common along the three Case Studies. Third, the merge of the methodology with the list of factors to state a common structure for the three proposed Case Studies and subsequently an appropriate induction for the effective identification of the factors of success. Fourth, the "a priori" choice of indicative qualitative and quantitative indicators that will measure the effects of the already selected factors along the three proposed Case Studies. As a result there has been stated a sequential time-line process of four phases with their characteristic selected factors belonging to each of them and having this approach the final aim of the brownfield's recovery (see figure page 186 phases of the selected factors). Then, throughout the description and analysis of the three proposed Case Studies, it is aimed to, through a process of induction: First, register the effects of the selected factors through their chosen indicators. Second, target the previously mentioned two-folded categorization of Drivers and Barriers for the redevelopment of the brownfield. Third, the identification of the factors of success from the comparison of the common selected factors through the subsequent one of their common measurable indicators. Figure of logical flow in page 187 displays this process.

Discussion

The identification of the factors of success based on the evidences from the development of the three Case Studies (CS1, CS2 and CS3) show the complexity of a phenomenon with wide multi-disciplinary implications and multi-scale effects. The identified factors of success have a different weight of influence among the Case Studies and the phenomenon itself in general, but in any case there is a minimum number of factors that unavoidably are needed to be present in the analysis.

Summarizing the findings from the process of induction explained in figure page 187, it could be stated the following figure inpage 188 for an “a posteriori” indicative statement of the key interconnections among the different factors of success:

The achievement of the recovery of a brownfield case in Spain, based on the evidences and findings after this non-exhaustive analysis, can be reached through the inclusion (1) of the project of redevelopment in the legislation in force at all the necessary levels (from local to supra-national), including multidisciplinary implementations (2) to reach an integrating character with evident effects in a site and regional level, through a comprehensive implication (3) of all the possible stakeholders to overcome potential issues of blockage related with the Land Tenure (4) of the affected area. The failure of CS1 and CS2, being both still unresolved, present similar characteristics and conclusions based on a general lack of political will from all the local, regional and national level of the Administrations. By contrast, the success of CS3, states a point of departure of probably and exemplary way of action through: First, stating implementations of ‘common sense’, with respect, restoration and put in value of the cultural, historical and natural assets inherited. Second, adding endogenous initiatives of transition and shift related with the cooperation with the local authorities and the responsible enterprises liable for the pollution or at least the owners of the affected areas. Third, aiming clear integrating effects that would reinforce the territorial cohesion of the area, permitting positive effects all along the region. Fourth, affecting directly the political context with the approval of regional regulations with direct and indirect impact on the affected area. Finally, obtaining as a consequence of the large-scale integration and comprehensive perspective of the implementations, national funding and supra-national co-funding, through a clear political will.

The conclusions

This project has been achieved with the genuine aim of finding positive inputs for a phenomenon that has been conditioning numerous scenarios across the Spanish territory, looking for a certain systematization of the processes od redevelopment, having each of the cases a divergent range of circumstances, agents and conditions.
One of its strengths has been the identification of an appropriate methodology related with the Spatial Planning that has been perfectly adapted to the brownfields phenomenon, stating point of departure of a new possible approach with a valid sequential process, where the numerous elements that shape the phenomenon can be included, analyzed and assessed coherently.
It can be also insisted on the pioneer character of the project, for a phenomenon which awareness in Europe has increased strongly but has not the deserved importance in Spain that it should, according to the huge number of existing cases that are registered and addressed already, and also those numerous ones that haven’t been identified and addressed yet.

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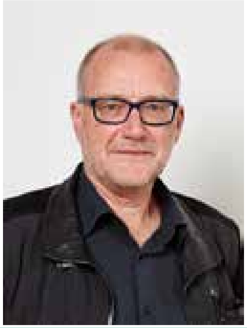
Research

3. Utilisation of in-situ techniques in remediation of oil-polluted sites in Finland

LOCATION	Jalasjärvi, Halikko and Lintuvaara, Finland
POLLUTANT	Oil carbons, hydrocarbons, PAHs and Voc's
SOURCE	Former fuel station
GENERAL CLEAN UP OBJECTIVES	Soil and grounwater remediation
REMEDIATION ACTIONS	Biodegradation, soil vapour extraction, biostimulation, bioaugmentation and chemical oxidation
SITE/END USE	Non specified
SOCIAL-LEGAL ISSUES	Land reclamation, lack of standards and high quality methods
KEY LEARNING/ EXPERIENCE TO SHARE	Identification of cost-effective and high-quality remediation methods

Author’s profile



Seppo Nikunen, is an engineer of Community Technnique. He has been working as a Project Manager in Pöyry Finland Oy in National Soil Remediation Programmes since the beginning of 1997. He has also been involved in several working groups for national environment legislation, instructions and in the testing of practices. He has been managing more than 1500 investigation and remediation projects including nearly 100 in situ projects in Finland. In 1980’s and 1990’s he was also working in Construction areas for example in Libya, China, Saudi-Arabia, Sweden, Norway and USA.

Sanna Pyysing is a legal advisor in the Oil Pollution Compensation Fund’s national JASKA-project for investigation and remediation of oil contaminated soils and groundwater. Sanna received her Master of Technology in environmental engineering from the Lappeenranta University of Technology and her Bachelor of Science in environmental sciences from the University of Eastern Finland. Prior to coordination of the JASKA-project, she worked as a research worker at chemistry laboratories and also educated the Finnish youth for several years.

Harri Talvenmäki, is a doctoral student working for EU/Interreg funded project INSURE (Innovative Sustainable Remediation) in University of Helsinki, dpt. of Environmental Sciences. Talvenmäki received his bachelor’s degree in environmental biotechnology from Lahti University of Applied Sciences in 2010 and master’s degree in environmental ecology from UHEL in 2016. In between the studies he worked for UHEL as a research technician with a primary focus on in situ remediation of contaminated soils and groundwater.

Author's profile

John Allen, received a bachelor of science in geology from the University of Georgia, USA in 2002. He then worked for nearly ten years in the environmental regulatory and compliance field in the US, focused on water quality issues. In 2013, moved with his family to Finland, where he enrolled in the Lahti University of Applied Sciences' masters degree programme in environmental technology and began working as a research technician in the University of Helsinki's Department of Environmental Ecology. John's research at LUAS focused on retention of polycyclic aromatic hydrocarbon contaminates in municipal snow disposal site sediments. He received a master of engineering degree from LUAS in 2016. While working for the University of Helsinki, John has been involved in projects examining the use of nanotechnologies in brownfields remediation, the effects of street trees on urban air quality, and the ecosystem services provided by urban green spaces.

Martin Romantschul, leads a research group of 10 scientists, four of which are postdoctoral fellows. The research of the group deals with both basic and applied aspects of environmental biotechnology. One of the main research topics of the group is soil bioremediation with particular emphasis on technology used in situ. In total he has supervised 21 PhD theses and published over 100 scientific articles in international scientific periodicals with a peer review practice. Romantschuk has also successfully led and taken part in a number of large national and international projects, some of which have led to practical applications used by the industry.

Hannu Silvennoinen, M.Sc. in Applied Geophysics and Mining, is the CEO of Nordic Envicon Oy providing clean-up and investigation services for contaminated soils, landfills and polluted air. Mr. Silvennoinen is an experienced trainer of environmental issues with an extensive knowledge and experience on project planning and management; biotechnical soil and groundwater remediation techniques; industrial, mining and nuclear waste; soil and storage studies; ground water studies and exploration in arid areas. This experience has been shared through lectures and a number of articles published in environmental magazines. He has also participated in several national and international symposiums in Europe and North America.

Utilisation of in-situ techniques in remediation of oil-polluted sites in Finland

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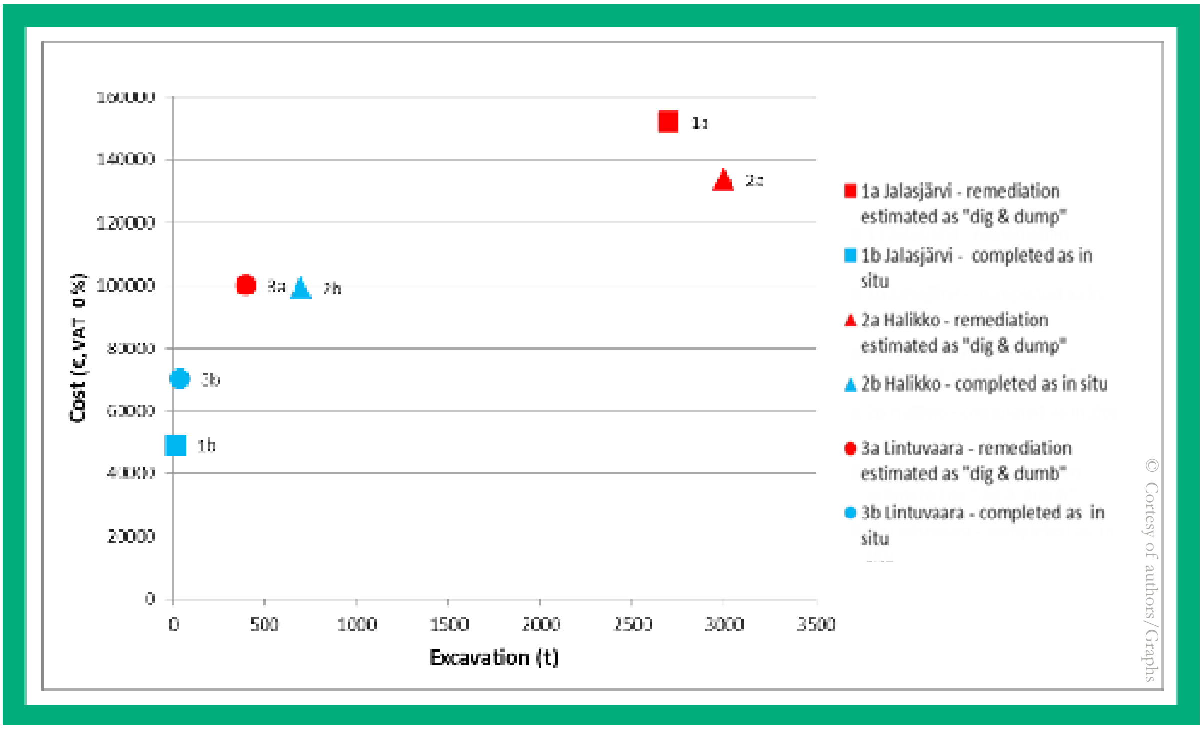
There have been two major national remediation programmes for oil-polluted sites in Finland. The first was SOILI (1997-2015) and the second is JASKA (2012). More than 1 200 sites have been investigated and about 800 sites have been remediated during these national programmes. The main operator is the Oil Industry Service Centre, with consultation from Pöyry Finland Oy's Lappeenranta office, which is responsible for the project management of both programmes. Project funding comes from the Finnish Oil Pollution Compensation Fund, which is administered by the Ministry of the Environment. The primary aim of our national remediation programmes is to eliminate environmental and health hazards by utilising cost-effective and high-quality methods. All of the programmes' remediation contracts and other services (consultants, laboratory analysis, etc.) are put out to bid.

Keywords: *bioaugmentation, biodegradation, biostimulation, biosurfactants, diesel, electrokinetics, Finland, in situ, Jaska, oil, remediation, SOILI, soil vapour extraction.*

Introduction

At the beginning of the SOILI programme, soil remediation was mainly based on excavation, transportation to treatment plants and backfilling with transported unspoiled soil (*dig and dump*). The first in situ projects from 1998 were completed by soil vapour vacuum extraction methods, sometimes feeding warm air into the ground from a catalytic burner to accelerate removal of gasoline from the soil, which also created a certain amount of biodegradation influence. Biodegradation has come into greater importance since 2007 in order to remediate effluents contaminated mainly by middle distillates (C_{10}- C_{21}).

From 2007 to 2015, in situ methods were used at 72 sites. Fourteen sites are planned to begin in situ treatment during 2016. Currently, about 40% of all remediation sites are remediated by utilising some of the in situ methods, such as biodegradation accelerated by nutrients and oxygen, soil vapour extraction into active carbon or catalytic burner, electrical osmosis and chemical oxidation. After the biodegradation phase, excavation has often been used to remove the remainder of the contamination down to predetermined target values. In situ methods alone (with no excavation needed) have been sufficient in approximately 10% of the completed projects. In 5% of all remediated sites, in situ methods have been used to treat associated



The original evaluations of the mass to be excavated and the cost of remediation estimated as *dig&dump* compared to the actual values for the in situ cases Jalasjärvi, Halikko and Lintuvaara.

groundwater contamination. In some cases soil and water purification systems have been successfully connected by circulating purified water through the oil-contaminated soil.

The project management team selects the sites where in situ methods could be beneficial and makes the final decision by comparing the bids received from contractors. There are many sites where excavation is required for removal of buried oil storage tanks. However, damage to surface areas can be minimised, if in situ remediation is utilised even as a combined method with excavation.

Before the competitive bidding stage, the environmental consultant always performs a site investigation and risk assessment to determine the extent of the contamination and to set target values for the remediation project. The investigation plan is based on a site history report which has been prepared by the programme operator. A cost estimate for remediation activities is prepared by the consultant after the site investigation. Usually the preliminary remediation design and cost estimate made by the environmental consultant are based on *dig and dump* techniques. The final price for in situ remediation is determined after the bids have been received.

The contract format, which has been used for in situ remediation is so called a turnkey contract, where the contractor is committed to reaching the target values within a fixed price. Moreover, there is also a condition in the bidding documents which states that, before the contract agreement, the chosen contractor shall conduct their own investigation of the site to confirm the applicability of the offered in situ method and the required extent of the remediation. The cost of this investigation is included in the offered contract price. After the site investigation, the contractor shall prepare the technical work specification for the method they have proposed. This document shall be attached to the general remediation plan made by the environmental consultant chosen by the operator.

The duration of the biodegradation phase has typically been about 1 year. This long remediation period is seen as the only disadvantage for using in situ methods. During in situ remediation, the site may continue to be used normally; the amount of contaminated soil is decreased on average by 60-70% and the concentration of oil in the soil is significantly reduced. Thus, the cost of transport and offsite treatment of

a) Lysimeter and **b)** soil column for an in situ pilot test at the UHEL lysimeter field station.

contaminated soil are lower when compared to the cost of treating soil with the original level of the contamination. In cases when it is estimated that the original target values cannot be reached by reasonable activities and cost, there is a possibility to perform a risk analysis to determine if the obtained residual concentration values are acceptable to protect public health and the environment. Total cost savings from the 72 sites remediated by in situ methods have been approximately 40% (savings of about 3.2 M €, VAT 0) over conventional *dig and dump* treatment. Cost of remediation estimated graph (go on see page 196 graph above) presents the difference between the original cost estimate for the remediation method performed as *dig and dump* and the actual cost for in situ remediation, as well as the difference between the original evaluation of the excavated mass and the excavation done during in situ treatment for clean-up cases (Jalasjärvi, Halikko and Lintuvaara) used as an example by the contractor (Nordic Envicon Oy).

In the next chapters, the contractor (Nordic Envicon Oy), which has won the most in situ remediation contracts for our programmes, will discuss in more detail the research behind the remediation technique and will give a few examples of successful remediation cases. This research has been conducted by the University of Helsinki's Department of Environmental Sciences in Lahti.

Research

Bioavailable and degradable pollutants in soils can be remediated naturally via biological, chemical and physical processes, with soil-dependent redox reactions playing a major role (Penttinen, 2001; Tuomi et al., 2004). Additional active measures may be contemplated when contaminant concentrations appear to be at stasis. These methods concern the removal of bottlenecks (e.g., suboptimal temperature, especially in deeper soil layers in boreal regions, lack of electron acceptors and insufficient nutrient-to-organic carbon ratio) that hinder further biological degradation (Margesin, 2000; Romantschuk et al., 2000).
For the most common bottlenecks, some general in situ procedures have been developed. Usually, heat, electron acceptors and nutrients are injected into the polluted zone. The treatment typically calls for an aquatic carrier (Penttinen, 2001; Pyy, 2009). Steady circulation of such a carrier has the potential to increase degradation in itself, even without additives, by increasing both the dissolved and hence more bioavailable fractions of the pollutant (Khalladi et al., 2009; Simpanen et al., 2016a) and oxygen levels. Since aerobic degradation is often more potent than

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From a-d : **a)** Jalasjärvi site, **b)** the installation of perforated tubes and **c)**, **d)** the electrokinetic in situ treatment.

anaerobic, oxygen is added as either carbon or calcium peroxide or as gas into the circulated fluid (Kondo, 2006; Suni et al., 2007; Tarasov et al., 2004). Other electron acceptors with alternative benefits (NO_3^-, So_4^{-2} etc.) exist, but they come with environmental risks and their use is restricted, especially in groundwater areas (Van Cauwenberge et al., 1998).

Organic pollutants increase the amount of carbon in soil and the resulting high organic carbon-to-nutrient ratio is a major hindering factor in biodegradation (Chaineau et al., 2005). In terrestrial systems, nitrogen is often the limiting nutrient, and it can be added using common agricultural fertilisers such as urea. Methylene urea is used instead at times to overcome the problems of fluctuating pH and the associated leaching of nitrogen (Peltola et al., 2004), but its low solubility makes it a poor fit for any water circulation applications.

Biostimulation

RIMA (Risk Management and Remediation of Chemical Accidents, 2011-2013) was a collaboration between the University of Helsinki (UHEL) and the Estonian National Institute of Chemical Physics and Biophysics which focused on the risk management of chemical accidents and the development of innovative remediation methodologies. A pilot-scale simulation was formed around a faux accident mimicking a tanker crash with both petrol and diesel oil leakage. In the project the actual accident was also piloted on a smaller scale with soil received from the accident spot. In both experiments biostimulation was compared with chemical oxidation and a control treatment representing monitored natural attenuation. Whereas with chemical oxidation the soil characteristics set certain challenges to be overcome, biostimulation proved to be a relatively reliable and straightforward method, at least when accessibility of the polluted zone was not a factor. In the smaller-scale experiment both biostimulation and chemical oxidation had a positive effect on the control as measured in concentrations in soil. The time frames and concentration end points of the former two were rather similar, hinting at the possibility that, even in the latter, the reductions were likely to have been caused by enhanced aerobic digestion (Tervo, 2013). In the larger-scale test of close to 2 m^3 soil columns (Picture of soil column for an in sity pilot test at the UHEL lysimeter at page 197), biostimulation affected the total amount of bacteria (16S rRNA gene) in a positive manner, and this was also the case with chemical oxidation, underlining its secondary biostimulative role. In both treatments the concentrations in the soil dropped significantly over 16 months. However, it was observed that this was in part due to the mobilisation of diesel oil with chemical oxidation. With biostimulation the dissolved fractions were also successfully degraded and were not transported downwards with water leachate (Gerlach, 2015; Simpanen et al., 2016b).

Bioaugmentation vs biostimulation

One of the more problematic bottlenecks for biodegradation is the lack of degradative power or no expression of degradative genes in native soil bacteria. Attempts to overcome this bottleneck use bioaugmentation techniques. In some cases introducing a selected species with a proven digestion capability has shortened the bacterial adaptation period (Sarand et al., 2000; Szulc et al., 2013). In a study comparing the benefits of bioaugmentation versus those of mere biostimulation, adding bacteria capable of degrading the target pollutant was not found to be a successful way to overcome the problems of the low metabolic potential of the native soil bacteria (Kauppi et al., 2011). When moving the experiment from a laboratory to a natural environment, bioaugmentation did not improve the effects of biostimulation or influence the microbial community composition. The adaptation of the imported species is mostly related to the soil conditions to which the local species are by default better adjusted, and thus they are easily superseded. Also, with aged contaminants, native bacteria usually have already generated the ability to utilise the pollutant as a carbon source, and the problem is instead related to the low number of cells. This dilemma can be dealt with by removing the bottlenecks with biostimulation (Kauppi et al., 2011).
A more successful variation of bioaugmentation is importing naturally occurring communities from other environments to the contaminated zone via soil transplants. A soil with a history of contamination promoted the degradation of further contamination over pristine soil in the case of both diesel oil (Kauppi et al., 2012) and PAHs (Koivula et al., 2004). Also, because the microbes in the humus layer are capable of degrading the naturally occurring complex heteropolymetric substances, both chlorophenol and PAH pyrene were found to degrade even faster in the humus layer than in a previously contaminated soil (Koivula et al., 2004; Sinkkonen et al., 2013).

Surfactants

Another concern in in situ biostimulation may be the low bioavailability of the pollutant (Szulc et al., 2013). The Biokunto project (2007-2010) studied the role of enhanced carbon bioavailabity on the breakdown of pollutants via the biological route. One of the primary interests was the benefit of the use of biosurfactants, mainly β-cyclodextrin. The use of surfactants and biosufactants increases the bioavailability of hydrophobic contaminants by including them in an emulsion or a complex with heightened solubility (Del Valle, 2004; Khalladi et al., 2009). Cyclodextrin is an oligosaccharide that forms a guest–host-type complex with the target molecule trapped at its hydrophobic centre with a van der Waals interaction and no changes in covalent bonds occurring (Del

Valle, 2004). The enhanced solubility affects the bioavailability in a positive manner, but the increased mobilisation can be seen as a potential risk if the biological degradation itself is for some other reason insufficient or lagging behind (Simpanen et al., 2016a).
In a pilot study for diesel soil from a depot area, cyclodextrin enhanced biostimulation and resulted in a tenfold number of colony-forming units (1/5 TGY plates) compared to control soil, and also lower remnant concentrations during a 5-month treatment. The differences in concentrations were apparent after 4 months of water circulation, suggesting that the constant circulation itself was efficient enough during the early stages when carbon availability had less of a restricting role (Talvenmäki, 2010). A pine emulsifier was tested as an alternative surfactant, but was found inapplicable for biostimulation purposes since it served as a more readily available carbon source for bacterial digestion than either diesel or PAHs.
PAHs responded to the usage of cyclodextrin in a similar manner to diesel. It was observed that after a few weeks of circulation the use of cyclodextrin began having a notable effect, lowering PAH concentrations in soil by increasing them in the water phase. This would suggest that the mobilising effect may indeed outpace the biodegradation, especially in freshly polluted soil. The efficiency of the cyclodextrin treatment correlated positively with both the molecule size of the PAHs and with the concentrations (Mäkelä, 2010; Simpanen et al., 2016a).
The effect of cyclodextrin on creosote PAH-contaminated soil was further tested in a full-scale field application. As with the smaller-scale test, optimisation of nutrient ratios proved to be the most important factor concerning the positive outcome, and liquid circulation tended to have a positive effect overall. However, the use of cyclodextrin did have an extra effect on more complex PAH structures that ultimately form the bulk of the contaminant in an aged contaminated soil. The results indicate that, as with diesel-contaminated soil, the use of cyclodextrin may be a financially sound decision after the more bioavailable fractions have already been degraded. This would also lessen the risk of mobilisation (Mäkelä, 2010; Simpanen et al., 2016a).
In the Tankki project (2012-2015) of Lahti University of Applied Sciences, UHEL and Nordic Envicon collaborated on developing in situ methods for oil-contaminated areas. In a lab-scale experiment, the results for β-cyclodextrin on diesel-contaminated soil followed those of the earlier projects. Additionally a 3:1 mixture of mono- and dirhamnolipid, a naturally emulsifying agent produced from Pseudomonas aeruginosa, was tested. The outcome of rhamnolipid-aided biostimulation may be dose dependant since, with larger concentrations, diesel may be trapped within the micelle core, resulting in diminishing bioavailability (Wang, 2011). The antimicrobial and phytotoxic traits may also endanger biological activity (Haba et al., 2003; Vatsa et al., 2010).
While the experiment with dosing of rhamnolipid (dose 300 ppm) did appear to positively affect the total amount of bacterial cells in the soil locally, as measured from 16S rRNA gene abundance, it did not have a similar effect on the removal of diesel (Talvenmäki, 2016). As with pine emulsifier, the additive may have become the carbon source, competing with the pollutant for resources and bacterial digestion potential. Methylated urea also may have a potential inhibiting role for similar reasons, and the problem should be taken into account with all carbon-including additives (Talvenmäki, 2016). This factor highlights why bioaugmentation practices may result in a negative outcome (Kauppi et al., 2010).

Clean-up cases

Lintuvaara case study

On the epremises of a former fuel station, was agreed to be treated with a combination of in situ biostimulation and mass exchange. In situ was chosen because of the low risk level, requiring no immediate solution, and because lowering the groundwater for mass exchange was deemed problematic. The area consisted of two residential lots, on which planned building development required remediation activities, and of a nearby park with risks associated with volatile compounds but not with heavier fractions if no major changes in land use were to occur.
In the residential area the remediation objective, based on case-dependent risk assessment, had the upper guideline value for fractions C_{10}-C_{21} (1000 mg/kg) and 55 mg/kg for volatile

compounds as both were present. The treatable area with oil carbon concentrations exceeding the lower guideline values was 400 m^3 in volume. Water samples taken from the west side of the site, where groundwater elevation was highest, showed high concentrations of volatile compounds which may originate from an unrelated, natural source. The polluted sandy zone was covered by a clayey surface layer 1 m in depth and devoid of contamination. A circulation well for reagent injection and sampling was installed to cover the area through connected sieve tubing. A fertiliser and water mixture containing nitrogen and phosphorus was injected monthly into the well. The nutrient mix was fed through the contaminated zone via injection channels and kept in circulation using a submersible pump installed in the well. After 22 months of treatment the objectives were reached in the residential area. In the park area the concentration of volatile compounds was lower than the target value and thus the endpoint was acceptable according to the original assessment. In water samples taken from west side of the area after the remediation the mid-heavy to heavy fractions had decreased slightly from 0.10 mg/l to 0.06 mg/l and no petrol compounds were detected.

Halikko case study

In some cases remediation objectives cannot be met with in situ treatment and so some portion of the polluted soil may need to be removed and replaced. Even in such cases the total volume requiring removal can be drastically reduced by employing in situ biostimulation prior to mass exchange. In Salo, southern Finland, a former fuel station area was successfully treated with a combination of these two methods in 2012-2013. The original evaluation of the polluted mass was 2 800 t, with peak C_{10}- C_{40} concentrations above 20 000 mg/kg and benzene levels surpassing the lower guideline value mg/kg in some samples. Sieve tubing was installed in the area and 9 m^3 of a nutrient-rich biostimulation solvent was introduced into the soil over a 5-month period. The positive effect of biostimulation was recorded, with the highest measured concentrations no more than 50% of the original peak values. However, it was necessary to remove 700 t of soil from the site for further processing in order to meet the project objectives. Both the 75% reduction in the mass treated off site, as well as the lower concentrations, still signified notable savings.

The combination of in situ and off-site treatment resulted in the successful removal of hydrocarbons from a 0.5 m × 40 m^2 volume at approximately 3 m in depth, with benzene concentrations surpassing the lower guideline value. The contaminated volume in question was situated under yard/unbuilt surfaces and was contained within soil that was clayey from the near surface to a depth of at least 18 m, and so the spreading of benzene either to indoor air or to groundwater was considered a minute risk. The remediation activities themselves were not found to have a negative effect on groundwater quality.

Jalasjärvi case study

Because with many former fuel stations the contamination consists of both volatile fractions that are difficult to degrade by biological means and heavier compounds for which biostimulation is often suitable, a combination of different methods may be worth pursuing. In one such case — a former fuel station area in Jalasjärvi, Finland — the soil was remediated electrokinetically. The biostimulation solvent was dispersed in a soil with low permeability by forming an electromagnetic current, which attracted charged particles contained and thus moved the whole water matrix through viscous forces (picture of Jalasjärvi site page 198). Because of the resulting dewatering effect, the volatile compounds could be treated by soil vapour extraction. Vapour extraction had been tested prior to biostimulation to no avail, and biostimulation by itself was found to have very little effect on BTEX compounds.

In more detail, the procedure was the following: The contaminated area was 30 m^2 and 6 m deep. The fuel pumps had been seated on coarse sand, but the natural soil underneath was dense and silty. A row of four stainless steel rods were installed as anode electrodes inside perforated plastic tubes standing ca 1.2 m apart and reaching down to a depth of 5-6 m. Ca. 5 m from the anode row, on the opposite side of the contaminated target soil, four cathodes were installed at a similar depth. The anodes and the cathodes thus formed four electrode pairs. The electrodes were then connected in parallel with a portable power supply of 270 V DC, causing a voltage of 0.54 V/cm. During the initial phases of the treatment, nutrient-amended water was introduced by slow infiltration and electrokinetic pumping into the contaminated soil. Diesel and some of BTEX in the coarse layer were treated successfully with biostimulation, and although the diesel was successfully removed by biodegradation also in the dense soil layers, high levels of BTEX remained in the natural dense soil. After the biostimulation the current was kept on for 6 more months without any infiltration of liquids other than natural rain and snowmelt. The resultant dewatering of the soil inspired a lab-scale test that revealed the degree of wetting, indeed corresponding negatively with the concentrations of volatile fractions as measured with PID. Encouraged by the results, SVE tubing was installed on the site, and after applying the vacuum for 3 months the C_5- C_{10} residues were under the target concentrations, and the condition of the site was found acceptable. The whole treatment lasted 24 months, of which approximately half could have been cut off with a more methodical approach (Martin Romantschuk, personal communication).

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VOC-YHDISTEIDEN POISTAMINEN POHJAVEDESTÄ VETYPEROKSIDIN KUPLITUS -MENETELMÄLLÄ

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Tiivistelmä – Referat – Abstract

Pohjavesien pilaantuminen on merkittävä ympäristöongelma. Esimerkiksi jotkut haihtuvat orgaaniset yhdisteet (VOC), kuten metyyli-tert-butyylieetteri (MTBE) sekä trikloorietyleeni (TCE), ovat saastuttaneet laajojakin pohjavesialueita. Pohjavesien kunnostuksessa ongelmana on, että nykyisillä menetelmillä pohjavettä on vaikeaa ja kallista puhdistaa. Perinteisessä pump & treat –menetelmässä vesi pumpataan maan päälle puhdistettavaksi, ilman että vuosienkaan jälkeen pitoisuudet välttämättä laskevat merkittävästi. Air sparging on edullisempi ja nopeampi menetelmä, mutta menetelmän soveltuvuus on tapauskohtaista. Myös kemiallinen hapetus on kohdespesifinen ja siksi toimivuudeltaan epävarma menetelmä. Näin ollen uusille puhdistustekniikoille on todellista tarvetta.

Yksi mahdollinen vaihtoehto voisi olla uusi vetyperoksidin kuplitus -menetelmä, joka perustuu vetyperoksidin (H_2O_2) hajoamisreaktioiden kykyyn mobilisoida ja haihduttaa pohjavedessä sijaitsevia VOC-aineita. Pohjavesikerrokseen korkeana pitoisuutena syötetty H_2O_2 leviää ja luonnostaan esiintyvä rauta katalysoi sen hajoamista. Hajoamisreaktioiden käynnistyessä vapautuvan kaasun oletetaan johtavan ilmastuksen ja strippauksen kaltaisiin vaikutuksiin, johtaen VOC-yhdisteiden haihtumiseen. Etuna ilmastukseen verrattuna olisi se, että vaikutussäde olisi nestettä lisäämällä mahdollista saada suuremmaksi kuin ilmaa syöttämällä. Vaikka käytetyt reagenssit ovat samoja kuin kemiallisessa hapetuksessa, toimintaperiaatteen takia menetelmän ei uskota olevan yhtä kohderiippuvainen.

Tässä pro gradu –tutkielmassa selvitettiin vetyperoksidin kuplitus –menetelmän soveltuvuutta VOC-yhdisteiden poistamiseen pohjavedestä. Tutkielma koostui laboratorio-, lysimetri- ja kenttäkokeista. Laboratoriokokeissa selvitettiin menetelmän soveltuvuutta ominaisuuksiltaan erilaisille VOC-yhdisteille. Lisäksi selvitettiin, miten eri muuttujat (H_2O_2- ja rautakonsentraatio sekä kelaattilisäys) vaikuttavat H_2O_2:n hajoamisreaktioaikaan sekä MTBE:n poistumaan. Pilot-mittakaavan lysimetrikokeissa testattiin MTBE:n poistamista sekä pelkästä vesifaasista että hiekkamaasta. Kokeissa käytettiin bensiini- ja TCE-saastunutta vettä sekä keinotekoista MTBE-vettä, jonka pitoisuus oli 750 mg/l. Menetelmän toimivuutta täydessä mittakaavassa testattiin entisellä polttoaineiden jakeluasemalla yhdessä Nordic Envicon oy:n kanssa.

Laboratoriokokeissa sekä pilot-kokeen vesikokeessa saavutettiin lähes 100 %:n puhdistumistulos. Pilot-vaiheen hiekkakokeessa MTBE:n poistuma oli noin 94 % ja toistetulla käsittelyllä lähes 97 %, mutta seisotuksen myötä pitoisuudet nousivat, jolloin poistuma jäi 85 ja 66 prosenttiin. Kenttäkokeessa vetyperoksidin havaittiin levinneen koko koealueelle, mutta epätasaisesti. Puhdistumista tapahtui alueella, jonne vetyperoksidia oli levinnyt eniten, ja jossa pitoisuuden oletettiin olleen riittävä tutkitun vaikutuksen aikaansaamiseksi. BTEX- ja bensiinijakeiden pitoisuudet laskivat muutamassa kuukaudessa jopa 88–97 %. Vaikka pitoisuuksien laskun kannalta kokeet olivat onnistuneita, ei vetyperoksidin kuplitus -menetelmää pystytty hypoteesien vastaisesti erottamaan kemiallisesta hapetuksesta. Sen sijaan hapettumista sekä haihtumista tapahtuu tulosten perusteella samanaikaisesti. Täyden mittakaavan sovellutuksia varten menetelmää onkin tarpeen vielä tutkia ja optimoida esimerkiksi massatasapainokokeiden avulla.

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VOC-yhdisteet, MTBE, TCE, pohjavesi, in situ -kunnostus

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Tiivistelmä – Referat – Abstract

Groundwater contamination is a worldwide problem. For example, some volatile organic compounds (VOCs), such as methyl tert-butyl ether (MTBE) and trichloroethylene (TCE) have contaminated large groundwater bodies. To minimize the health risks, contaminated groundwater needs to be remediated, but it is often difficult and expensive. In pump & treat, water is pumped onto the ground for remediation. The pumping may take from years to decades without significant decrease in concentrations. Air sparging, on the other hand, is a more cost-effective and faster method, but the suitability of the method is case-dependent. Chemical oxidation is also site-specific and therefore an uncertain method. Thus, there is a demand for new remediation techniques.

One alternative could be a new method called hydrogen peroxide (H_2O_2) sparging. It is based on the ability of H_2O_2 degradation reactions to mobilize and volatilize VOCs from groundwater. In peroxide sparging, H_2O_2 is injected in high concentrations into the groundwater, where it spreads and naturally occurring iron catalyzes its degradation. When the degradation reactions start, the released gas is assumed to cause air sparging- and stripping-like effects, resulting in the volatilization of VOCs. The advantage over aeration would be that the radius of influence would be increased by supplying liquid instead of air. Although the reagents are the same as in chemical oxidation, the method is not supposed to be as site-specific, due to the operation principle.

The aim of this Master's Thesis was to investigate the suitability of H_2O_2 sparging for the removal of VOCs from soil pores and groundwater. The thesis consisted of laboratory, lysimeter and field experiments. In laboratory scale experiments, the suitability of the method for removal of VOCs with different physicochemical properties was studied. The effect of different parameters (H_2O_2 and iron concentrations and chelate addition) to the reaction time of H_2O_2 and the degradation of MTBE was also studied. In pilot scale lysimeter experiments the aim was to test the removal of MTBE both from aqueous phase and sandy soil. The tests were executed with groundwater contaminated with gasoline or TCE and with MTBE spiked water at a concentration of 750 mg/l. The full-scale functionality of the method was tested at the former fuel station together with Nordic Envicon Oy.

In the laboratory and pilot tests, nearly 100% removal was achieved. In the pilot experiment with sandy soil, the removal rate of MTBE was 94% and with repeated treatment almost 97%. Concentrations rebounded after about a month, lowering the removal rate to 85 and 66 %. In the field experiment, H_2O_2 was found to spread unevenly throughout the test area. Removal occurred in the area where H_2O_2 had spread most and where the concentration was supposed to be sufficient to produce the observed effect. BTEX and gasoline concentrations decreased by as much as 88–97% in just a few months. Although the experiments were successful in degreasing concentrations, the principle of H_2O_2 sparging could not be distinguished from the chemical oxidation, which was opposite to the hypothesis. Based on the results, oxidation and volatilization will occur simultaneously. Before full-scale applications, it is necessary to study and optimize the method, for example by studying in more detail the mass balance.

Avainsanat – Nyckelord – Keywords
VOCs, MTBE, TCE, groundwater, *in situ* remediation

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SISÄLLYSLUETTELO

1. Johdanto

Pohjavesien pilaantuminen on vakava maailmanlaajuinen ongelma. Pohjavesiä käytetään monin paikoin talousvetenä, joten pilaantuessaan ne voivat aiheuttaa terveysriskejä. Esimerkiksi pilaantuneet maa-alueet voivat uhata niiden kuntoa. Pilaantuminen voi olla seurausta muun muassa haitta-aineiden käytöstä, valmistuksesta ja varastoinnista aiheutuvista päästöistä tai satunnaisista vahingoista. Suomessa on vuonna 2013 tehdyn selvityksen mukaan yli 23 000 pilaantuneeksi epäiltyä, todettua tai kunnostettua maa-aluetta, joista 18 % sijaitsee luokitetuilla pohjavesialueilla. Näistä yli 80 % kuuluu luokkaan I, eli vedenhankinnan kannalta tärkeisiin pohjavesialueisiin. Pohjaveden kuntoa uhkaavia toimialoja ovat muun muassa polttoaineen jakelu, kaatopaikat, moottoriajoneuvojen huolto sekä ampumaradat. (Pyy ym. 2013). Haitta-aineista esimerkiksi haihtuvat orgaaniset yhdisteet (VOC), kuten bensiini ja sen lisäaineet (mm. metyyli-tert-butyylieetteri eli MTBE) tai liuottimet, kuten trikloorietyleeni (TCE) voivat aiheuttaa pilaantumista.

Terveys- ja ympäristöriskien ehkäisemiseksi pilaantuneita pohjavesiä on tarpeen kunnostaa. Nykyisillä menetelmillä kunnostaminen on kuitenkin monesti kallista ja vaivalloista. Esimerkiksi perinteisissä pumppaus ja käsittely (pump & treat) -menetelmissä vesi täytyy pumpata maan päälle puhdistettavaksi, ilman että vuosienkaan käsittelyn jälkeen pitoisuudet maassa välttämättä laskevat merkittävästi (Mackay & Cherry 1989). Ilmastus (air sparging) puolestaan on suhteellisen edullinen, nopea ja tehokas kunnostusmenetelmä (Reddy ym. 1995) mutta sen soveltuvuus on tapauskohtaista. Ilma nimittäin pyrkii nousemaan helpointa reittiä ylöspäin, jolloin erityisesti heterogeenisessä maaperässä menetelmän vaikutussäde voi jäädä hyvinkin pieneksi (Reddy & Adams 2001). Myös kemiallinen hapetus on kohdespesifinen ja siten toimivuudeltaan epävarma menetelmä (Petri ym. 2011).

Yksi vaihtoehto näille menetelmille on vetyperoksidin kuplitus -menetelmä, jossa VOC-yhdisteitä haihdutetaan pohjaveteen syötetyn vetyperoksidin hajoamistuotteiden seurauksena muodostuvan kaasun avulla. Tämän pro gradu -tutkielman tarkoituksena oli selvittää vetyperoksidin kuplitus -menetelmän soveltuvuutta ominaisuuksiltaan erilaisille VOC-yhdisteille. Lisäksi tutkielmassa pyrittiin erottelemaan menetelmän toimintaperiaate Fenton-kemiaan perustuvasta kemiallisesta hapetuksesta, jossa käytetään samoja reagensseja orgaanisten yhdisteiden hajottamiseksi.

Tutkielma on osa INNOVOC- ja INSURE-hankkeita. INNOVOC on osittain rahoitettu Pirkanmaan ELY-keskuksen organisoimasta pilaantuneiden maa-alueiden kokeiluhankkeesta, jolla pyritään kiihdyttämään pilaantuneiden maa-alueiden kestävien riskinhallintamenetelmien kehittämistä ja käyttöönottoa (YM 2015). INSURE (Innovative Sustainable Remediation) puolestaan on EU:n Interreg Central Baltic -ohjelman osittain rahoittama projekti, jonka yhtenä tarkoituksena on tutkia kestävämpiä kunnostusmenetelmiä.

1.1. VOC-yhdisteet

VOC-yhdisteillä (volatile organic compounds) tarkoitetaan haihtuvia orgaanisia yhdisteitä. Tarkkaa yksittäistä määritelmää VOC-yhdisteille ei ole (Rivett ym. 2011), mutta esimerkiksi Euroopan Unionin direktiivin 2004/42/EY mukaan haihtuviksi orgaanisiksi yhdisteiksi luetaan ne yhdisteet, joiden kiehumispiste on enintään 250 °C normaali-ilmanpaineessa (101,3 kPa). Teollisuuden päästödirektiivissä (2010/75/EU) VOC:t puolestaan määritellään orgaanisiksi yhdisteiksi, joiden höyrynpaine 20 °C:n lämpötilassa on vähintään 0,01 kPa. Haihtuvat orgaaniset yhdisteet voivat olla joko luonnollista alkuperää (biogeenisiä) tai ihmistoiminnasta aiheutuvia (antropogeenisia). Biogeenisten VOC-yhdisteiden merkittävin lähde on kasvillisuus. Antropogeenisiin lähteisiin puolestaan lukeutuvat muun muassa fossiiliset polttoaineet, biomassojen polttaminen, jätehuolto sekä lukuiset teolliset prosessit, kuten liuottimien valmistus. (Koppmann 2007)

Vaikka VOC:t ovat haihtuvia yhdisteitä, osa niistä voi saastuttaa merkittävästi pohjavesiä. Yleisiä pilaantumanaiheuttajia ovat esimerkiksi öljyhiilivedyt sekä klooratut liuottimet. VOC-aineet esiintyvät pohjavedessä pääasiassa joko liukenemattomassa faasissa (non-aqueous phase liquid, NAPL) tai pohjaveteen liuenneina. (Adams ym. 2011). Ne voivat muodostaa laajoja, nopeastikin levittäytyviä haitta-ainevanoja (Reddy ym. 1995). Haitta-aineet kulkeutuvat pääasiassa virtaavan veden eli advektion, virtausnopeuksien pienimuotoisten vaihteluiden (dispersion) sekä diffuusion avulla (Reddy & Tekola 2004).

Tarkasteltaessa VOC-yhdisteiden ympäristökohtaloa yksi tärkeä ominaisuus on Henryn lain vakio. Henryn laki kuvaa riippuvuutta kaasun osapaineen ja nesteeseen liuenneen kaasun määrän välillä, eli sen avulla voidaan arvioida haitta-aineen haihtumista vesifaasista. Jos kahden yhdisteen konsentraatio vedessä on sama, yhdiste, jonka Henryn vakio on suurempi, haihtuu herkemmin kaasufaasiin. (Reddy & Tekola 2004). Henryn lain vakiosta käytetään usein myös yksikötöntä muotoa, joka saadaan jakamalla Henryn lain vakio kaasuvakion ja lämpötilan tulolla. Yhdiste, jonka yksikötön vakio on suurempi kuin 0,05, haihtuu vedestä. (Squillace ym. 1997)

VOC-aineisiin kuuluu useita erilaisia yhdisteitä, jotka voidaan ominaisuuksien perusteella jakaa omiin ryhmiinsä. Tässä tutkielmassa VOC-yhdisteet ovat jaettu alifaattisiin, aromaattisiin ja halogenoituihin hiilivetyihin sekä eettereihin, mikä on myös joidenkin laboratorioiden tapa jakaa VOC:t. Alifaattiset hiilivedyt ovat suoraketjuisia, haaroittuneita tai rengasrakenteisia yhdisteitä, jotka eivät sisällä bentseenirengasta. Niiden vesiliukoisuus ja haihtuminen heikkenevät molekyylikoon kasvaessa. (YM 2014). Esimerkiksi lyhytketjuiset alifaattiset hiilivedyt ovat merkittäviä bensiinin komponentteja (Watts ym. 2000). Suomessa bensiinijakeisiin luetaan hiililuvun perusteella C5–C10-hiilivedyt (YM 2014: 207).

Aromaattiset hiilivedyt puolestaan sisältävät vähintään yhden bentseenirenkaan, jossa kuusi hiiliatomia on sitoutunut renkaaksi. Ne voidaan jakaa bentseenirenkaiden määrän mukaan monoaromaattisiin ja polyaromaattisiin (PAH) hiilivetyihin. Aromaattiset hiilivedyt, erityisesti monoaromaattiset BTEX-yhdisteet (bentseeni, tolueeni, etyylibentseeni ja ksyleenit) ovat alifaattisten hiilivetyjen ohella merkittäviä fossiilisten polttoaineiden komponentteja. Alifaattisiin hiilivetyihin verrattuna monoaromaattiset yhdisteet ovat vesiliukoisempia mutta myös kulkeutuvampia, sillä ne eivät pidäty yhtä vahvasti maaperän orgaaniseen ainekseen. (Watts ym. 2000). Ne ovat kuitenkin alifaattisia yhdisteitä heikommin haihtuvia (YM 2014: 209). Lisäksi monoaromaattiset hiilivedyt ovat toksisempia kuin saman hiililuvun alifaattiset hiilivedyt (Watts ym. 2000).

Halogenoidussa hiilivedyissä puolestaan yksi tai useampi vety on korvattu halogeenilla, kuten kloorilla tai bromilla. Monet niistä ovat vettä raskaampia. Ominaisuuksiensa vuoksi niillä on ollut laajaa teollista käyttöä muun muassa liuottimina sekä jäähdytysaineina. Monet halogenoidut hiilivedyt ovat kuitenkin mahdollisia karsinogeeneja. (Huang ym. 2014). Eetterit taas ovat yhdisteitä, joissa kaksi hiilivetyrunkoa on sitoutunut toisiinsa happiatomin välityksellä. Ne ovat poolisia, mikä tekee eettereistä poolittomia hiilivetyjä vesiliukoisempia. Eetterien molekyylit eivät voi muodostaa vetysidoksia keskenään, minkä vuoksi niillä on molekyylipainoltaan samankokoisten hiilivetyjen kaltaisesti suhteellisen alhainen kiehumispiste. (Ouellette & Rawn 2014). Eettereitä on käytetty usein muun muassa polttoaineiden lisäaineina (Koppmann 2007: 138).

Tähän työhön valittiin tarkasteltavaksi kaksi ominaisuuksiltaan erilaista VOC-yhdistettä, eettereihin kuuluva metyyli-tertiääri-butyylieetteri (MTBE) sekä halogenoituihin hiilivetyihin kuuluva trikloorietyleeni (TCE). MTBE on vesiliukoista ja vettä kevyempää (Squillace ym. 1997), kun taas TCE on heikommin veteen liukenevaa ja vettä raskaampaa (Pant & Pant 2010). Kummankin yhdisteen tuotantomäärät ovat olleet suuria ja käyttö maailmanlaajuista, minkä seurauksena monia pohjavesialueita on saastunut. Ominaisuuksiensa vuoksi näitä yhdisteitä on ollut haasteellista poistaa pohjavedestä perinteisin kunnostusmenetelmin (Lewis ym. 2009, Innocenti ym. 2014).

1.1.1. MTBE

Metyyli-tertiääri-butyylieetteri eli MTBE on synteettinen yhdiste, jota on käytetty pääasiallisesti bensiinin lisäaineena kohottamaan oktaanilukua sekä lisäämään happipitoisuutta. Tarkoituksena on ollut tehostaa polttoaineen tasaista palamista sekä vähentää autojen hiilimonoksidipäästöjen muodostumista. (Stefan ym. 2000). MTBE:ä on lisätty polttoaineisiin 1970-luvun lopulta lähtien (van Wezel ym. 2009) ja Suomessa sitä on käytetty vuodesta 1991 (Tidenberg ym. 2009). MTBE:n tuotantomäärät ovat olleet maailmanlaajuisesti suuria, esimerkiksi vuonna 1999 MTBE:ä tuotettiin yhteensä noin 21 miljoonaa tonnia (van Wezel ym. 2009). Suomessa vastaavana vuonna MTBE:n tuotanto oli noin 108 000 t ja käyttö noin 136 000 t (Tidenberg ym. 2009).

Vaikka MTBE:n lisäämisellä polttoaineeseen on ollut ilmanlaadun kannalta suotuisia vaikutuksia, on sen käyttö herättänyt huolta mahdollisten terveydelle haitallisten vaikutusten vuoksi (Stefan ym. 2000). MTBE:n on todettu aiheuttavan eläimillä syöpää, minkä vuoksi MTBE on luokiteltu mahdollisesti ihmisille karsinogeeniseksi (Squillace ym. 1997). Lisäksi MTBE on erittäin vesiliukoinen ja suhteellisen heikosti haihtuva yhdiste (taulukko 1) eivätkä mikrobit hajota sitä helposti (Hwang ym. 2010). Näin ollen MTBE:ä päätyy helposti pohjaveteen, jossa se on melko pysyvä. MTBE:llä on matala haju- ja makukynnys (15 ja 40 µg/l), joten sen esiintyminen jo pieninä pitoisuuksina voi rajoittaa pohjaveden käyttöä talousvetenä (Tidenberg ym. 2009). MTBE:ä päätyy ympäristöön esimerkiksi vuotavista maanalaisista polttoainesäiliöistä sekä tahattomien polttoainevuotojen seurauksena (Hwang ym. 2010). Myös kulkeutuminen ilman kautta hajapäästöinä on mahdollista (Innocenti ym. 2014).

MTBE:n aiheuttamat vuodot ovat olleet ongelmana erityisesti Yhdysvalloissa, jossa suurien vuotojen myötä pitoisuudet julkisissa vedenottamoissa ovat nousseet paikoitellen niin korkeiksi, että vedenottamoita on jouduttu poistamaan käytöstä. Myös pienemmät esiintymät ovat olleet yleisiä. Tämän johdosta MTBE:n käyttö on kielletty joko osittain tai kokonaan monissa Yhdysvaltojen osavaltioissa, ja esimerkiksi vuoteen 2007 mennessä MTBE:n käyttö bensiinissä oli vähentynyt lähes olemattomalle tasolle. Euroopassa puolestaan käyttömäärät ovat olleet vähäisempiä, eikä MTBE:lle ole asetettu käyttökieltoa. (Lindsey ym. 2017). Biopolttoainedirektiivin myötä MTBE:n tuotanto on kuitenkin vähentynyt ja MTBE:ä on korvattu erityisesti etanolipohjaisella etyyli-tert-butyylieetterillä (ETBE) (van Wezel ym. 2009, Tidenberg ym. 2009).

1.1.2. TCE

Trikloorietyleeni (trikloorieteeni, TCE) on kloorattu liuotin, jota on käytetty pääasiassa metallien puhdistuksessa ja rasvanpoistossa, mutta myös muun muassa vaatteiden kemiallisessa pesussa sekä lääkkeiden, kylmäaineiden ja palonestoaineiden valmistuksessa. Trikloorietyleenin käyttö alkoi 1900-luvun alkupuolella, käytön ollessa huipussaan Yhdysvalloissa 1960- ja 1970-luvun taitteessa. Trikloorietyleenin käyttöä alettiin rajoittaa 1970-luvulla, sillä sen epäiltiin olevan osallinen otsonin ja savusumun muodostumisessa. Lisäksi TCE:n epäiltiin olevan karsinogeeninen. (Doherty 2000). Myös Euroopassa trikloorietyleenin käyttö on vähentynyt 1970-luvun puolivälin jälkeen yli 50 %, tuotannon ollessa vuonna 2001 140 000 tonnin tienoilla (EC 2004). Suomessa vuoden 2008 tietojen mukaan TCE:ä valmistettiin 16,4 tonnia ja tuotiin 110,6 tonnia. Nykyisellään TCE:n käyttöä Euroopan unionissa on rajoitettu muun muassa REACH-asetuksella. (Tukes 2009)

Trikloorietyleeniä päätyy ympäristöön esimerkiksi teollisuudesta ja kuluttajatuotteista sekä vääränlaisen varastoinnin ja hävittämisen seurauksena (EC 2004, Pant & Pant 2010). Maaperään ja pintavesiin päätyvä TCE poistuu pääasiassa haihtumalla ilmakehään (Wu & Schaum 2000), jossa sen puoliintumisaika on noin viikko. Toisin kuin 1970-luvulla uskottiin, TCE:ä ei pidetä merkittävänä tekijänä alailmakehän otsonin muodostumisessa. Trikloorietyleeni pidättyy heikosti tai kohtalaisesti maapartikkeleihin, joten se on maaperässä kulkeutuva yhdiste. (EC 2004). TCE liukenee kohtalaisen heikosti veteen, ja vettä raskaampana yhdisteenä se voi kerrostua pohjavesipinnan alapuolelle omaksi faasikseen, jota on vaikea puhdistaa. (Pant & Pant 2010). Trikloorietyleeni onkin yksi yleisimmin pohjavedestä havaituista haitta-aineista (muun muassa Squillace ym. 1999, Yu ym. 2015), ja mahdollisten terveyshaittojen vuoksi TCE:llä pilaantuneet pohjavedet ovat herättäneet huolta (Pant & Pant 2010).

Trikloorietyleeni on biohajoava, mutta hajottamista rajoittaa sen toksisuus sekä heikko vesiliukoisuus (Xin-De ym. 2012). Mikrobit voivat hajottaa TCE:ä anaerobisissa oloissa, jolloin optimaalisessa tilanteessa lopputuotteena syntyy etaania tai eteeniä. (Pant & Pant 2010) Mikäli hajoaminen ei ole täydellistä, voi muuntumistuotteena syntyä muun muassa vinyylikloridia, joka on TCE:ä toksisempaa (Xin-De ym. 2012). Aerobisissa oloissa on mahdollista saavuttaa TCE:n täydellinen mineralisaatio (Pant & Pant 2010).

Taulukko 1. MTBE:n (Tidenberg ym. 2009) ja TCE:n fysikaalis-kemialliset ominaisuudet (Alleman ym. 2010: 33).

Ominaisuus	MTBE	TCE
Molekyylipaino, g/mol	88,15	131,4
Tiheys	0,741 (20 °C)	1,46 (25 °C)
Kiehumispiste, °C	55	86,7
Vesiliukoisuus, g/l	42 (20 °C)	1,1 (25 °C)
Höyrynpaine, kPa (20 °C)	27	8,6 [a]
Log K_{ow} (25 °C)	1,06	2,53
Henryn lain vakio (H) (Pa m^3/mol) (20 °C)	42,8	1030 [a]
Henryn lain vakio (H/RT)	0,018	0,423
CAS-numero	1634-04-4	79-01-6

[a] (EC 2004)

1.2. Pilaantuneiden alueiden kunnostus

Useimmissa kunnostettavissa kohteissa ympäristöä pilaava toiminta on tapahtunut vuosikymmeniä sitten (YM 2015). Tarve pilaantuneiden maa-alueiden kunnostamiselle syntyy tavallisesti maankäytön muutoksen tai kaivamisen ja rakennustöiden seurauksena. Useimmiten kunnostuksen tarkoituksena on vähentää mahdollisia terveysriskejä rakennettavilla asuinalueilla tai pohjavesialueilla. (Pyy ym. 2013). Tavoitteena on saavuttaa haitta-aineiden osalta tietty pitoisuustaso, joka määritellään tavallisesti PIMA-asetuksen (Valtioneuvoston asetus maaperän pilaantuneisuuden ja puhdistustarpeen arvioinnista, 214/21007) riskiperustaisten ohjearvojen perusteella. Ohjearvot määräytyvät pääasiallisesti maankäytön mukaan. (YM 2015)

Pohjavedelle ei ole annettu vastaavanlaisia ohjearvoja, vaan kunnostuksen tavoitteet määräytyvät lähinnä käyttötarkoituksen perusteella. Juomavesikäyttöön tarkoitetun veden tulee täyttää talousveden laatuvaatimukset taikka muut erikseen määritellyt laatuvaatimukset. Näiden puuttuessa vertailuarvona voidaan käyttää myös WHO:n juomaveden enimmäispitoisuuksia. Mikäli pohjavettä käytetään muuhun tarkoitukseen, esimerkiksi pesuun tai kasteluun, vertailuarvot määritetään riskiperustaisesti käytön mukaan. Näitä arvoja on esitetty muun muassa ruotsalaisen Kemakta Konsult AB:n julkaisemassa selvityksessä ”Riktvärden för ämnen i grundvatten vid bensinstationer”. (YM 2014: 89–90)

Pilaantuneiden alueiden kunnostusmenetelmät voidaan jakaa sen perusteella, missä kunnostus tapahtuu. *Ex situ* (off site) -menetelmissä pilaantunut pohjavesi tai maa-alue pohjavesi kuljetetaan muualle kunnostettavaksi. Suomessa pilaantuneiden alueiden kunnostaminen toteutetaan pääosin juuri *ex situ* -massanvaihtona (Pyy ym. 2013). On site -menetelmissä pilaantunut pohjavesi pumpataan pois tai maamassa kaivetaan ylös, mutta kunnostus tapahtuu paikan päällä. *In situ* -menetelmissä puolestaan pilaantuneet alueet käsitellään kohteessa ilman, että pohjavettä tai maa-ainesta tarvitsee poistaa. Suomessa aloitetaan vuosittain noin 250–300 pilaantuneiden maiden kunnostushanketta, joista vain 10–15 kohteessa kunnostus toteutetaan *in situ*. *In situ* -tekniikoiden käyttöönottoa rajoittavat muun muassa niiden vähäinen tarjonta sekä alueidenkäytön suunnittelua ja rakentamista koskevat käytännöt. (YM 2015)

Kunnostusmenetelmät voidaan jakaa myös fysikaalisiin, kemiallisiin ja biologisiin menetelmiin. Menetelmän valinta riippuu erityisesti haitta-aineen ja maaperän ominaisuuksista. Haihtuville orgaanisille yhdisteille soveltuvia maaperän *in situ* -kunnostusmenetelmiä ovat muun muassa huokosilmakäsittely sekä maan huuhtelu. VOC-aineiden sijaitessa pohjavedessä voidaan kunnostuksessa käyttää esimerkiksi pohjaveden pumppaus ja käsittely (pump & treat) -menetelmiä, ilmastusta (air sparging) tai kemiallista hapetusta. (Penttinen 2001, Khan ym. 2004). Nämä pohjaveden kunnostusmenetelmät on esitelty tarkemmin seuraavissa kappaleissa.

1.2.1. Pohjaveden pumppaus ja käsittely

Pohjaveden kunnostusmenetelmistä yleisimpiä ovat pumppaus ja käsittely (pump & treat) –menetelmät (Khan ym. 2004). Pilaantunut pohjavesi pumpataan maan päälle puhdistettavaksi, eli kunnostaminen tapahtuu ”on site” tai *ex situ*. Vesi voidaan käsitellä usealla eri menetelmällä, joista yleisin on aktiivihiilisuodatus. Muita käsittelyvaihtoehtoja ovat muun muassa kemiallinen hapetus, strippaus eli haihdutus sekä bioreaktorit. Käsittelymenetelmän valintaan vaikuttavat erityisesti haitta-aineen ominaisuudet. (Penttinen 2001). Käsittelyn jälkeen vesi voidaan palauttaa takaisin maaperään, johtaa pintavesiin tai viedä jatkokäsiteltäväksi jätevedenpuhdistamolle (Penttinen 2001, Khan ym. 2004).

Olennaista pumppaus ja käsittely -menetelmissä on eristää tai poistaa varsinainen haitta-aineen lähde, sillä muutoin päästölähde toimii jatkuvana haitta-aineen lähteenä ja kunnostukseen vaadittava aika pitenee (Brusseau ym. 2006: 321). Pumppaus ja käsittely -menetelmien ongelmana onkin, että puhdistaminen voi olla erittäin hidasta, kestoltaan jopa useita kymmeniä vuosia (Khan ym. 2004). Menetelmien avulla voidaan kyllä ehkäistä haitta-aineiden leviämistä ja siten mahdollisia haitta-aineista aiheutuvia terveysriskejä, mutta pitkäaikainen pumppaus ja käsittely tuovat merkittäviä kustannuksia kunnostamiselle (Mackay & Cherry 1989). Menetelmien tehokkuutta heikentävät maaperän heikosti läpäisevät alueet, sillä veteen liuenneet kemikaalit voivat diffundoitua heikosti läpäisemättömiin kerroksiin, kun taas pohjavesi virtaa pääasiassa niiden ympäriltä. Pumppaus ja käsittely -menetelmät eivät myöskään sovi haitta-aineille, jotka pidättyvät lujasti maapartikkeleihin tai jotka eivät liukene veteen. (Brusseau ym. 2006: 321). Pinta-aktiivisia aineita lisäämällä voidaan kuitenkin lisätä maapartikkeleihin pidättyneiden haitta-aineiden kulkeutuvuutta ja liukoisuutta, mikä voi parantaa kunnostuksen tehoa. Epävarman toimivuutensa vuoksi pumppausta ja käsittelyä ei nykyään pidetä parhaana kunnostusvaihtoehtona. Merkittävästi saastuneilla alueilla se voi silti olla hyödyllinen, sillä menetelmän käyttöönotto on yksinkertaista ja nopeaa. (Khan ym. 2004)

1.2.2. Pohjaveden ilmastus

Pohjaveden ilmastus (air sparging, stripping) on *in situ* -menetelmä, jossa pyritään nopeuttamaan haihtuvien yhdisteiden poistumista maaperästä. Menetelmässä paineistettua ilmaa syötetään injektioputkien kautta pilaantuneen pohjavesikerroksen alapuolelle. Nosteen seurauksena injektoitu ilma nousee pilaantuneen alueen läpi kohti maanpintaa irrottaen samalla haitta-aineita maasta tai pohjavedestä. Ilmastus edesauttaa haitta-aineiden poistamista myös lisäämällä liuenneen hapen määrää maaperässä ja pohjavedessä, jolloin aerobinen hajotus tehostuu. (Reddy & Tekola 2004). Esimerkiksi monet öljyhiilivety-yhdisteet ovat aerobisissa oloissa biohajoavia, mutta useimmissa polttoaineella saastuneissa kohteissa hapen puute rajoittaa niiden hajotusta (Johnson ym. 1993). Ilmastus voidaan yhdistää huokosilmakäsittelyyn (soil vapor extraction, SVE), jossa haitta-aineet poistetaan alipaineen avulla maaperästä. Kontaminoitunut ilma voidaan tämän jälkeen käsitellä esimerkiksi aktiivihiilisuodattamalla tai polttamalla. (Adams ym. 2011). Ilmastuksen ja huokosilmakäsittelyn yhdistelmää on pidetty tehokkaana ja ekonomisena VOC-yhdisteillä pilaantuneiden alueiden kunnostusmuotona (Reddy ym. 1995).

Ilmastus soveltuu parhaiten yhdisteille, joilla on korkea Henryn vakio (Benner ym. 2002). Esimerkiksi MTBE:ä poistettaessa ilmastuksella saavutettava hyöty voi olla rajallinen, sillä MTBE:n suhteellisen alhainen Henryn lain vakio rajoittaa sen jakautumista vesifaasista ilmaan (Innocenti ym. 2014). Ilmastuksen tehokkuus riippuu merkittävästi myös maaperän ominaisuuksista sekä käytettävän menetelmän muuttujista (Reddy & Tekola 2004), joita ovat esimerkiksi injektioputkien määrä sekä ilmansyötön nopeus, paine ja jaksotus (Benner ym. 2002). Maaperä on usein hyvin heterogeenistä, mikä heikentää ilmastuksen tehokkuutta. Ilma nimittäin pyrkii nousemaan vähiten vastuksellisinta reittiä pitkin ylöspäin, joten heikosti läpäisevillä alueilla ilma jakautuu epätasaisesti. (Reddy & Adams 2001). Ilman syöttäminen hienojakoiseen maaperään vaatii suurta syöttöpainetta, mikä puolestaan voi aiheuttaa maaperän murtumista. Murtumisten seurauksena saattaa syntyä kanavia, joiden kautta ilma voi karata. Ilmastus soveltuukin parhaiten homogeeniselle maalle (Reddy & Tekola 2004) ja karkeille maalajeille, kuten hiekalle tai soralle. (van Dijke ym. 1995)

Ilmastuksessa riskinä on, että haitta-aineet leviävät puhtaille alueille liiallisen paineistuksen seurauksena tai kohdatessaan heikosti läpäiseviä pintakerroksia. Lisäksi haitallisten kaasujen leviäminen ei-toivotuille alueille, kuten asuintaloihin, on mahdollista. Riskien välttämiseksi on välttämätöntä ymmärtää perustiedot ilmastusprosessista, erityisesti injektoidun ilman kulkusuunta sekä tärkeät haitta-aineen kulkeutumis- ja muuntumisprosessit (Reddy ym. 1995).

1.2.3. Kemiallinen hapetus

Kemiallinen hapetus on *in situ* -menetelmä, joka perustuu hapettimen kykyyn muuttaa maaperässä ja pohjavedessä olevia haitta-aineita vähemmän haitalliseen muotoon. Tyypillisimpiä kemiallisia hapetuksessa käytettyjä hapettimia ovat otsoni, permanganaatti, persulfaatti sekä vetyperoksidi, joista jälkimmäinen on kaikkein laajalti käytetyin (Innocenti ym. 2014). Vetyperoksidi kykenee hapettamaan suoraan itse joitakin orgaanisia yhdisteitä, mutta pääasiassa kohtuullisilla vetyperoksidipitoisuuksilla orgaanisten yhdisteiden kanssa tapahtuvat hapetusreaktiot ovat liian hitaita ollakseen merkittäviä. Tämän vuoksi vetyperoksidia käytetään yleensä yhdessä katalyytin kanssa. (Neyens & Baeyens 2003, Watts & Teel 2005)

Parhaiten tunnettu vetyperoksidia hyödyntävä menetelmä perustuu Fenton-kemiaan. Fenton-prosessin käynnistää ferroraudan ja vetyperoksidin välinen reaktio, jota kutsutaan Fenton-reaktioksi. Reaktiossa ferrorauta (Fe^{2+}) käynnistää ja katalysoi vetyperoksidin (H_2O_2) hajoamisen tuottaen hydroksyyliradikaaleja ja hydroksidi-ioneja (R1). Samalla rauta hapettuu ferriraudaksi (Fe^{3+}).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-} \tag{R1}$$

Reaktiossa muodostuvat hydroksyyliradikaalit ovat voimakkaita epäspesifisiä hapettimia, jotka voivat reagoida monien orgaanisten yhdisteiden kanssa. (Neyens & Baeyens 2003). Fenton-reaktio käynnistää myös sarjan jatkoreaktioita, joissa rauta esiintyy kahden- ja kolmenarvoisen raudan muodossa (Lewis ym. 2009). Lisäksi jatkoreaktioissa muodostuu haitta-aineita hajottavia radikaaleja ja katalyyttejä, joista merkittävimpiä hydroksyyliradikaalien ohella ovat superoksidi ($O_2^{\bullet -}$), perhydroksyyliradikaali ($HO_2^{\bullet}$) sekä hydroperoksidianioni (HO_2^{-}) (Watts & Teel 2005). Kemiallisista olosuhteista riippuu, mitkä radikaalit hallitsevat reaktioita. Reaktioreitin valintaan vaikuttavat muun muassa hapettimen konsentraatio, katalyytti, liuenneet orgaaniset ja epäorgaaniset aineet sekä pH. Tämän vuoksi jotkut haitta-aineet saattavat hajota vain tietyissä kemiallisissa oloissa. Ihanteellisessa tilanteessa tapahtuu täydellinen mineralisaatio, jolloin haitta-aine hajoaa hiilidioksidiksi, vedeksi ja suoloiksi. (Petri ym. 2011)

Liukoisen ferroraudan lisäksi ferrirauta (Fe^{3+}), muut siirtymämetallit sekä maaperän mineraalit voivat toimia katalyytteinä (Watts & Teel 2005). Tällaisia

Fenton-reaktion muunnelmia kutsutaan termeillä ”muunneltu Fenton” tai ”Fentonin kaltainen”. Selkeyden vuoksi näistä käytetään nykyään usein myös yhteistä nimitystä ”katalysoitu vetyperoksidi” (catalyzed hydrogen peroxide, CHP). (Petri ym. 2011)

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \qquad (R2)$$

Hapetuksen tehokkuuteen vaikuttaa merkittävästi ympäröivä pH. Reaktio (R1) on yksinkertaistettu eikä ota huomioon pH:n vaikutusta. Optimaalinen pH Fenton-prosessille on hieman alle 3, jolloin rauta on pääosin liukoisessa muodossa. Tätä alhaisemmassa pH:ssa protonit alkavat kuluttaa hydroksyyliradikaaleja, kun taas korkeammassa pH:ssa Fe^{3+} saostuu rauta(III)hydroksidiksi ($Fe(OH)_3$). (Pignatello ym. 2006, Garrido-Ramírez ym. 2010). Saostuminen estää kolmenarvoisen raudan pelkistymisen takaisin ferroraudaksi sekä saattaa aiheuttaa tukoksia injektioputkiin (Lewis ym. 2009), joten hapetuksen tehostamiseksi maan pH:ta on usein tarpeen laskea. Maaperän pH on kuitenkin usein lähellä neutraalia tai lievästi hapanta (Petri ym. 2011), ja lisäksi maaperällä on yleensä hyvä puskurointikyky, minkä vuoksi maaperän pH:ta voi olla haastavaa muuttaa (Matta ym. 2007). Kelatoivia aineita lisäämällä voidaan kuitenkin ylläpitää riittävä liukoisten siirtymämetallien konsentraatiota myös lähellä neutraalia pH:ta (Vicente ym. 2011).

Suurin ongelma kemiallisessa hapetuksessa on se, että vetyperoksidi hajoaa maaperässä nopeasti, yleensä vain tunneissa tai päivissä. Vetyperoksidin reaktionopeudesta johtuen vetyperoksidin syöttäminen maanpinnan alapuolelle on haastavaa. (Petri ym. 2011). Vetyperoksidia on kuitenkin mahdollista stabiloida esimerkiksi kelaatinmuodostajien avulla. Kelaatinmuodostajalla tarkoitetaan yleensä orgaanista yhdistettä, joka voi toimia ligandina sitoen keskusatomin, kuten metalli-ionin, kahdesta tai useammasta kohdasta. Tapahtumaa kutsutaan kelaatioksi ja muodostuvaa kompleksia kelaatiksi. (Siegrist ym. 2011: 562). Muun muassa trinatriumsitraatti on osoittautunut tehokkaaksi kelaatinmuodostajaksi, sillä se voi tuottaa puskuriefektin, jolloin maaperää ei tarvitse happamoida. Etuna on myös sen biohajoavuus. (Vicente ym. 2011). Natriumsitraatin avulla voidaan hidastaa vetyperoksidin hajoamista (Watts ym. 2007) sekä tehostaa haitta-aineiden poistamista (Lewis ym. 2009, Vicente ym. 2011).

1.3. Tutkielman tavoitteet, hypoteesit ja käytetyt menetelmät

Tämän pro gradu -tutkielman päätavoitteena oli selvittää VOC-yhdisteiden poistamista pohjavedestä uudella vetyperoksidin kuplitukseen perustuvalla *in situ* -menetelmällä. Menetelmän oletettu teho perustuu vetyperoksidin hajoamisreaktioiden kykyyn mobilisoida ja haihduttaa pohjavedessä esiintyviä VOC-aineita. Kuplitusmenetelmässä vetyperoksidia syötetään korkeana pitoisuutena siiviläputkien kautta pohjavesikerrokseen, jolloin laimennuttuaankin vetyperoksidia on tarpeeksi suurena konsentraationa vaadittavaan reaktioon. Maassa neste leviää ja luonnostaan esiintyvä rauta katalysoi vetyperoksidin hajoamista. Oletuksena on, että hajoamisreaktiot alkavat vasta viiveellä, jolloin neste ehtii levitä laajemmalle alueelle. Vetyperoksidin hajoamisreaktioiden käynnistyessä vapautuvan kaasun puolestaan oletetaan johtavan ilmastuksen ja strippauksen (haihtuvien aineiden poistaminen nestefaasista kaasuvirran avulla) kaltaisiin vaikutuksiin, johtaen haihtuvien orgaanisten yhdisteiden mobilisaatioon ja haihtumiseen. Menetelmän etu ilmastukseen verrattuna olisi edellä mainitun perusteella se, että vaikutussäde olisi nestettä lisäämällä mahdollista saada suuremmaksi kuin ilmaa syöttämällä. Vaikka käytetyt reagenssit ovat samoja kuin kemiallisessa hapetuksessa, toimintaperiaatteen takia menetelmän ei uskota olevan yhtä kohderiippuvainen ja epävarma.

Tutkielma koostui laboratorio-, lysimetri- ja kenttäkokeista. Laboratoriomittakaavan kokeissa tutkittiin menetelmän soveltuvuutta ominaisuuksiltaan erilaisille VOC-yhdisteille. Lisäksi laboratoriossa tutkittiin eri muuttujien (vetyperoksidi- ja katalyyttikonsentraatio, kelatoivana aineena toimiva sitraattilisäys) vaikutusta metyyli-tert-butyylieetterin (MTBE) poistumaan. Erityisesti kelaattilisäyksen avulla haluttiin selvittää, voidaanko menetelmän toimintaperiaate erotella kemiallisesta hapetuksesta. MTBE:n poistamista vesifaasista sekä hiekkamaasta tutkittiin myös pilot-mittakaavan lysimetrikokeissa. MTBE valittiin tarkasteluun sen vesiliukoisuuden ja laajan esiintyvyyden vuoksi sekä siksi, että perinteisin menetelmin sitä on vaikea poistaa pohjavedestä. Lisäksi tutkielmaan kuului yhdessä Nordic Enviconin kanssa toteutettu kenttäkoe, jossa testattiin kuplitusmenetelmän toimivuutta täydessä mittakaavassa entisellä polttoaineiden jakeluasemalla. Hypoteesina tutkielmassa oli, että menetelmä toimii kaikille VOC-yhdisteille sekä laboratorio- että täydessä mittakaavassa. Lisäksi sen oletettiin olevan toimiva vaihtoehto ilmastukselle sekä kemialliselle hapetukselle ohittaen näihin menetelmiin liittyvät rajoitukset ja ongelmat.

Tutkielman tarkoituksena oli siis selvittää:
1) Soveltuuko menetelmä kaikkien, sekä vettä kevyempien että raskaampien, VOC-aineiden poistamiseen maa- ja pohjavedestä?
2) Onko laboratorio- ja pilot-kokeissa havaittuja tuloksia mahdollista siirtää täyteen mittakaavaan?
3) Voidaanko vetyperoksidin kuplitus -menetelmän toimintaperiaate erottaa kemiallisesta hapetuksesta?

Tutkielma sisälsi paljon työtä, mutta kokonaisuuden kannalta tärkeitä osioita ei haluttu jättää pois. Tämän vuoksi työtä jaettiin niin, että Harri Talvenmäki suoritti VOC-pilaantuneilla pohjavesillä tehdyt kokeet sekä osallistui pilot-vaiheen kokeisiin. Suoritin itsenäisesti keinotekoisella MTBE-vedellä tehdyt kokeet sekä vastasin kenttäkokeen toteutuksesta. Vastuullani oli koota sekä tulkita kaikista kokeista saadut tulokset.

2. Aineisto ja menetelmät

2.1. Reagenssit

Vetyperoksidi (35- ja 50-prosenttinen liuos) ostettiin Bang & Bonsomer Group oy:ltä (Suomi). Rauta(III)sulfaatti ($Fe_2(SO_4)_3 \cdot xH_2O$, puriss. p.a.) sekä sitraatti (natriumsitraattidihydraatti, ≥ 99 %, elintarvikelaatu) ostettiin Sigma-Aldrichilta (Saksa) ja rauta(II)sulfaattiheptahydraatti ($FeSO_4 \cdot 7H_2O$, puriss.) Honeywell Flukalta (Saksa). MTBE (puhtausaste ≥ 99 %) hankittiin Merck Schuchardt OHG:lta (Saksa).

2.2. Fysikaaliset ja kemialliset analyysit

Ilmasta mitattuja VOC-pitoisuuksia (ppm) seurattiin laboratorio- ja pilot-kokeissa kannettavalla Microtip Photovac Mp-100 -valoionisaatiodetektorilla (photoionization detector, PID) ja kenttäkokeessa UltraRAE 3000 -mittarilla. PID-mittari ei havaitse yksittäisiä yhdisteitä, vaan sillä voidaan mitata haihtuvien orgaanisten yhdisteiden summapitoisuutta. Laboratorio- ja pilot-kokeissa oli kuitenkin oletettavissa, että mitatut pitoisuudet olivat pääasiassa MTBE:ä, minkä vuoksi jäljempänä näiden kokeiden ilmamittausten yhteydessä puhutaan selkeyden vuoksi kokonais-VOC-pitoisuuksien sijaan MTBE-pitoisuuksista.

Vetyperoksidipitoisuudet mitattiin puolikvantitatiivisilla vetyperoksidiliuskoilla (Quantofix® Peroxide), joiden mittausalue on 0–100 mg/l (1–100 mg/l = 0,0001–0,01 % = 0,03–3 mM). Rautasulfaatti- ja sitraattilisäyksen vaikutuksia pH-arvoon selvitettiin erillisessä tarkastelussa. Tutkittavien maiden pH mitattiin pH-mittarilla (WTW inoLab pH 720) 0,01 M kalsiumkloridi ($CaCl_2$) -maasuspensiosta, jossa maan ja vesiliuoksen massasuhde oli 1:5. Laboratoriokokeessa käytetyn hiekkamaan kosteusprosentti mitattiin kuivaamalla noin 30 g maata yön yli 105 °C:ssa. Lysimetrikokeessa maan kosteus mitattiin lysimetrin omalla kosteusanturilla. Muut maan ominaisuudet oli analysoitu valmiiksi ennen tutkielman aloittamista. Analyysien tulokset on esitetty taulukossa 2.

Taulukko 2. Laboratorio- ja lysimetrikokeissa käytetyn hiekkamaan fysikaalis-kemiallisia ominaisuuksia.

Ominaisuus	Arvo	Yksikkö
Raekokojakauma		
Hiekka (0,06–2 mm)	60	%
Sora (<8 mm)	40	%
Orgaaninen aines	8,6 ± 2,8	mg/kg kuivapaino
Rauta, alkuainemuotoinen	14,2 ± 1,7	g/kg kuivapaino
pH	6,2	
Kosteus	2,0 – 5,6	%

Pilaantuneilla pohjavesillä suoritettujen laboratoriokokeiden vesinäytteet sekä pilot-kokeen vesi- ja maanäytteet analysoitiin Eurofins Environment Testing Finland oy:n Lahden laboratoriossa. VOC-pitoisuudet määritettiin menetelmällä RA4050 (mod. ISO 11423-1 ja mod. EN ISO 10301) käyttäen HS/GC/MS-tekniikkaa. Kenttäkokeen vesinäytteet analysoitiin Novalabissa (nykyinen SYNLAB Analytics & Services Finland oy) käyttäen sisäistä menetelmää (Novalab 040) sekä akkreditoitua menetelmää (ISO 20595:2018, mod.). Ilmanäytteenotossa käytetty adsorbenttikeräin analysoitiin kaasukromatografisesti Työterveyslaitoksella käyttäen akkreditoitua KEMIA-TY-006-menetelmää.

2.3. Laboratoriomittakaavan kokeet

2.3.1. Haihdutuskokeet keinotekoisella MTBE-vedellä

Haihdutuskokeessa, jossa malliaineena käytettiin MTBE:ä, selvitettiin eri muuttujien vaikutusta vetyperoksidin reaktionopeuteen sekä MTBE:n poistumiseen. Käytettävät muuttujat olivat vetyperoksidikonsentraatio (0,5, 1, 2 ja

5 M), rauta(III)sulfaattikonsentraatio (0, 0,6, 2 ja 20 mM) sekä kelaattina toimiva trinatriumsitraattilisäys (0 ja 50 mM). Lisäksi raudan hapetusasteen vaikutusta testattiin käyttämällä katalyyttinä 20 mM rauta(II)sulfaattia, jolloin lisätyn raudan määrä oli puolet ja sulfaatti-ionien määrä kolmasosa rauta(III)sulfaattiin verrattuna. Jokaisesta eri käsittely-yhdistelmästä tehtiin kolme rinnakkaista koetta, jolloin kokeita tehtiin yhteensä 120. Lisäksi tehtiin kolme rinnakkaista kontrollia, joihin lisättiin pelkkää MTBE:ä ja ionivaihdettua (Milli-Q®) vettä. Kokeita pelkällä rauta- tai sitraattilisällä ei suoritettu, sillä ilman vetyperoksidia näillä ei voida olettaa olevan vaikutusta MTBE-pitoisuuteen.

Kokeet suoritettiin 1000 ml:n lasipulloissa, joihin lisättiin litra puhdasta hiekkaa. Käytetyn hiekan ominaisuudet on esitetty taulukossa 2. Ionivaihdettua vettä ja vetyperoksidia lisättiin koeasetelmien mukaisissa suhteissa niin, että pulloihin lisätyn nesteen kokonaistilavuus oli aina 200 ml. Kokeissa, joissa käytettiin rautaa ja sitraattia, aineet sekoitettiin suoraan hiekkaan ennen nesteen lisäämistä. MTBE, jonka pitoisuus oli 750 mg/l, lisättiin nesteeseen juuri ennen pulloihin kaatamista. Nestelisäyksen jälkeen pullojen suut peitettiin parafilmillä (Parafilm® M) haihtumisen ehkäisemiseksi. Pulloista mitattiin lämpötila laittamalla lämpömittari parafilmistä läpi, minkä jälkeen samasta reiästä mitattiin välittömästi PID-mittarilla MTBE-pitoisuus. Mittaukset suoritettiin välittömästi nestelisäyksen jälkeen sekä 15 minuutin välein kahden tunnin ajan. Kahden tunnin jälkeen tarkkailuväliä pidennettiin puoleen tuntiin ja tarkkailua jatkettiin neljänteen tuntiin asti. Viimeiset mittaukset suoritettiin kokeesta seuraavana päivänä. Mittausten jälkeen pullojen suut peitettiin aina ehjällä parafilmillä.

2.3.2. Kokeet VOC-pilaantuneilla pohjavesillä

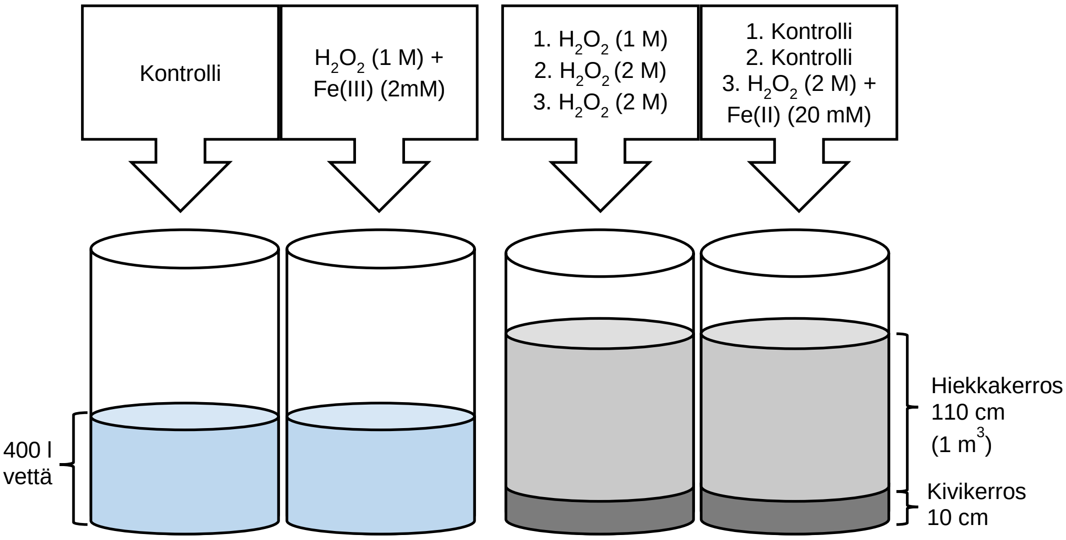
Laboratoriomittakaavassa testattiin myös vetyperoksidin kuplitusmenetelmän soveltuvuutta toiselle malliaineelle, trikloorietyleenille (TCE). Koe suoritettiin 1000 ml:n borosilikaattidekantereissa. Kontrolleja sekä itse kokeita tehtiin yhteensä kuusi, kummastakin kolme rinnakkaista. Dekantereihin laitettiin ensin

300 ml puhdasta, kuivaa kvartsihiekkaa, johon sekoitettiin 20 mM rauta(III)sulfaattia. Kontrolleihin ei lisätty rautaa. Tähän hiekkamäärään sekoitettiin myös 120 ml nestettä, josta 110 ml oli Motalasta (Ruotsi) 23.3.17 otettua, TCE:llä pilaantunutta pohjavettä. Kontrollidekanttereihin lisättiin TCE-veden lisäksi 10 ml Milli-Q® -vettä ja muihin 10 ml vetyperoksidia (1 M). Lopuksi dekanttereihin lisättiin vielä 700 ml puhdasta ja kuivaa kvartsihiekkaa ja reaktion annettiin jatkua yön yli. Kokeesta seuraavana päivänä otettiin vesinäytteet. Kuiva kvartsihiekka kaadettiin ensin pois, ja märästä kvartsihiekasta kaadettiin suppilon läpi ultrapuhtaiden dekantterilasien avulla 40 ml:n VOC-pulloihin vettä.

Toisessa vastaavassa kokeessa testattiin vetyperoksidin kykyä haihduttaa haitta-aineita bensiinisaastuneesta pohjavedestä, jota oli tuotu pilaantuneelta alueelta Nastolasta. Koe suoritettiin TCE-kokeen mukaisesti, mutta kymmenkertaisessa mittakaavassa ja vetyperoksidikonsentraatiolla 2 M. Kvartsihiekalla tehtyjen kokeiden lisäksi suoritettiin kokeet pelkässä vesifaasissa käsittelemällä 1,2 l saastunutta vettä vetyperoksidilla (0,5, 1 ja 2 M). Jokaisesta edellä mainitusta käsittelystä tehtiin kolme toistoa.

2.4. Pilot-mittakaavan lysimetrikokeet

Pilot-mittakaavan lysimetrikokeet suoritettiin maaperäntutkimuskeskus Soiliassa, Lahdessa. Tarkoituksena oli tutkia MTBE:n puhdistamista pelkästä vesifaasista sekä maan huokostilassa olevasta vedestä. Kokeet suoritettiin kahdessa teräksisessä sylinterin muotoisessa lysimetrissä (tilavuus 1,7 m^3, korkeus 194 cm). Ensimmäisessä kokeessa lysimetrit täytettiin kuvan 1 mukaisesti vedellä ja toisessa kokeessa kivillä ja hiekalla.



Kuva 1. Kaavakuva koeasetelmasta. Lysimetrien korkeus oli 194 cm ja tilavuus noin 1,7 m^3.

Lysimetrikoe aloitettiin vedellä 7.6.2017. Kontrollilysimetriin kaadettiin 400 l vesijohtovettä. Toiseen lysimetriin lisättiin vettä ja vetyperoksidia (35 %) yhteensä 400 l, jolloin vetyperoksidikonsentraatio oli 1 M. Tämän jälkeen kumpaankin lysimetriin lisättiin MTBE:ä 400 ml (750 mg/l), eli viisinkertaisesti Lopella sijaitsevan kenttäkohteen korkeimpaan mitattuun MTBE-pitoisuuteen verrattuna. Lopuksi vetyperoksidireaktioiden katalysoimiseksi vetyperoksidia sisältävään lysimetriin lisättiin 2 mM rauta(III)sulfaattia ($Fe_2(SO_4)_3$).

Ensimmäisenä päivänä lysimetreistä otettiin näytteet veden pinnasta ennen rautasulfaatin lisäämistä sekä kolme tuntia kokeen alkamisen jälkeen. Kummastakin lysimetristä otettiin kaksi rinnakkaista vesinäytettä VOC-pulloihin, jotka vietiin jääkaappiin (+4 °C) säilytykseen. Lisäksi lysimetreistä mitattiin lämpötila sekä PID-mittarilla ilman MTBE-pitoisuus. Näytteenotto toistettiin vuorokauden jälkeen. Käsitellystä vedestä määritettiin H_2O_2-pitoisuus. Liuskatuloksen perusteella vetyperoksidireaktio oli kulunut vuorokaudessa loppuun, joten koetta ei ollut tarpeen jatkaa. Kontrollikokeesta otettiin vielä kuuden päivän kuluttua näyte todentamaan, ettei tilanne näytteenottojen välillä ole muuttunut.

Lysimetrikoe hiekalla aloitettiin 14.6.2017. Lysimetrin pohjalle laitettiin noin 10 sentin kerros (noin 80 l) isokokoisia kiviä ja päälle 1 m^3 (1,42 t) hiekkaa (ominaisuudet taulukossa 2), jolloin koko maapatsaan korkeudeksi tuli 120 cm. Hiekasta kosteusanturilla määritetyn kosteuden (5,6 %) perusteella kyseisen hiekkamäärän arvioitiin sisältävän noin 1,34 t hiekkaa ja 80 l vettä. Kontrollilysimetriin lisättiin vielä 80 litraa vettä. Vetyperoksidia sisältävään lysimetriin lisättiin 80 l nestettä, jonka vetyperoksidikonsentraatio oli 2 M. Kumpaankin lysimetriin lisättiin 165 ml (1 500 mg/l) MTBE:ä. Sekä vetyperoksidia että MTBE:ä laitettiin kaksinkertaiset pitoisuudet, sillä hiekan sisältämän veden takia laskettiin laimenevan puoleen lysimetrissä. Vetyperoksidi ja MTBE sekoitettiin ensin veteen, minkä jälkeen neste kaadettiin lysimetreihin. Koska hiekka sisälsi luonnostaan rautaa, rautalisäystä ei tehty.

Lysimetreistä mitattiin lämpötila mahdollisimman pohjasta otetusta kairanäytteestä. Ilman MTBE-pitoisuudet mitattiin PID-mittarilla kairakuopasta. Lysimetrien pohjassa olevien hanojen kautta otettiin MTBE-vesinäytteet VOC-pulloihin ennen kokeen aloittamista sekä ensimmäisen, toisen ja viidennen vuorokauden jälkeen. Kaksi päivää kokeen aloituksesta H_2O_2 oli vetyperoksidiliuskatestin perusteella kulunut lähes loppuun, minkä perusteella pystyttiin päättelemään, ettei merkittäviä reaktioita enää tapahdu. Viisi päivää kokeen aloituksesta käsittely toistettiin kaksinkertaisella vetyperoksidipitoisuudella (2 M). Konsentraatiota laskettaessa otettiin huomioon ensimmäisessä vaiheessa lisätty vesi, ja uudeksi nestetilavuudeksi tuli 200 l. Lisäksi kumpaankin lysimetriin lisättiin 750 mg/l MTBE:ä tasaamaan nestelisäyksestä aiheutuvaa laimenemista. Vesinäytteet otettiin kontrollista välittömästi lisäyksen jälkeen sekä kummastakin lysimetristä ensimmäisen ja toisen vuorokauden jälkeen.

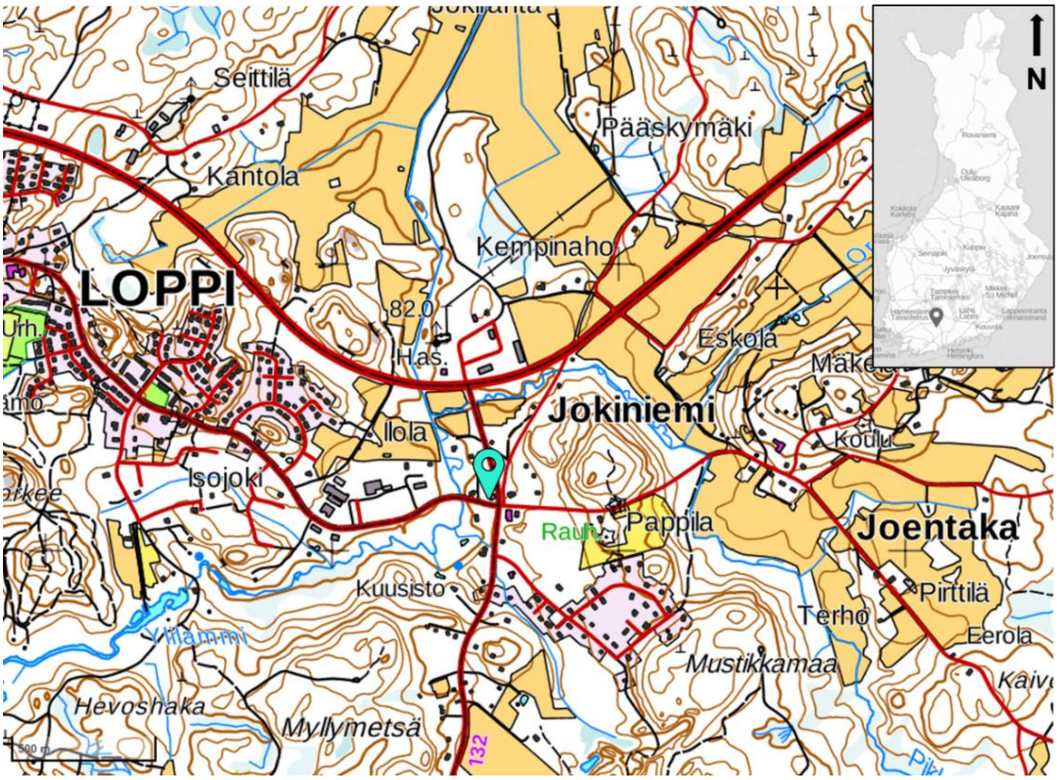
Saatujen tulosten perusteella suoritettiin vielä kolmas koe, jossa testattiin, onko edellisellä lisäyskerralla saavutettu puhdistusteho mahdollista toistaa. Käsittelylysimetriin lisättiin 40 l vetyperoksidia, jolloin lysimetrin sisältämän nesteen kokonaistilavuudeksi tuli arviolta 240 l ja vetyperoksidikonsentraatioksi 2 M. Kontrollikäsittelyn sijaan toisessa lysimetrissä testattiin ylimääräisen rautalisän vaikutusta puhdistumistehokkuuteen. Lysimetriin lisättiin 40 l vetyperoksidia sekä 20 mM rauta(II)sulfaattia ($FeSO_4$). Rauta lisättiin mahdollisimman syvälle kairattuihin koloihin. Kolot tehtiin lähelle toisiaan, jotta voitiin varmistaa raudan ja vetyperoksidin kohtaaminen reaktion aikana. Lisäksi kumpaankin lysimetriin lisättiin vetyperoksidin mukana jälleen 40 ml (750 mg/l) MTBE:ä. Vesinäytteet otettiin ennen kokeen aloitusta sekä tunnin, vuorokauden ja 28 vuorokauden jälkeen.

Lysimetrikoe lopetettiin, kun kolmannen kokeen aloituksesta oli kulunut 28 päivää ja koko hiekkakokeen aloituksesta 49 päivää. Kummastakin lysimetristä otettiin pohjalta vesinäytteet. Lisäksi kokeen purkamisen yhteydessä käsittelylysimetristä otettiin neljä maanäytettä eri syvyyksiltä varmentamaan, ettei pintamaa toimi MTBE:n lähteenä ja että MTBE on tasaisesti jakautunut alueelle.

2.5. Kenttäkoe

2.5.1. Tutkimuskohteen kuvaus

Tutkimuskohde, Salosen Autokorjaamo, sijaitsee Lopella Kanta-Hämeen maakunnassa osoitteessa Jokiniementie 260, 12640 Jokiniemi (kuva 2). FCG Suunnittelu ja tekniikka oy on toteuttanut kohteessa perustutkimuksen vuonna 2014 ja Nordic Envicon oy maaperätutkimuksen vuonna 2016. Kohteessa on toiminut polttoaineiden jakelupiste korjaamotoiminnan yhteydessä vuodesta 1950 noin vuoteen 2002 asti. Kohteessa myytiin bensiiniä, dieseliä ja polttoöljyä, joita varastoitiin maanalaisissa säiliöissä. Korjaamotoiminnan loputtua säiliöt tyhjennettiin mutta niitä ei poistettu. Nykyään kohteessa harjoitetaan pienimuotoista korjaamotoimintaa.

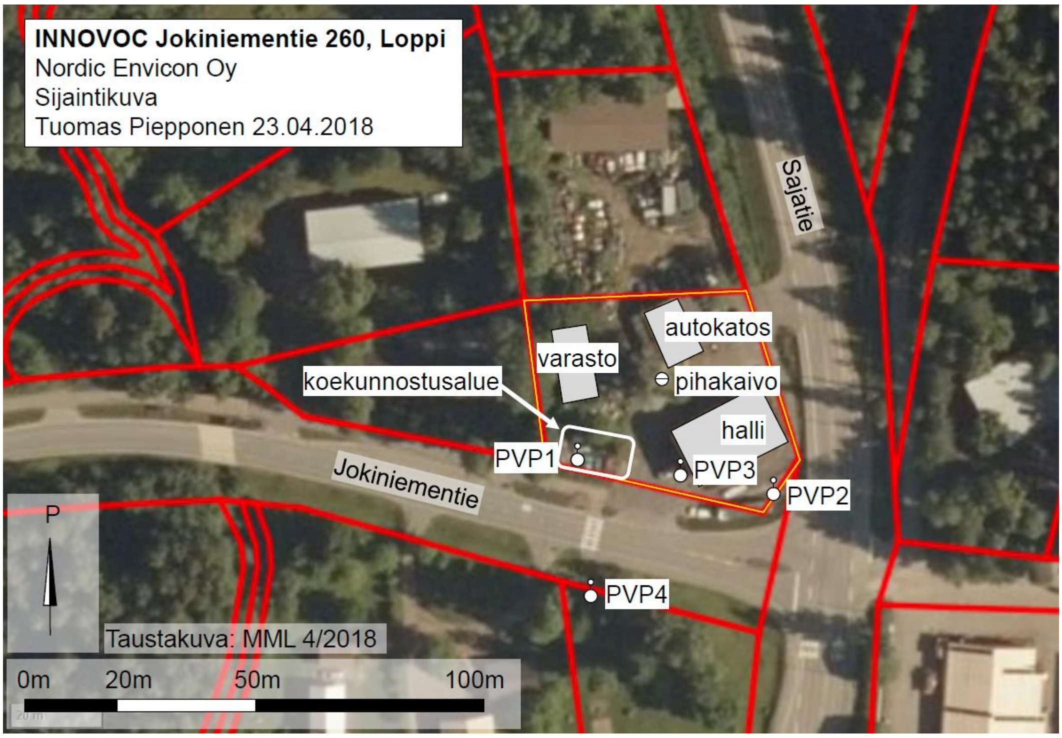


Kuva 2. Tutkimuskohteen (Jokiniementie 260, 12640 Jokiniemi) sijainti (Maanmittauslaitos, Karttapaikka). Mittajana (500 m) on esitetty kuvan vasemmassa alareunassa.

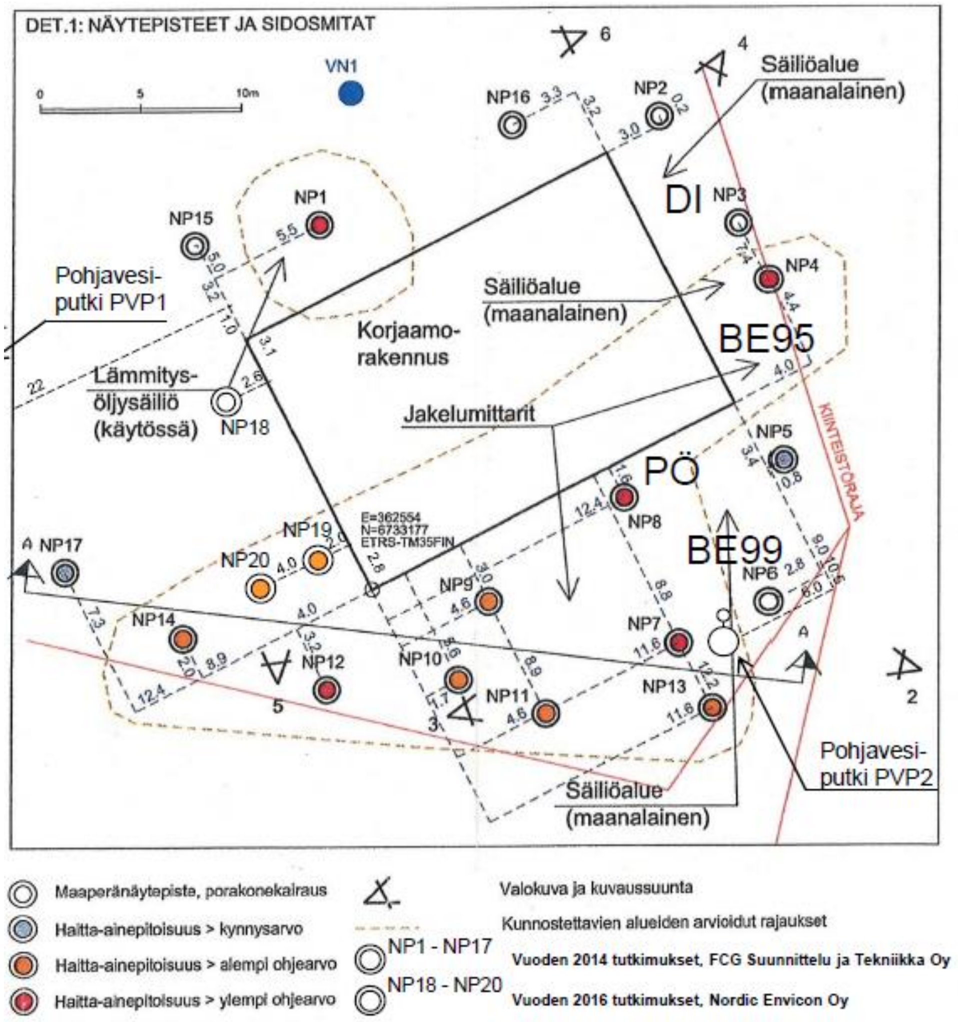
Kohteen piha-alueella on noin metrin paksuinen sorakerros. Piha on pääosin asvaltoitu. Sorakerroksen alapuolinen perusmaa (noin 1–6 m) on silttistä savea, jossa on ohuita hiekkaisia kerrostumia (liite 2). Kohde sijaitsee luokan II pohjavesialueella (Jokiniemi 80443304) ja pohjaveden pinta on noin 3–4 metrin syvyydessä. Kiinteistöllä sijaitsee kaivo, jonka vettä ei käytetä talousvetenä. Lähialueen kaivoista tai niiden käytöstä ei ole tarkkaa tietoa. Pohjaveden arvioitu virtaamissuunta on luoteiseen tai länteen kohti viereistä Nummistenjokea eli Isojokea.

Alueelta otetuista pohjavesinäytteistä on havaittu useita VOC-yhdisteitä. Vuonna 2014 tutkimuksen yhteydessä pihakaivosta otetusta vesinäytteestä (VN1) havaittiin kohonneita bentseenin, oksygenaattien (MTBE ja TAME eli tert-amyylimetyylieetteri) sekä 1,2-dikloorietaanin pitoisuuksia. Kaivo sijaitsee noin 20 m päässä pilaantuneeksi todetusta entisen jakelumittarikentän alueesta (kuvat 3 ja

4), minkä perusteella kulkeutumista on arvioitu tapahtuneen. Koska haitta-aineiden kulkeutuminen pohjaveden mukana kohteen ulkopuolelle on mahdollista, FCG arvioi pohjaveden kunnostukselle olevan tarve. Nordic Enviconin vuonna 2016 suorittamissa lisätutkimuksissa pohjavesiputkessa PVP1 havaittiin oksygenaatteja, muiden haitta-aineiden ollessa alle määritysrajan. Entisen mittarikentän lähellä (PVP2 ja PVP3) puolestaan havaittiin öljyjakeita ja BTEX-yhdisteitä, mutta ei oksygenaatteja. Myös vedellä täyttyneen entisen bensiinisäiliön vesi tutkittiin, ja sen havaittiin sisältävän muun muassa suuria määriä MTBE:ä (150 mg/l). Lisäksi maaperässä on havaittu haitta-aineita ylemmät ohjearvot ylittävinä pitoisuuksina. Maaperästä ja pohjavedestä aiemmin havaitut haitta-aineiden maksimipitoisuudet on esitetty liitteessä 3.



Kuva 3. Tutkimuskohteen koekunnostusalueen, pohjavesiputkien (PVP1–4) sekä pihakaivon (VN1) sijainnit (Nordic Envicon oy).

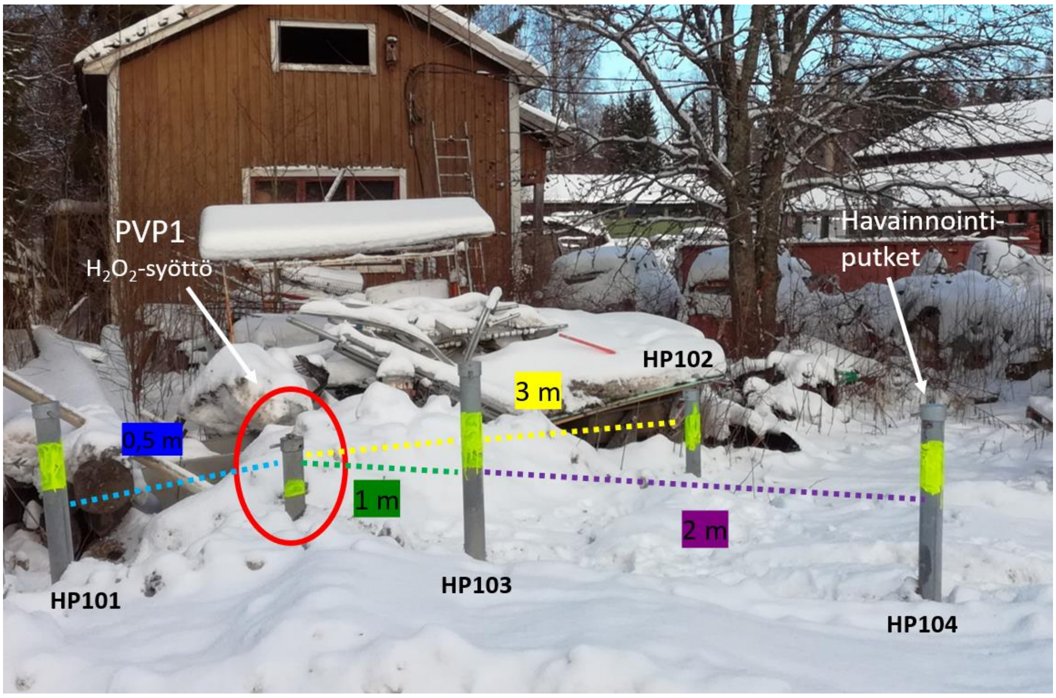


Kuva 4. Kohteen aiempi tutkimuspistekartta, josta näkyy katkoviivoin merkittynä haitta-ainepitoisuuksien perusteella pilaantuneeksi luokiteltu alue (FCG & Nordic Envicon oy).

2.5.2. Koejärjestelyt

Kenttäkoe aloitettiin asennustöillä 8.2.2018. Koealueeksi valittiin pohjavesiputken PVP1 läheinen alue, sillä kyseisestä putkesta vuonna 2016 otetuissa vesinäytteissä oli havaittu MTBE:ä kohonneina pitoisuuksina (0,034 mg/l). Lisäksi valitun alueen oletettiin olevan alkuperäisten pitoisuustietojen perusteella riskitön vaihtoehto kunnostettavaksi koealueeksi, sillä kyseisellä alueella ei ollut havaittu keskiraskaita tai raskaita öljyhiilivetyjakeita. Näitä öljyhiilivetyjakeita ei pystytä haihduttamaan maasta VOC-yhdisteiden tavoin, joten ne voivat mahdollisesti aiheuttaa kulkeutumisriskin. Kohteen muista alueista poiketen koealueella ei myöskään ollut asvalttipinnoitusta, mikä helpotti kairaustöitä.

Koetta varten maahan kairattiin neljä pystyputkea noin 5,5 metrin syvyydelle. Putket asennettiin pohjavesiputkina, joissa siiviläkerros alkoi 0,5 metrin syvyydeltä. Putkien ympärille asennettiin noin metrin syvyyteen ulottuvat vandaaliputket. Pohjavesiputket asennettiin kuvan 5 osoittamille etäisyyksille toisistaan.



Kuva 5. Syöttöputken sekä havainnointiputkien etäisyydet toisistaan.

Syöttö aloitettiin noin viikko asennustöiden jälkeen. Ennen kokeen alkua syöttö- sekä havainnointiputkista otettiin vesinäytteet 40 ml:n EPA-pulloihin VOC-analyysia varten. Putkista määritettiin myös VOC-pitoisuudet PID-mittarilla. Havainnointiputkesta HP101, josta mitattiin korkein PID-lukema, kerättiin lisäksi pumpulla (SKC 222-3) aktiivinen VOC-näyte adsorbentilla täytettyyn keräimeen.

Koetta varten tyhjään IBC-säiliöön (1 m^3) pumpattiin 50-prosenttista vetyperoksidiliuosta sekä kiinteistön kaivosta vettä yhteensä noin 550 litraa, jolloin vetyperoksidilaimennoksen pitoisuudeksi tuli noin 17 % (5 M). Vetyperoksidin laimenemista maaperässä ei voitu etukäteen päätellä, mutta oletuksena oli, että kyseisellä pitoisuudella päästäisiin tutkittavalla koealueella lähelle pitoisuutta 2 M, joka oli laboratoriomittakaavan kokeissa havaittu tehokkaaksi pitoisuudeksi. Ensimmäisellä syöttökerralla vetyperoksidia saatiin syötettyä pohjavesiputkeen (PVP1) vain noin 100 l, joka oli kymmenesosan alun perin suunnitellusta syöttömäärästä. Syöttö aloitettiin uudelleen viisi päivää myöhemmin käyttäen pienempää pumppua, jolloin syöttö saatiin suoritettua hitaasti ja hallitusti. Kuitenkin vain noin 200 l peroksidia saatiin syötettyä pohjaveteen, sillä oletettavasti pakkasen kiristyttyä H_2O_2-laimennos alkoi jäätyä, eikä pumppu kyennyt pumppaamaan jäätyvää liuosta. Kolmen viikon kuluttua säiliö täytettiin ja H_2O_2-käsittely toistettiin. Tällä kertaa pohjaveteen syötettiin noin 900 litraa 17-prosenttista H_2O_2-liuosta. Kunnostuksen aikana pohjavesiputkista tarkkailtiin lämpötilaa, happi- ja vetyperoksidipitoisuuksia syöttöpäivänä sekä vuorokauden, viikon ja kolmen viikon jälkeen.

Menetelmän toimivuutta testattiin myös sulan maan aikaan. Ensimmäinen käsittely tehtiin toukokuussa, kun edellisestä syöttökerrasta oli kulunut kaksi kuukautta. Tällä kertaa pohjaveteen lisättiin noin 250 litraa 25-prosenttista vetyperoksidilaimennosta, ja lisäys tehtiin kaikkiin koealueen pohjavesiputkiin. Kaksi viikkoa myöhemmin syöttö päätettiin aloittaa koealueen ulkopuolella korjaamorakennuksen vierellä sijaitsevaan putkeen PVP3 (kuva 3, liite 4), sillä varsinainen koealue oli osoittautunut pohjavesinäytteiden perusteella puhtaaksi. Lisäksi haluttiin selvittää, kulkeutuuko vetyperoksidi oletetun pohjaveden virtaussuunnan mukaisesti kohti koealuetta. Syöttäminen PVP3-putkeen oli kuitenkin hidasta, ja ensimmäisellä kerralla vain noin 60 l liuosta saatiin lisättyä pohjaveteen. Tämän vuoksi syöttämistä jatkettiin loppuvaiheessa valuttamalla vetyperoksidia kolme kertaa viikon ajan hitaasti PVP3-putkeen. Lisäksi putkeen PVP2, josta myös oli havaittu vesinäytteiden perusteella korkeita VOC-pitoisuuksia, syötettiin toiseksi viimeisellä valutuskerralla päivän aikana 100 litraa H_2O_2-liuosta. Käsittelyt lopetettiin 13.7.18, jolloin koko koekunnostuksen kesto ensimmäisestä syöttöpäivästä alkaen oli 150 päivää. Viimeiset vesinäytteet otettiin kuukausi tämän jälkeen. Taulukossa 3 on esitetty koekunnostuksen aikataulu.

Taulukko 3. Koekunnostuksen aikataulu. Päivinä, jolloin ei ole suoritettu injektointia tai vesinäytteenottoa, on seurattu pohjaveden happi- ja vetyperoksidipitoisuuksia, lämpötilaa sekä pinnankorkeutta.

Päivämäärä	Syöttö	Vesinäytteet	Aika syötöstä (n.)	Syöttömäärä (l)
14.2.18	kyllä, PVP1	kyllä	0	100
19.2.18	kyllä, PVP1	ei	0	200
20.2.18	ei	ei	1 vrk	
26.2.18	ei	ei	1 vk	
5.3.18	ei	kyllä	2 vk	
12.3.18	kyllä, PVP1	kyllä	3 vk	900
13.3.18	ei	ei	1 vrk	
20.3.18	ei	ei	1 vk	
3.4.18	ei	kyllä	3 vk	
14.5.18	kyllä, HP101–4, PVP1	kyllä	2 kk	250
15.5.18	ei	ei	1 vrk	
18.5.18	ei	ei	4 vrk	
28.5.18	kyllä, PVP3	kyllä	2 vk	60
29.5.18	kyllä, PVP3	ei	1 vrk	20
4.6.18	kyllä, PVP3	ei	1 vk	
6.6.18	kyllä, PVP3	ei	0	100 (2 vrk:n aikana)
12.6.18	kyllä, PVP3	ei	0	150 (1 vk:n aikana)
26.6.18	ei	kyllä	2 vk	
29.6.18	kyllä, PVP3	ei	2,5 vk	
6.7.18	kyllä, PVP2–3	ei	0	100 (1 vk:n aikana), PVP2: 100
13.7.18	ei	ei	0	200 (1 vk:n aikana)
14.8.18	ei	kyllä	1 kk	

2.6. Tilastolliset analyysit

Keinotekoisella MTBE-vedellä suoritetun laboratoriokokeen tulosten normaalisuus sekä varianssien samankaltaisuus testattiin IBM SPSS Statistics 24 -ohjelmistolla (IMB Corp., 2016). Aineisto ei ollut log-muunnoksellakaan normaalisti jakautunut eivätkä varianssit yhtä suuret, minkä vuoksi aineistolle tehtiin ei-parametrinen Kruskal-Wallisin *H*-testi. Analyysissä verrattiin eri käsittelyjä (vetyperoksidi- ja rautakonsentraatio sekä sitraattilisäys) keskenään eri mittausajankohtina. Testin suorittamiseksi kaikki saman mittausajankohdan mittaustulokset yhdistettiin, asetettiin suuruusjärjestykseen ja korvattiin järjestysluvuillaan SPSS:ssä. Järjestysluvuille suoritettiin SPSS:ssä normaali useampisuuntainen varianssianalyysi, mutta tilastolliseen testaukseen käytettiin SPSS:n antaman testisuureen *F* sijasta testisuuretta *H*. Tämä testisuure laskettiin kaavan 1 mukaisesti kullekin käsittelylle eri mittausajankohtina käyttäen apuna varianssianalyysin antamia neliösummia (SS):

$$H = \frac{SS}{MS_{TOTAL}} \tag{1}$$

Jossa H = testisuure
SS = järjestyslukujen neliösumma
MS_{TOTAL} = kokonaiskeskineliö

Nimittäjässä esiintyvä termi MS_{TOTAL} laskettiin kaavan (2) mukaisesti:

$$MS_{TOTAL} = \frac{N(N+1)}{12} \tag{2}$$

Jossa N = havaintojen määrä
12 = vakio (Ranta ym. 2012: 332).

Testisuureen *H* arvoja verrattiin χ^2-taulukon (Ranta ym. 2012: 544) kriittisiin arvoihin riskitasoilla $\alpha = 0{,}05$, 0,01 ja 0,001 vastaavien neliösummien vapausasteita käyttäen. Tulokset, jotka olivat suurempia kuin taulukon arvot, olivat tilastollisesti merkittäviä. Lopuksi pylväskuvaajien avulla tarkasteltiin, mitkä käsittelyistä erosivat tilastollisesti merkittävästi toisistaan.

Lisäksi rautasulfaattikäsittelyille suoritettiin parittainen vertailu mittatikun avulla. Mittatikun pituus laskettiin kaavan (3) mukaisesti:

$$W_I = Q_{0,05(I,\infty)}\sqrt{\frac{n_0(n_0 I)(n_0 I+1)}{12}} \tag{3}$$

Jossa W_I = mittatikun pituus

$Q_{0,05(I,\infty)}$ = lukuarvo taulukosta 5 %:n riskillä testattaessa (Ranta ym. 2012: 550)

n_0 = kustakin käsittelystä saatujen havaintojen lukumäärä

I = vertailtavien käsittelyjen määrä

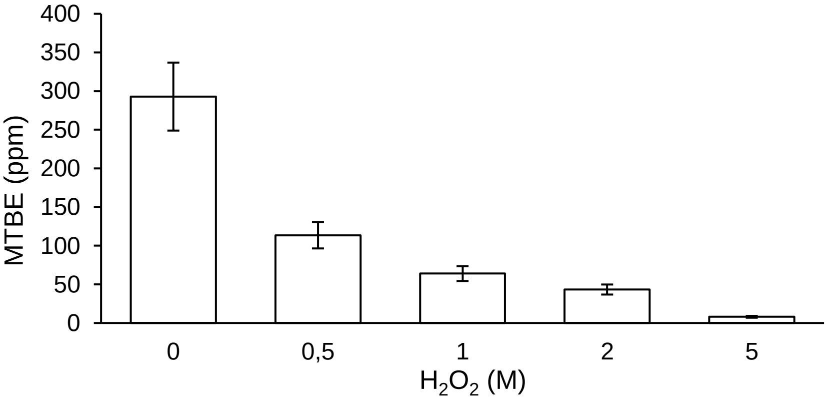
Tämän jälkeen jokaiselle eri rautasulfaattikäsittelylle laskettiin järjestyslukusummat laskemalla käsittelyn järjestysluvut yhteen. Käsittelyiden järjestyslukujen erotukset laskettiin taulukkoon ja erotuksia verrattiin mittatikun pituuteen. Käsittelyiden välinen ero oli merkitsevä, mikäli erotustulos oli suurempi kuin mittatikun pituus.

Lysimetrikokeiden tuloksia vertailtiin luottamusvälien avulla, sillä näytteitä ei ollut mahdollista ottaa tarpeeksi tilastollista analyysiä varten. Vertailussa käytettiin 85 % luottamusvälejä. Keskiarvot, joiden luottamusvälit eivät risteä, eroavat tilastollisesti merkittävästi toisistaan (Cumming 2009). Yleensä tapana on käyttää 95 % luottamusvälejä, mutta tällöin ei-päällekkäisten luottamusvälien merkitsevyystaso on todellisuudessa alle 0,05, eli tapa on turhan jyrkkä keskiarvojen välisten erojen testaamiseen. Paras riskitason $\alpha = 0,05$ approksimaatio saavutetaankin käyttämällä 85 % luottamusvälejä. (Payton ym. 2000)

3. Tulokset

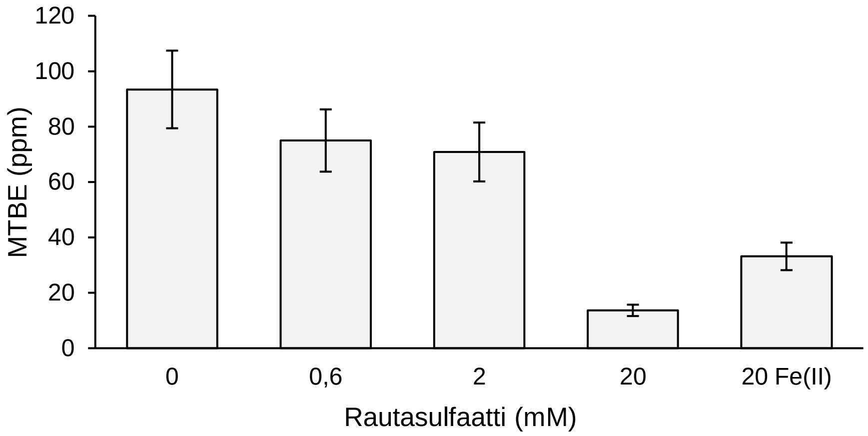
3.1. Haihdutuskokeet keinotekoisella MTBE-vedellä

Laboratoriossa suoritettujen haihdutuskokeiden tulosten perusteella paras MTBE:n poistuma saavutettiin käsittelyllä, jossa oli 5 M vetyperoksidia ja 20 mM rauta(III)sulfaattia. Saavutettu keskiarvopitoisuus (3,1 ppm) oli 99 % lähtöpitoisuutta pienempi. Kuvassa 6 on esitettynä vetyperoksidikonsentraation vaikutus MTBE-pitoisuuteen viimeisellä mittauskerralla (1 vrk kokeen alkamisesta). Kaikissa käsittelyissä, joissa vetyperoksidikonsentraatio oli 5 M, saavutettiin yli 90 %:n poistuma. Vastaavasti missään alle 1 M vetyperoksidikäsittelyissä yli 90 %:n poistumaan ei ylletty. Heikoin puhdistumistulos kontrollia lukuun ottamatta saavutettiin käsittelyllä 0,5 M H_2O_2, jolloin saavutettiin vain 17 % poistuma. Kontrollissa puolestaan loppupitoisuus oli lähes 37 % lähtöpitoisuutta suurempi. Erot vetyperoksidikonsentraatioiden välillä osoittautuivat Kruskal-Wallisin testillä tilastollisesti merkitseväksi kolmella viimeisellä mittauskerralla (120 min, 180 min ja 1 vrk kokeen alusta).



Kuva 6. Vetyperoksidikonsentraation vaikutus MTBE-pitoisuuteen viimeisellä mittauskerralla (*keskiarvo ± 85 % luottamusväli, n=30, kontrollissa n=3).*

Kokeissa, joissa ei lisätty rautasulfaattia, MTBE-pitoisuudet jäivät viimeisellä mittauskerralla selvästi korkeammiksi kuin kokeissa, joissa rautasulfaattilisäys tehtiin (kuva 7). Rauta(III)sulfaatin lisääminen jo pieninä konsentraatioina (0,6 ja 2 mM) tehosti MTBE:n poistumista, tosin näissä tapauksissa yli 95 %:n puhdistuminen saavutettiin vain silloin, kun vetyperoksidikonsentraatio oli suuri, 5 M. Selvästi paras poistuma saavutettiin suurimmalla rautasulfaattikonsentraatiolla (20 mM). Kokeissa, joissa lisättiin 20 mM rauta(II)sulfaattia, MTBE:n poistuma oli keskimäärin 86 %, mutta pitoisuudet jäivät yli kaksi kertaa korkeammiksi kuin kokeissa, joissa lisättiin 20 mM rauta(III)sulfaattia (kuva 7). Erot rautasulfaattikonsentraatioiden välillä osoittautuivat Kruskal-Wallisin testillä tilastollisesti merkitseväksi kaikilla muilla paitsi ensimmäisellä (0 min) mittauskerralla. Mittatikun avulla tehdyn parittaisen vertailun perusteella pitoisuudet rauta(II)- ja rauta(III)sulfaattikäsittelyiden välillä eivät kuitenkaan eronneet tilastollisesti merkittävästi (taulukko 4).

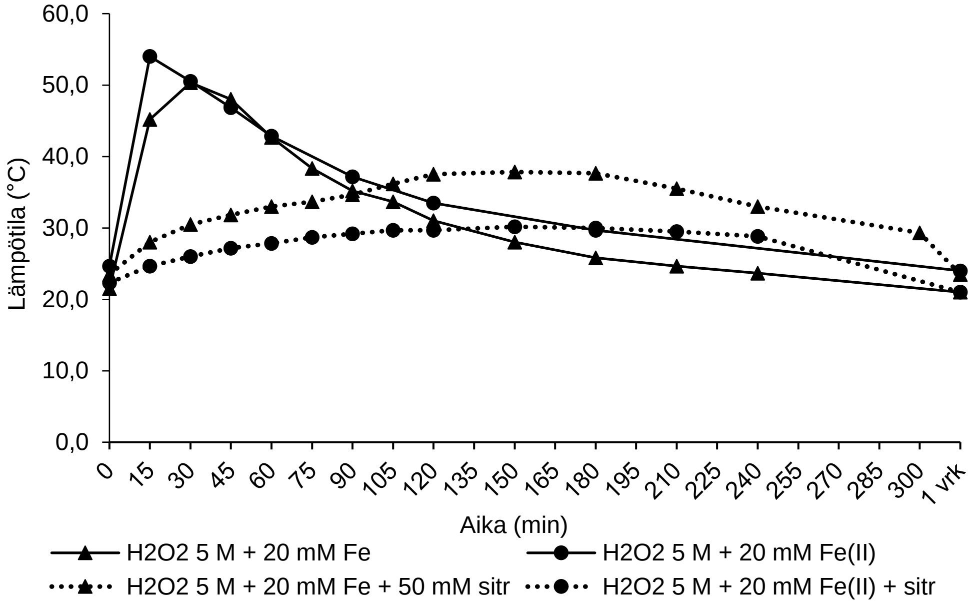


Kuva 7. Rautasulfaattilisäyksen vaikutus MTBE-pitoisuuteen viimeisellä mittauskerralla (*keskiarvo ± 85 % luottamusväli, n = 24).*

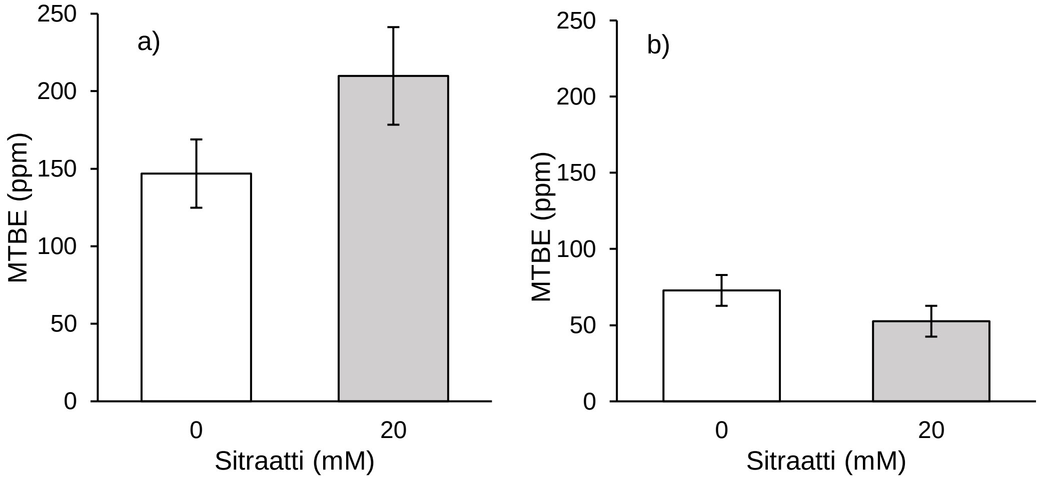
Taulukko 4. Rautasulfaattikäsittelyiden järjestyslukusummien erotukset. Tähdellä merkityt erotukset ovat suurempia kuin mittatikun pituus (657,8), ja siten käsittelyt eroavat toisistaan tilastollisesti merkittävästi.

Pitoisuus (M)	0,6	2	20	20 (Fe(II))
0	79,00	227,5	1182*	810,0*
0,6		148,5	1103*	731,0*
2			954,0*	582,5
20				371,5

Sitraatin lisääminen hidasti vetyperoksidin hajoamisreaktioita. Tämä näkyi kokeiden alkupuolella alhaisempina lämpötiloina (kuva 8) sekä korkeampina MTBE-pitoisuuksina (kuva 9a). Sitraattilisäyksen negatiivinen vaikutus MTBE:n poistumaan oli tilastollisesti merkittävä aikavälillä 0–180 min. Viimeisellä mittauskerralla (1 vrk kokeen alkamisesta) sitraattilisäyksellä ei kuitenkaan havaittu selvää vaikutusta. Kokeissa, joissa tehtiin sitraattilisäys, MTBE:n poistuma viimeisellä mittauskerralla oli keskimäärin 9 prosenttiyksikköä suurempi kuin kokeissa, joissa sitraattia ei lisätty (kuva 9b). Näin ollen sitraattilisäys vaikutti lievästi tehostavan MTBE:n poistumaa kokeen lopussa. Ero käsittelyiden välillä ei kuitenkaan ollut Kruskal-Wallisin testillä tilastollisesti merkittävä.

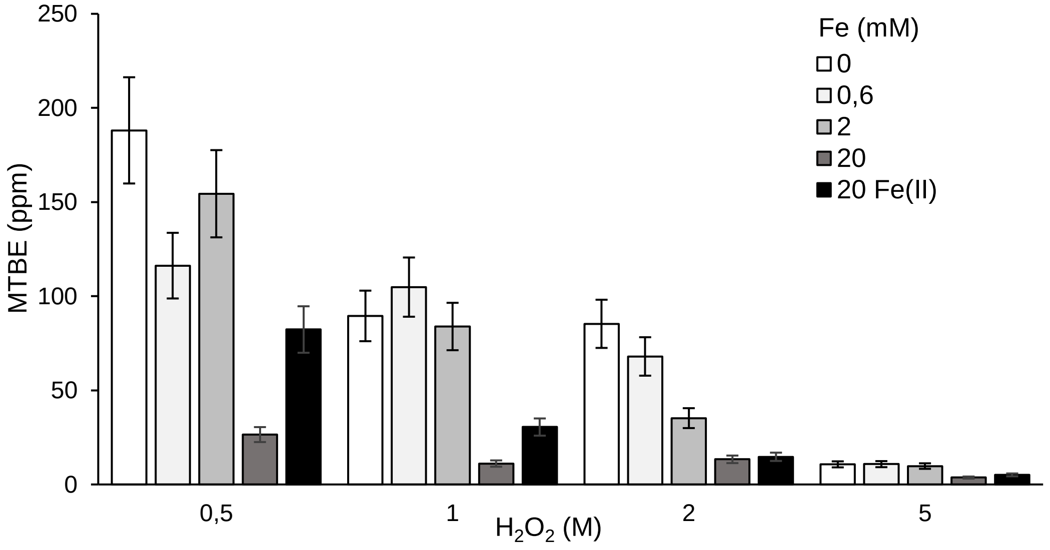


Kuva 8. Sitraattilisäyksen (sitr) vaikutus lämpötilaan (°C) (*keskiarvo, n = 3)* 0–300 min ja 1 vrk:n aikana kokeissa, joissa oli käytetty 5 M vetyperoksidia sekä 20 mM rauta(III)- tai rauta(II)sulfaattia.



Kuva 9a-b. Sitraattilisäyksen vaikutus MTBE-pitoisuuteen a) 60 min jälkeen ja b) 1 vrk jälkeen kokeen aloituksesta (*keskiarvo ± 85 % luottamusväli, n = 60).*

Rautasulfaattilisäyksen vaikutus oli suhteellisen samankaltainen jokaisella vetyperoksidikonsentraatiolla (kuva 10), mikä viittaa siihen, ettei käsittelyiden välillä ole yhdysvaikutusta. Yhdysvaikutuksia vetyperoksidin ja raudan välillä ei todettu myöskään Kruskal-Wallisin testillä (taulukko 5). Yhdysvaikutuksella tarkoitetaan eri faktoreiden tasojen vaikutusten välistä riippuvuutta (Ranta ym. 2012: 276). Tässä tapauksessa faktoreiden tasoja ovat rauta- ja H_2O_2-konsentraatiot sekä sitraattilisäys. Yhdysvaikutus puolestaan tarkoittaisi esimeriksi sitä, että suurimmalla vetyperoksidikonsentraatiolla raudan lisäämisellä ei olisi lainkaan vaikutusta MTBE:n pitoisuuksiin, tai että esimerkiksi rautalisäyksen vaikutus kulkisi toiseen suuntaan kuin pienemmillä H_2O_2-konsentraatioilla. Myöskään vetyperoksidin ja sitraatin välillä ei ollut tilastollisesti merkittävää yhdysvaikutusta. Sen sijaan rautasulfaatin ja sitraatin sekä vetyperoksidin, rautasulfaatin ja sitraatin välillä oli tilastollisesti merkittävä yhdysvaikutus ajan hetkellä 0 (taulukko 5). Näin ollen esimeriksi sitraatin vaikutus on voinut olla erilainen eri rauta- ja vetyperoksidipitoisuuksilla. Yhdysvaikutusta on havainnoitu kuvissa 11a-b. Muilla mittaushetkillä yhdysvaikutusta ei ollut.

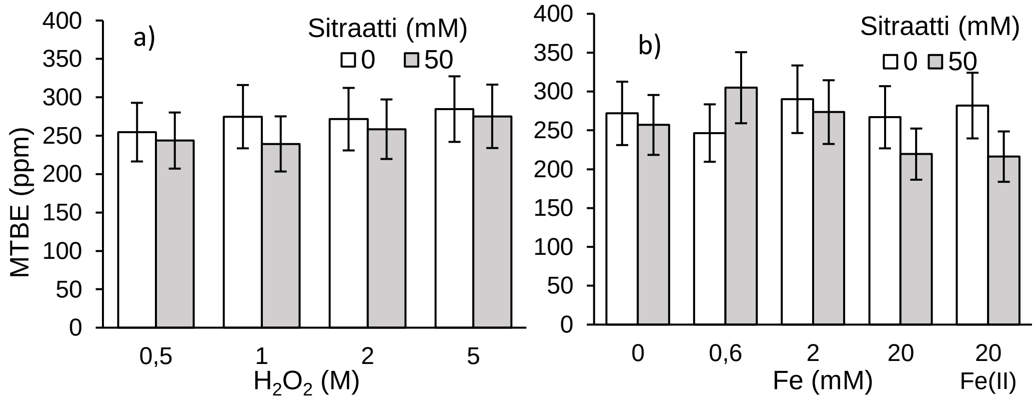


Kuva 10. Vetyperoksidin ja rautasulfaatin vaikutus MTBE-pitoisuuteen viimeisellä mittauskerralla (*keskiarvo ± 85 % luottamusväli, n = 6)*. Käsittelyillä ei ollut tilastollisesti merkittävää yhdysvaikutusta.

Taulukko 5. Vetyperoksidi-, rautasulfaatti- sekä sitraattikäsittelyiden pää- ja yhdysvaikutukset MTBE-pitoisuuksiin. H_2O_2 = vetyperoksidi, Fe = rautasulfaatti, sitr = sitraatti.

		0	15	30	45	60	90	120	180	1 vrk
	df	*H*	*H*	*H*	*H*	*H*	*H*	*H*	*H*	*H*
H_2O_2	4	5,4	3,4	2,9	1,7	1,7	9,2	24,2***	43,6***	59,7***
Fe	4	9,3	46,7***	48,6***	41,3***	45,7***	53,2***	43,7***	41,1***	34,5***
Sitr	1	4,8*	12,3***	17,3***	19,7***	16,2***	14,9***	7,6**	5,9*	0,1
H_2O_2 x Fe	12	20,8	9,8	7,2	9,2	11,1	7,0	6,9	6,6	7,3
H_2O_2 x sitr	3	0,8	5,9	3,6	4,0	7,2	7,1	4,6	6,0	1,0
Fe x sitr	4	14,2**	2,7	3,6	5,8	5,9	3,0	6,2	3,3	4,1
H_2O_2 x Fe x sitr	12	22,6*	13,4	9,7	14,3	12,2	7,9	7,3	4,3	2,5

*α<0,05; **α<0,01; ***α<0,001



Kuva 11a–b. Sitraatin ja a) vetyperoksidin (ei yhdysvaikutusta) sekä b) rautasulfaatin (yhdysvaikutus) vaikutus MTBE-pitoisuuksiin ajan hetkellä 0 min (*keskiarvo ± 85 % luottamusväli, n = 15 kuvassa a ja n=24 kuvassa b).*

3.2. Kokeet VOC-pilaantuneilla pohjavesillä

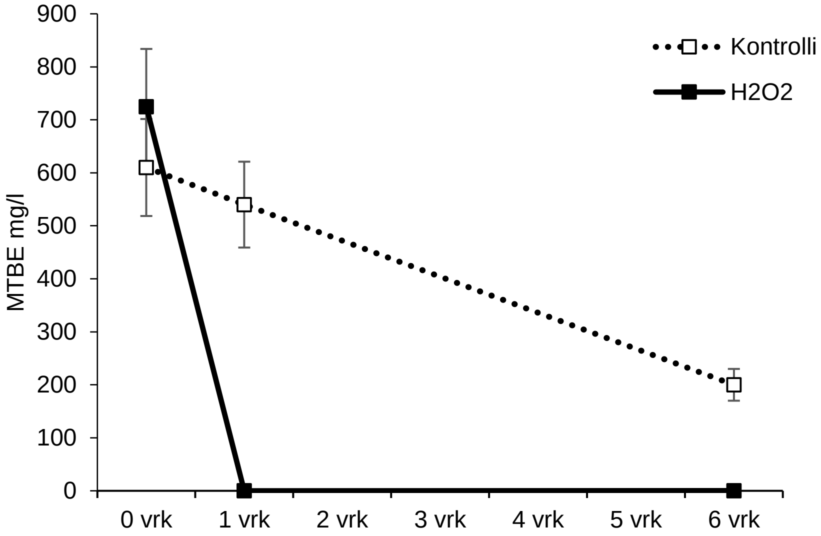
Laboratoriokokeessa, jossa tutkittiin Motalasta (Ruotsi) tuodun, TCE:llä pilaantuneen pohjaveden puhdistumista, ei alitettu määritysrajaa. Pitoisuuksissa saavutettiin kuitenkin yli 99 %:n poistuma. Nastolasta tuodulla, bensiinisaastuneella vedellä, pitoisuudet laskivat alle määritysrajan jo pienimmällä vetyperoksidikonsentraatiolla (0,4 M), kun kokeet suoritettiin vesifaasissa. Myös hiekassa suoritetuissa kokeissa päästiin kaikkien yhdisteiden osalta alle määritysrajan, kun vetyperoksidikonsentraatio oli 2 M. Vetyperoksidin vaikutus oli samankaltainen kaikissa yhdisteryhmissä (halogenoidut, aromaattiset, eetterit ja alifaattiset yhdisteet). Taulukossa 6 on esitetty TCE- ja bensiinisaastuneella vedellä suoritettujen kokeiden tulokset. Alkutilannetta korkeammat kontrollipitoisuudet johtuvat todennäköisesti veden kerrostumisesta koetilanteessa, kun taas alkutilanteessa vesi oli hyvin sekoittunutta.

Taulukko 6. Motalasta (Ruotsi) ja Nastolasta tuotujen vesien laboratoriokokeiden tulokset.

Yhdisteryhmä	Yhdiste	Pitoisuus (µg/l)						
Halogenoidut							Vesi kiintoaineessa	
Motala		Alku					Kontrolli	1 mol/l
	TCE	3700					310	2
				Irrallinen vesifaasi			Vesi kiintoaineessa	
Nastola		Alku	Kontrolli	0,4 mol/l	1 mol/l	2 mol/l	Kontrolli	2 mol/l
	1,2-dibromietaani	1	1	<0,1	<0,1	<0,1	1	<0,1
Aromaattiset								
	Bentseeni	2	4	<0,1	<0,1	<0,1	1	<0,1
	Tolueeni	130	250	<1	<1	<1	69	<1
	Etyylibentseeni	79	120	<0,1	<0,1	<0,1	3	<0,1
	m+p-ksyleeni	130	230	<0,1	<0,1	<0,1	170	<0,1
	o-ksyleeni	120	200	<0,1	<0,1	<0,1	140	<0,1
	n-propyylibentseeni	0,1	0,3	<0,1	<0,1	<0,1	<0,1	<0,1
	Isopropyylibentseeni	0,2	0,2	<0,1	<0,1	<0,1	<0,1	<0,1
	2-etyylitolueeni	10	14	<0,1	<0,1	<0,1	10	<0,1
	3-etyylitolueeni	10	15	<0,1	<0,1	<0,1	12	<0,1
	4-etyylitolueeni	7	11	<0,1	<0,1	<0,1	7	<0,1
	1,2,3-trimetyylibentseeni	8	12	<0,1	<0,1	<0,1	10	<0,1
	1,3,5-trimetyylibentseeni	1	13	<0,1	<0,1	<0,1	8	<0,1
	1,2,3,5-tetrametyylibentseeni	2	3	<0,1	<0,1	<0,1	2	<0,1
	1,2,4,5-tetrametyylibentseeni	1	2	<0,1	<0,1	<0,1	1	<0,1
	Naftaleeni	2	3	<0,5	<0,5	<0,5	5	<0,5
Eetterit								
	MTBE	2	3	<0,1	<0,1	<0,1	3	<0,1
	TAME	1	1	<0,1	<0,1	<0,1	0,6	<0,1
Alifaattiset								
	2-metyylipentaani	4	4	<1	<1	<1	2	<1
	3-metyylipentaani	3	3	<1	<1	<1	<1	<1
	Metyyli-syklopentaani	2	3	<0,5	<0,5	<0,5	1	<0,5
	Sykloheksaani	1	2	<0,5	<0,5	<0,5	0,7	<0,5

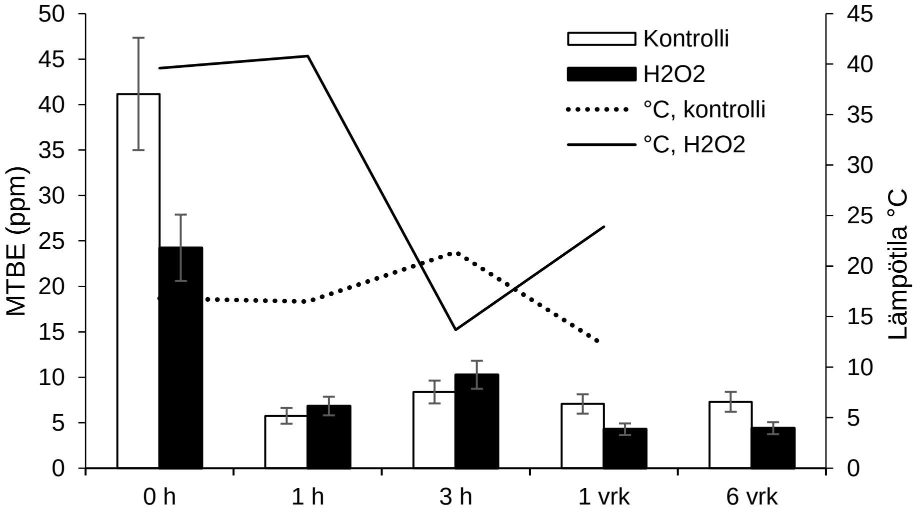
3.3. Pilot-mittakaavan lysimetrikokeet

Vedellä suoritetussa lysimetrikokeessa vetyperoksidiannoksella 1 M ja laskennallisella MTBE-pitoisuudella 750 mg/l käsitelty vesi puhdistui lähes 100-prosenttisesti yhdessä vuorokaudessa (kuva 12). Liuskatulosten perusteella vetyperoksidi oli kulunut loppuun jo vuorokaudessa, joten koetta ei ollut tarpeen jatkaa. Kuuden vuorokauden kuluttua kokeen aloituksesta otetuista näytteistä havaittiin, että kontrollilysimetrissä pitoisuudet olivat hieman laskeneet mutta odotetun kaltaisesti kuitenkin yhä korkeat (keskiarvo 200 mg/l). Poistuma kontrollilysimetrissä jäi vain 67 prosenttiin. Viiden vuorokauden seisotuksen jälkeen vetyperoksidilla käsitellyn veden MTBE-pitoisuus oli noussut pitoisuudesta 2,5 µg/l pitoisuuteen 18 µg/l.



Kuva 12. Käsittelyn vaikutus MTBE-pitoisuuteen (mg/l) vesifaasissa ajan suhteen (*keskiarvo ± 85 % luottamusväli, n=2*).

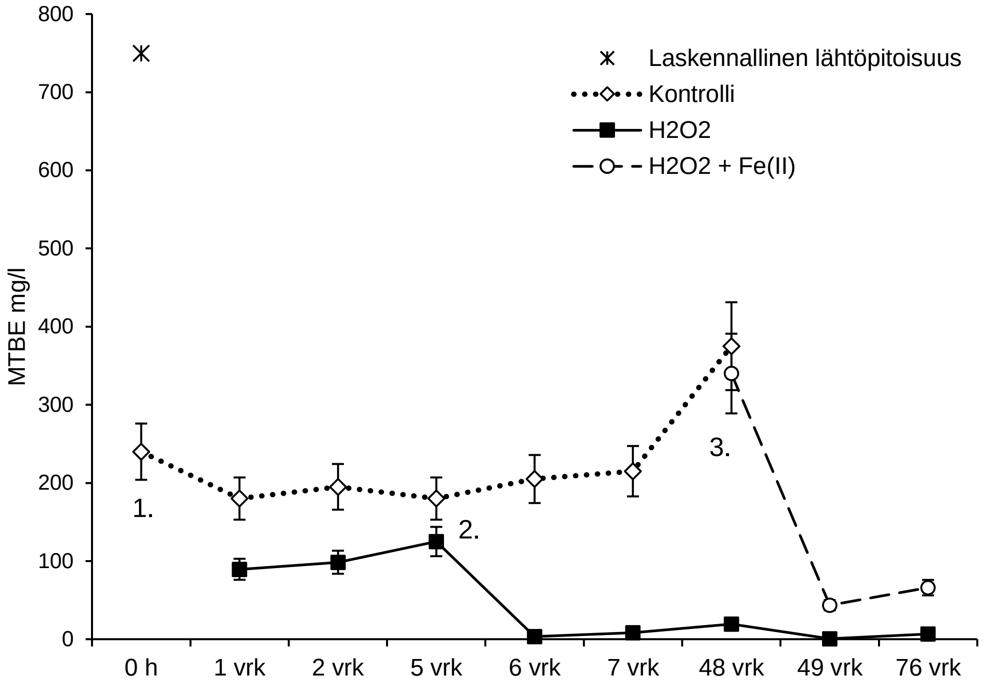
Lysimetrien ilmasta PID-mittarilla mitatut pitoisuudet laskivat ajan kuluessa kummassakin lysimetrissä noin 82 %, kontrollilysimetrissä pitoisuuksien jäädessä noin 3 ppm korkeammaksi kuin vetyperoksidilysimetrissä (kuva 13). Näin ollen vesianalyysituloksista ilmennyt teho ei heijastunut PID-tuloksiin. Ilman taustapitoisuus mittausten aikana oli noin 4 ppm, minkä vuoksi kokeessa ei tätä alhaisempia pitoisuuksia mitattu. Lämpötilakuvaajasta (kuva 13) nähdään, että vetyperoksidilisäys nosti lysimetrin veden lämpötilan heti lähes 40 °C:een. Kontrollilysimetrissä lämpötila oli 20 °C matalampi, lämpötilavaihteluiden mukaillessa vuorokauden lämpötilavaihteluja. Lysimetrien lämpötilojen välillä oli vielä seuraavanakin aamuna noin 10 °C:n ero.



Kuva 13. Pylväskuvaaja lysimetrien ilmasta mitatuista MTBE-pitoisuuksista (ppm) eri mittausajankohtina (*keskiarvo ± 85 % luottamusväli, n=7*) sekä viivakuvaaja lysimetrien lämpötiloista (°C) (aikasarja ei ole tasaisesti jatkuva).

Hiekalla suoritetussa lysimetrikokeessa ensimmäinen vetyperoksidikäsittely konsentraatiolla 1 M ei johtanut merkittävään MTBE-pitoisuuden laskuun (kuva 14). Pitoisuudet viidentenä päivänä käsittelystä olivat vain 31 % pienemmät kontrollikokeen pitoisuuksiin verrattuna. Lisäksi kokeessa havaittiin, että vain noin kolmasosa syötetystä MTBE:stä näkyi kontrollilysimetrin pohjalta otetusta näytteestä muutama tunti kokeen alkamisen jälkeen. Lysimetristä, jossa oli suoritettu vetyperoksidikäsittely, ei voitu ottaa heti käsittelyn jälkeen näytettä analysoitavaksi, sillä nestefaasi reagoi yhä kiivaasti.

Toisen H_2O_2-lisäyksen (2 M) jälkeen MTBE-pitoisuuksissa havaittiin selkeä lasku (kuva 14). Päivän jälkeen käsittelystä pitoisuudet olivat jopa alle 2 % kontrollikokeen pitoisuuksista, ja saavutettu poistuma oli lähes 94 %. Kuten vesifaasissa, myös hiekkakokeissa MTBE-pitoisuuksien havaittiin nousevan lievästi seisotuksen myötä, jolloin toisella käsittelykerralla saavutettu poistuma laski 85 %:iin. Kontrollikokeessa pitoisuudet lähes kaksinkertaistuivat noin 40 vuorokauden seisotuksen aikana.



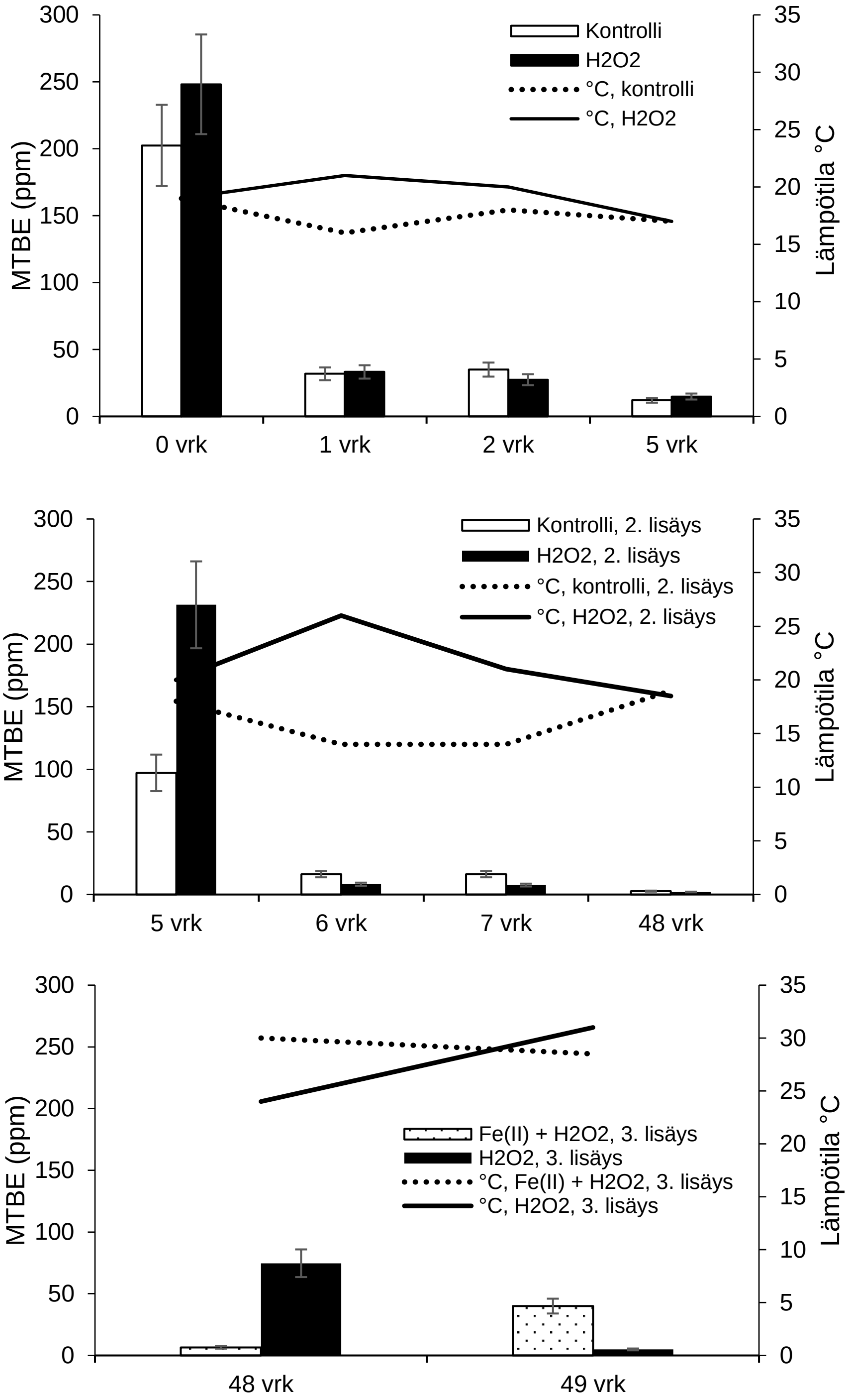
Kuva 14. Käsittelyn vaikutus MTBE-pitoisuuteen (mg/l) ajan funktiona (*keskiarvo ± 85 % luottamusväli, n =2*). Kuvaajassa on esitetty aikasarjana lysimetreissä hiekalla suoritetut käsittelyt: 1. MTBE-veden ja vetyperoksidin (1 M) syöttö maahan, 2. toinen H_2O_2-syöttö (2 M), 3. kolmas syöttö (2 M H_2O_2, kontrollissa 2 M H_2O_2 + 20 mM Fe(II)). Kokeen alussa (0 h) vetyperoksidikäsittelystä ei voitu ottaa näytettä, sillä reaktio oli yhä käynnissä. Aikasarja ei ole tasaisesti jatkuva.

Kolmas lisäys tehtiin, kun koko hiekkakokeen aloittamisesta oli kulunut 48 vuorokautta. Lysimetrissä, jossa toistettiin 2 M H_2O_2-käsittely, MTBE-pitoisuuksien havaittiin laskevan yhdessä vuorokaudessa jälleen lähes 97 % (kuva 14). Kuten toisella syöttökerralla, tälläkin kertaa vajaan kuukauden seisotuksen aikana MTBE-pitoisuudet olivat nousseet, minkä myötä viimeisen H_2O_2-käsittelyn teho jäi vain 66 %:iin. Kaikkien kolmen vetyperoksidikäsittelyn jälkeen lopullinen pitoisuus (6700 µg/l) oli jopa 99 % pienempi verrattuna syötettyyn laskennalliseen MTBE-pitoisuuteen.

Kontrollilysimetrissä MTBE-pitoisuus oli laskenut 48 vuorokauden aikana vain 50 % laskennallisesta alkupitoisuudesta (kuva 14). Kolmatta kontrollikäsittelyä ei tehty, vaan viimeisellä kerralla aiemmin kontrollina käytettyyn lysimetriin lisättiin rauta(II)sulfaattia (20 mM) ja vetyperoksidia (2 M). Tällä haluttiin testata katalyyttilisäyksen vaikutusta puhdistumistehokkuuteen pelkkään vetyperoksidikäsittelyyn verrattuna. Rautasulfaatin ja vetyperoksidin lisääminen näkyi selvänä MTBE-pitoisuuden laskuna, ja vajaan kuukauden seisotuksen jälkeen MTBE:n poistuma oli 82 %.

Hiekkakokeessa lysimetrien ilmasta PID-mittarilla mitatut MTBE-pitoisuudet laskivat myös selvästi ajan myötä (kuva 15a–c). Kaikissa sekä kontrolli- että H_2O_2-lysimetrissä suoritetuissa kokeissa pitoisuudet laskivat yli 90 % alkutilanteeseen nähden, joten myöskään hiekkakokeissa ilmasta mitatut pitoisuudet eivät heijastelleet vedestä mitattuja pitoisuuksia. Muista kokeista poiketen lysimetrissä, johon viimeisellä kerralla lisättiin vetyperoksidia sekä rauta(II)sulfaattia, ilman MTBE-pitoisuus nousi noin kuusinkertaiseksi. Ilman taustapitoisuus oli noin 4 ppm kaikkina muina mittauspäivinä paitsi 48. ja 49. päivä, jolloin taustapitoisuus oli suunnilleen 2 ppm.

Lämpötila hiekkakokeessa nousi vetyperoksidikäsittelyn seurauksena hitaammin kuin vesifaasissa suoritetussa kokeessa (kuva 15a–c). Poikkeuksen teki kolmannen reagenssilisäyskerran rauta(II)sulfaattilisäys, sillä lähes välittömästi reagenssilisäyksen jälkeen lämpötila lysimetrin pinnalla nousi yli mitta-asteikon (yli 100 °C) ja vesi alkoi höyrystyä. Syvemmältä lysimetristä kairalla otetusta näytteestä mitattiin lämpötilaksi 30 °C, joka sekin oli 4–10 °C korkeampi kuin lämpötilat pelkkien vetyperoksidilisäysten jälkeen.



Kuva 15a–c. Pylväskuvaajat lysimetrien ilman MTBE-pitoisuuksista (ppm) (*keskiarvo ± 85 % luottamusväli, n=7*) sekä viivakuvaajat lysimetrien lämpötiloista (°C) eri mittausajankohtina a) ensimmäisen, b) toisen ja c) kolmannen reagenssilisäyksen jälkeen. Viivakuvaajat eivät ole ajan suhteen tasaisesti jatkuvia.

Kokeen purkamisen yhteydessä otetuista maanäytteistä havaittiin, että MTBE-pitoisuus hiekassa nousi syvyyden mukaan (taulukko 7). Kaikkein alimmaisessa näytteessä (90–120 cm) oli suurin MTBE-pitoisuus. Toisaalta MTBE-pitoisuuksien ja kuiva-aineen massaprosentin välillä oli selvä negatiivinen korrelaatio (r=0,99). Mitä pienempi kuiva-aineen osuus eli mitä kosteampaa maa-aines oli, sitä suurempi oli MTBE-pitoisuus.

Taulukko 7. MTBE-pitoisuudet (mg/kg) sekä kuiva-aineen määrä massaprosentteina eri näytteenottosyvyyksillä.

Syvyys (cm)	MTBE (mg/kg)	Kuiva-aine (m-%)
0–30	<0,05	96
30–60	0,16	95
60–90	0,23	94
90–120	0,52	91

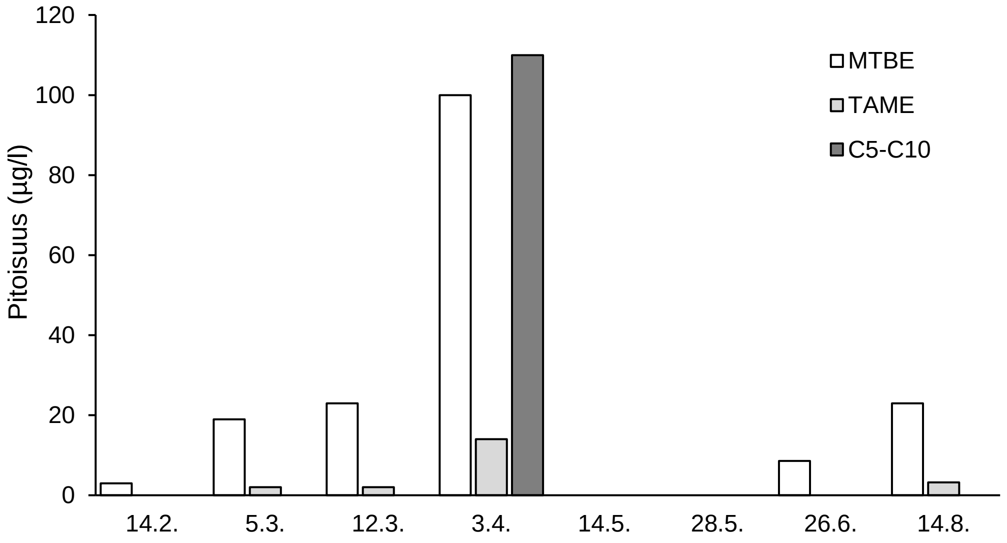
3.4. Kenttäkoe

Ennen kenttäkokeen alkua syöttö- ja havainnointiputkista otetuista vesinäytteistä osoittautui, että alue oli VOC-yhdisteiden osalta lähes puhdas. Vain MTBE:ä oli yli määritysrajan neljässä putkessa (taulukko 8), eikä muita VOC-yhdisteitä havaittu. Havainnointiputkesta HP101 (kuva 5, liite 1) pumpulla otetun aktiivisen ilmanäytteen perusteella TVOC-pitoisuus oli myös pieni, 4,7 mg/m3. Kahden kuukauden kuluttua kunnostuksen päättymisestä, ennen kenttäkokeen toista vaihetta, kaikki pitoisuudet olivat alle määritysrajan. Kunnostuksen aikana VOC-pitoisuuksia seurattiin havainnointiputkista HP101 sekä HP104. Pitoisuudet eivät laskeneet heti, vaan jopa nousivat ajan myötä (kuvat 16 ja 17). Lisäksi putkessa HP104 havaittiin kunnostuksen aikana MTBE:n ohella toista oksygenaattia TAME:a sekä bensiinijakeita (C5–C10). Kuukausi kunnostuksen toisen vaiheen jälkeen havaittiin, että MTBE-pitoisuudet näissä putkissa olivat nousseet jopa lähtöpitoisuuksia korkeammiksi (taulukko 8, kuvat 16 ja 17). Lisäksi kummastakin putkesta havaittiin TAME:a. Putkessa HP102 analysoitujen VOC-yhdisteiden pitoisuudet olivat yhä alle määritysrajan. Lopuista kahdesta putkesta ei otettu näytteitä aikaisempien puhtaiden näytteiden ja resurssien vuoksi.

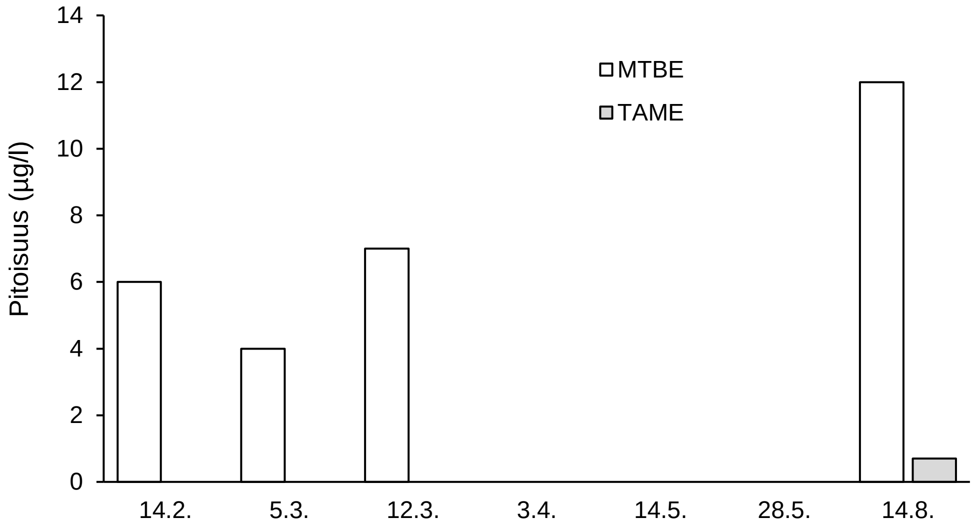
Taulukko 8. Koealueelta otettujen vesinäytteiden MTBE-pitoisuudet (µg/l) ennen kunnostuksen alkamista sekä noin kaksi kuukautta kunnostuksen päättymisen jälkeen.

Pvm	HP101	HP102	HP103	HP104	PVP1
14.2.18	6	<1	1	3	3
14.5.18	<0,5	<0,5	<0,5	<0,5	<0,5
14.8.18	12	<0,5	NA*	23	NA

*NA = ei analysoitu

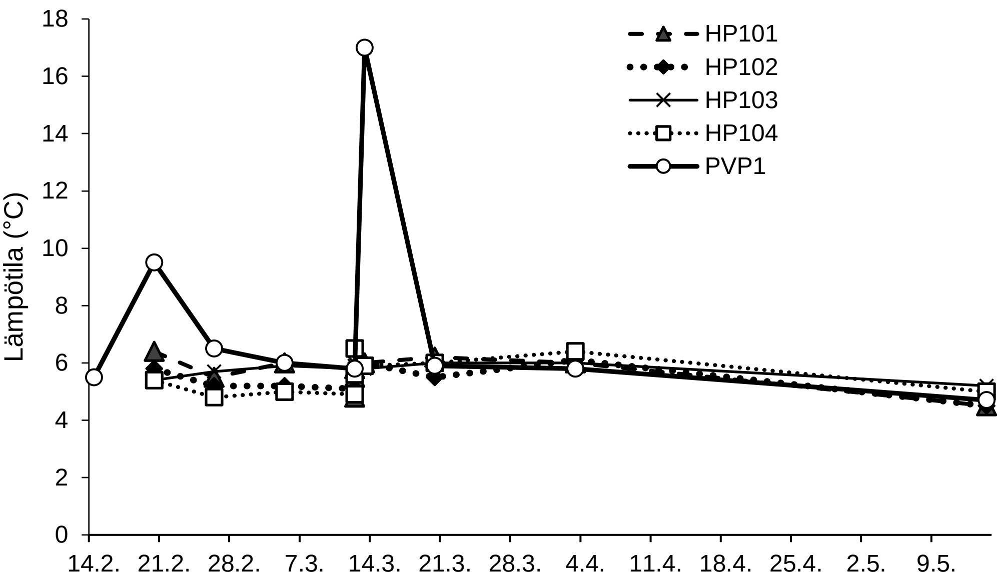


Kuva 16. VOC-yhdisteiden pitoisuuksien muutos havainnointiputkessa HP104. Päivinä 14.5. ja 28.5. pitoisuudet olivat alle määritysrajan.



Kuva 17. MTBE:n ja TAME:n pitoisuudet havainnointiputkessa HP101. Huhti-toukokuun mittauspäivinä pitoisuudet olivat alle määritysrajan.

Vetyperoksidin havaittiin levinneen epätasaisesti koko tutkittavalle koealueelle. Vetyperoksidireaktioiden aiheuttama lämpötilan nousu näkyi selvästi vain syöttöputkessa PVP1 (kuva 18). Sen sijaan vetyperoksidi- ja happipitoisuus nousivat selvästi syöttöputken lisäksi sitä lähinnä sijaitsevassa havainnointiputkessa HP101 (taulukko 9, kuva 19). Talven viimeisen syöttökerran jälkeisenä päivänä oli havaittavissa, että vetyperoksidi oli vaahdonnut maan pinnalle noin kolmen metrin päähän syöttöputkesta, pohjaveden virtauksen suuntaisesti luoteeseen kohti viereistä jokea ja näin ollen poispäin koealueesta (liite 7).



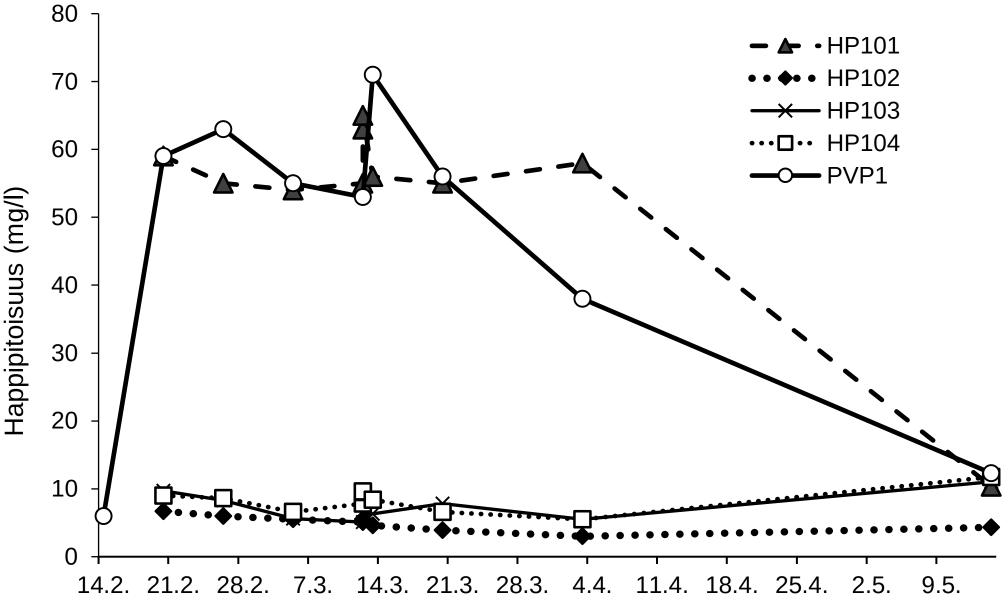
Kuva 18. Lämpötilan muutos syöttö- ja havainnointiputkissa kolmen ensimmäisen koekuukauden aikana.

Taulukko 9. Vetyperoksidipitoisuudet (mg/l) syöttö- ja havainnointiputkissa talven ja kevään aikana. Tulokset ovat puolikvantitatiivisia (liuskojen mittausalue 0–100 mg/l, 1–100 mg/l = 0,0001–0,01 % = 0,03–3 mM). Näytteitä ei voitu laimentaa, joten 100 mg/l vetyperoksidia sisältävissä näytteissä todellinen pitoisuus on voinut olla paljon tätä suurempi.

Pvm	HP101	HP102	HP103	HP104	PVP1
20.2.	100	3	10	3	100
26.2.	30	3	3	30	30
5.3.	30	0	1	1	30
12.3.[a]	30	0	0	1	30
12.3.[b]	30	10	30	10	NA*
13.3.	100	1	30	3	100
20.3.	30	1	3	1	30
3.4.	30	1	0	0	3
14.5.	0	0	0	0	0

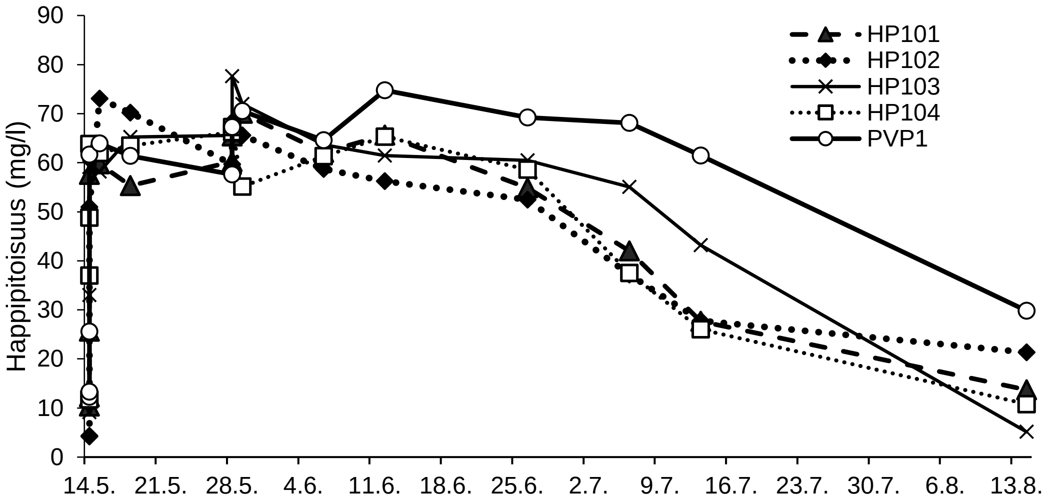
a) ennen syöttöä, b) syöttöpäivän jälkeen

*syöttö putkeen, pitoisuutta ei mitattu



Kuva 19. Happipitoisuuden (mg/l) muutos syöttö- ja havainnointiputkissa kolmen ensimmäisen koekuukauden aikana.

Toukokuussa sulan maan aikaan vetyperoksidi reagoi paljon nopeammin ja kiivaammin, joskin myös vetyperoksidin pitoisuus oli suurempi (25 %). Jo lähes välittömästi syötön alettua pintamaa alkoi paikoitellen kuplia vaahtomaisesti. Lisäksi mitattujen happipitoisuuksien perusteella voidaan päätellä, että käsittelyn vaikutussäde oli laajempi. Vaikka toukokuun 14. päivän jälkeen alkuperäiselle koealueelle ei enää syötetty lisää vetyperoksidia, alueen happipitoisuudet vaihtelivat, eivätkä laskeneet täysin tasaisesti (kuva 20). Happipitoisuuden nousu putkissa heijastelee päiviä, jolloin PVP3-putkeen on syötetty vetyperoksidia. Lisäksi koealueella havaittiin, että vetyperoksidin määrä alkukesästä nousi, vaikkei vetyperoksidia enää lisätty koealueen pohjavesiputkiin. Parhaimmillaan vetyperoksidin havaittiin levinneen kaikkiin kohteen pohjavesiputkiin (taulukko 10).



Kuva 20. Happipitoisuuden (mg/l) muutos syöttö- ja havainnointiputkissa kahden viimeisen koekuukauden aikana sekä kuukauden seisotuksen jälkeen.

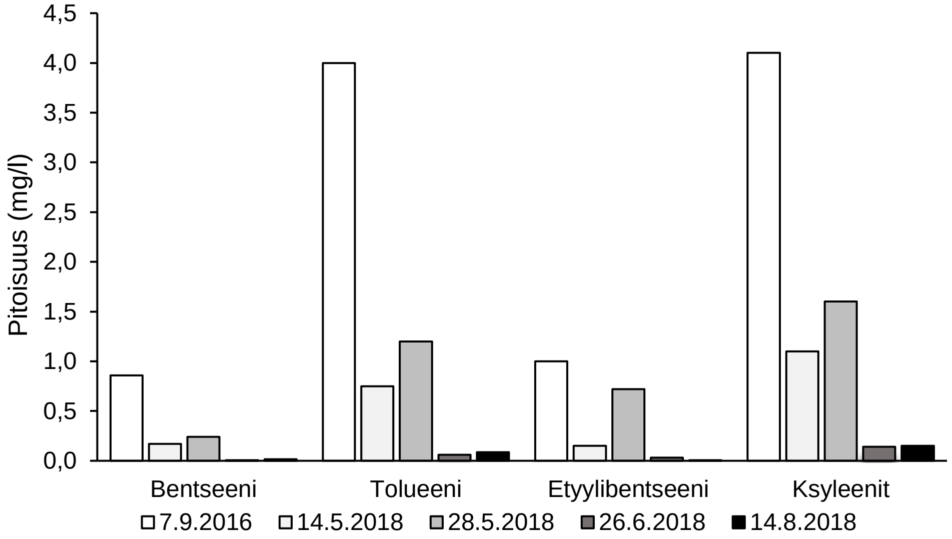
Taulukko 10. Vetyperoksidipitoisuudet (mg/l) syöttö- ja havainnointiputkissa sekä koealueen ulkopuolisissa pohjavesiputkissa (PVP2–4) sulan maan aikaan. Tulokset ovat puolikvantitatiivisia (liuskojen mittausalue 0–100 mg/l, 1–100 mg/l = 0,0001–0,01 % = 0,03–3 mM). Näytteitä ei voitu laimentaa, joten 100 mg/l vetyperoksidia sisältävissä näytteissä todellinen pitoisuus on voinut olla paljon tätä suurempi.

Pvm	HP101	HP102	HP103	HP104	PVP1	PVP2	PVP3	PVP4
14.5.	0	0	0	0	0	NA*	NA	NA
15.5.	100	100	100	100	100	10	30	10
18.5.	30	30	100	100	30	1	30	1
29.5.	NA	NA	30	30	NA	NA	100	3
6.6.	100	30	100	100	100	1	100	10
12.6.	100	30	100	100	100	10	100	1
26.6.	30	30	100	30	100	3	100	1
6.7.	10	3	30	3	100	0	100	0
13.7.	3	3	3	3	100	3	100	0
14.8.	1	0	1	1	0	0	0	0

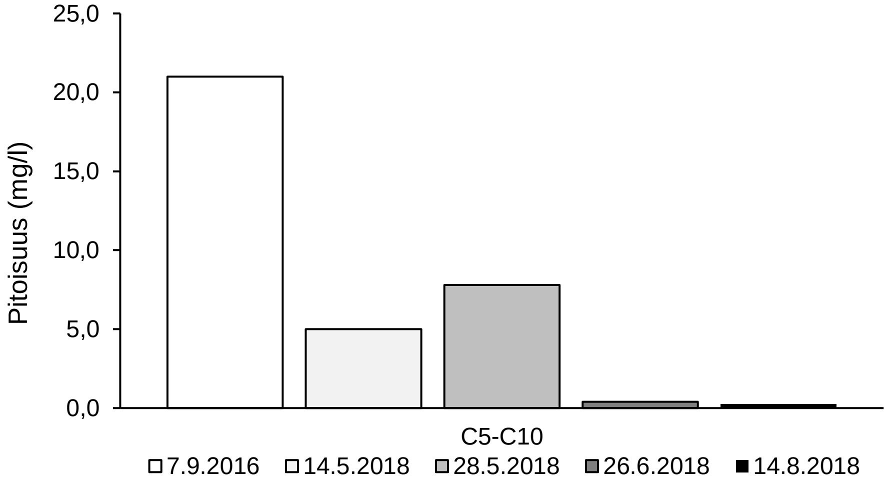
*NA = ei analysoitu

Koska koealueella kaikkien analysoitujen haihtuvien yhdisteiden osalta oli päästy alle määritysrajan, toukokuussa käsittelyjä päätettiin jatkaa pohjavesiputkessa PVP3. Kyseisestä putkesta on aiemmin vuonna 2016 havaittu BTEX-yhdisteitä ja bensiinijakeita talousveden laatuvaatimukset tai kasteluveden enimmäispitoisuudet ylittävinä pitoisuuksina. Parin vuoden aikana pitoisuudet ovat luontaisestikin laskeneet, yhdisteestä riippuen lasku on ollut 73–85 prosenttia (kuvat 21 ja 22).

Käsittelyiden alkupuolella BTEX- sekä bensiinijakeiden pitoisuudet nousivat hieman, mutta reilun kuukauden kuluessa pitoisuudet laskivat, ja kuukausi kokeen loputtua pitoisuudet olivat jopa 88–97 prosenttia matalammat kevään lähtötilanteesta.



Kuva 21. BTEX-yhdisteiden pitoisuuksien (mg/l) vaihtelu pohjavesiputkessa PVP3.



Kuva 22. Bensiinijakeiden (C5–C10-hiilivedyt) pitoisuuksien (mg/l) vaihtelu pohjavesiputkessa PVP3.

PID-mittausten perusteella haihtuminen koealueella oli melko vähäistä. Talvella VOC-pitoisuudet eivät nousseet yli 3,3 ppm:n edes silloin, kun pohjaveteen syötettiin lähes yksi kuutio 17-prosenttista vetyperoksidiliuosta (taulukko 11). Sulan maan aikaan ja korkeammalla vetyperoksidipitoisuudella (25 %) VOC-pitoisuudet nousivat selvemmin, tällöin korkein mitattu pitoisuus oli noin 33 ppm. Vaikutus oli kuitenkin vain hetkellinen ja rajoittui pääosin syötön jälkeiseen ensimmäiseen puoleen tuntiin.

Taulukko 11. VOC-pitoisuudet ilmassa (ppm) talven viimeisen ja kevään ensimmäisen syöttökerran aikaan.

Päivämäärä		HP101	HP102	HP103	HP104	PVP1
12.3.18	Ennen syöttöä	0,0	2,3	0,0	1,7	0,0
	+1 h syötöstä	3,3	0,0	0,0	0,0	0,0
	+3,5 h syötöstä	2,0	0,0	0,0	0,0	0,0
13.3.18	+ 24 h	0,0	0,0	0,0	0,0	0,0
14.5.18	Ennen syöttöä	0,0	0,0	0,0	0,0	0,0
	+ 0,5 h	0,0	13	19	16	33
	+1 h	0,4	0,5	0,3	0,6	0,4
	+ 4 h	2,0	0,5	0,4	0,4	0,3
15.5.18	+ 24 h	2,0	0,0	0,0	0,0	0,0

3.5. pH

Laboratorio- ja pilot-kokeissa käytetyn lysimetrihiekan pH oli lähellä kuutta ilman katalyytti- tai kelaattilisäystä (taulukko 12). Rauta(III)sulfaatin havaittiin laskevan tehokkaasti pH-arvoa, ja pH oli sitä matalampi, mitä suurempi oli rauta(III)sulfaatin konsentraatio. Vaikutus vaihteli eri näytematriiseissa, mikä todennäköisesti johtui eri matriisien kyvystä puskuroida pH-vaihteluita. Esimerkiksi suurimmalla rautakonsentraatiolla (20 mM) pelkässä vedessä pH laski jopa alle kahteen, kun taas lysimetri- ja kvartsihiekassa pH oli noin kolme. Rauta(II)sulfaatin havaittiin laskevan pH:ta rauta(III)sulfaattia vähemmän. Sitraatin puolestaan havaittiin nostavan maan pH:ta noin yhdellä ja puskuroivan melko tehokkaasti pH-vaihteluita.

Taulukko 12. Rautasulfaatin (Fe(III) ja Fe(II)) sekä sitraatin (50 mM) vaikutus pH-arvoon eri näytematriiseissa.

Näyte	Kontrolli	0,6 mM Fe(III)	2 mM Fe(III)	20 mM Fe(III)	20 mM Fe(II)
Loppi, maa	5,8			4,5	
Jokimaa, maa	5,9	5,7	5,0	3,2	4,7
Jokimaa, maa + sitraatti	6,6	6,3	6,2	4,5	6,0
Vesi				1,8	4,3
Vesi + sitraatti				6,5	4,3
Kvartsihiekka				2,8	

4. Tulosten tarkastelu

4.1. Vetyperoksidikonsentraation vaikutus

Laboratoriokokeissa osoitettiin, että pelkässä vesifaasissa jo pienimmällä tutkitulla vetyperoksidikonsentraatiolla (0,4 M, 1 %) päästiin tutkittujen yhdisteiden osalta alle määritysrajan, kun katalyyttinä käytettiin rauta(III)sulfaattia. Hiekalla suoritetuissa laboratorio- ja pilot-kokeissa ratkaisevaksi konsentraatioksi osoittautui 2 M (7 %), joskin laboratoriossa paras poistuma saavutettiin konsentraatiolla 5 M (17 %). Kemiallisessa hapetuksessa käytetyt vetyperoksidipitoisuudet vaihtelevat yleensä 2 ja 12 prosentin (0,6–3,6 M) välillä. Suuresta vetyperoksidipitoisuudesta on sikäli hyötyä, että se suosii hydroksyyliradikaalien lisäksi muiden etenemisreaktioissa muodostuvien reaktiivisten radikaalien syntymistä, mikä mahdollistaa erilaisten haitta-aineiden hajottamisen. (Watts & Teel 2005). Toisaalta korkeina pitoisuuksina vetyperoksidi voi heikentää hapetuksen tehoa kuluttamalla itse itseään (Petri ym. 2011). Koska vetyperoksidi on menetelmässä suurin kustannus asennustöiden ohella, ylimäärin lisätty vetyperoksidi tuo myös turhia lisäkustannuksia.

Vetyperoksidi koostuu noin 94-prosenttisesti hapesta, joten kaasumuotoinen happi voi olla joidenkin vetyperoksidireaktioiden merkittävä sivutuote. Lisäksi koska vetyperoksidireaktiot ovat eksotermisia, ne voivat nostaa pohjaveden lämpötilaa ja edistää siten kaasujen muodostumista (Petri ym. 2011). Esimerkiksi Baciocchi ym. (2010) havaitsivat yli 6-prosenttisen (1,8 M) H_2O_2-liuoksen lisäävän merkittävästi kaasuntuottoa, mikä puolestaan voisi heikentää hapettumisen etenemistä maaperässä. Tähän tutkimukseen osittain perustuen esimerkiksi Innocenti ym. (2014) ja Piscitelli ym. (2015) tutkivat MTBE:n poistumaa Fentonin-kaltaisissa käsittelyissä käyttäen korkeintaan 6-prosenttista vetyperoksidiliuosta. Chen ym. (2001) puolestaan havaitsivat, että vetyperoksidin lisääminen jo pienempänä pitoisuutena (10 g/l, 1 %) johti nopeaan kaasunmuodostumiseen, minkä seurauksena noin 70 % liuenneesta TCE:stä kulkeutui kaasufaasiin. Kemiallista hapettumista ei havaittu merkittävissä määrin. Toisaalta koe tehtiin hyvin pienessä mittakaavassa (kolonnin koko 43 mm x 76 mm), joten koe ei ole täysin vertailukelpoinen tämän tutkielman kanssa.

4.2. Rautalisäyksen vaikutus

Laboratoriomittakaavassa suoritettujen kokeiden perusteella raudan lisääminen tehosti MTBE:n poistumaa. Raudan hapetusasteella ei ollut tilastollisesti merkittävää eroa poistumaan, vaikka käytettäessä rauta(II)sulfaattia lisätyn raudan määrä oli puolet pienempi rauta(III)sulfaattiin verrattuna. MTBE:n keskiarvopitoisuudet rauta(II)sulfaattia lisätessä olivat kuitenkin noin kaksi kertaa suurempia kuin rauta(III)sulfaattia käytettäessä. Myös Watts ja Dilly (1996) havaitsivat dieselsaastuneen maaperän Fenton-kaltaista kunnostamista tutkiessaan kahdenarvoisten rautayhdisteiden olevan rauta(III)yhdisteitä heikompia katalyyttejä. Tämän uskottiin johtuvan siitä, että vetyperoksidia kului vetyperoksidin hapettaessa kahdenarvoista rautaa rauta(III)-muotoon. Muun muassa Wattsin ja Teelin (2005) mukaan suuria vetyperoksidipitoisuuksia käytettäessä onkin kannattavampaa lisätä katalyytiksi kolmenarvoista rautaa, sillä se ei kuluta vetyperoksidia välittömästi. Sen sijaan rauta(III) pelkistyy reaktiossa (R2) rauta(II)-muotoon, mikä toimii varsinaisen Fenton-reaktion käynnistäjänä. (Watts & Dilly 1996, Watts & Teel 2005).

Kolmenarvoista rautaa käytettäessä reaktio on kuitenkin reaktiota (R1) hitaampi, ja sen on havaittu käynnistyvän joissain tapauksissa vasta viiveen jälkeen (De Laat ym. 2004, Pignatello ym. 2006). Kenttäsovellusten kannalta pieni viive reaktion alkamisessa on eduksi, sillä tällöin vetyperoksidi ehtii mahdollisesti levitä laajemmalle alueelle. Tässä tutkielmassa selvää eroa rauta(II)- tai rauta(III)sulfaatin katalysoimien reaktioiden käynnistymisnopeudessa ei kuitenkaan havaittu kuin suurimmalla vetyperoksidipitoisuudella. Suurimmalla pitoisuudella (5 M) reaktio käynnistyi lähes välittömästi reagenssilisäyksen jälkeen ja reaktion aiheuttama lämpötilannousu oli aloitushetkellä noin kolme ja 15 minuutin kohdalla 9 °C suurempi käytettäessä rauta(II)- kuin rauta(III)sulfaattia. Pienemmillä H_2O_2-pitoisuuksilla puolestaan reaktio alkoi viiveellä raudan hapetusasteesta riippumatta. Toisaalta käsittelyt eivät ole täysin vertailukelpoisia keskenään, sillä kuten aiemmin mainittiin, rauta(II)sulfaattia käytettäessä raudan määrä oli puolet pienempi. Mikäli lisättävän reagenssin määrä olisi laskettu sen sisältämän raudan mukaan, rauta(II)sulfaatti olisi saattanut toimia voimakkaampana katalyyttina ja havaittu vaikutus olisi voinut olla toisenlainen.

Raudan hapetusasteen vaikutuksesta on saatu myös päinvastaisia tuloksia tutkittaessa rautamineraalien katalysointikykyä. Esimerkiksi Matta ym. (2007, 2008) havaitsivat, että kahdenarvoista rautaa sisältävät raudan oksidit olivat kolmiarvoisen raudan oksideja tehokkaampia katalyyttejä TNT:n (2,4,6-trinitrotolueeni) Fenton-kaltaisessa hapetuksessa sekä neutraalissa että happamassa pH:ssa. Lähellä neutraalia pH:ta TNT:n hajotuksen havaittiin hidastuvan nopeasti alun kiivaan vaiheen jälkeen, minkä uskottiin johtuvan rauta(II):n hapettumisesta ja saostumisesta (Matta ym. 2007). Tässä tutkielmassa rautasulfaattilisäyksen havaittiin alentavan pH:ta erityisesti heikosti puskuroiduissa systeemeissä. Rauta(III)sulfaatin havaittiin laskevan pH-arvoa rauta(II)sulfaattia enemmän, mikä selittänee ainakin osittain rauta(III)sulfaatilla saatuja parempia tuloksia. Suurimmalla rauta(III)sulfaattipitoisuudella (20 mM) maan pH laski noin kolmeen, mikä on otollinen pH kemialliselle hapetukselle (Garrido-Ramírez ym. 2010). Vastaavasti rauta(II)-lisäys laski pH-arvoa noin 4,5:een. Tämän perusteella on todennäköistä, että erityisen hyvät tulokset johtuisivatkin ainakin tässä tapauksessa kemiallisesta hapetuksesta.

Laboratoriokokeissa saatujen positiivisten tulosten perusteella myös pilot-kokeessa päätettiin lisätä katalyytiksi rautaa. Koska alustavien tulosten perusteella rauta(II) näytti toimivan kolmenarvoista rautaa paremmin, hiekkakokeessa viimeisellä syöttökerralla toiseen lysimetriin päätettiin lisätä rauta(II)sulfaattia. Reaktio lysimetrissä oli hyvin kiivas, minkä seurauksena syntyi runsaasti kaasua ja pintamaa lämpeni yli veden haihtumispisteen. Vetyperoksidi oletettavasti kului loppuun ennen kohdesyvyyttä, sillä lysimetrin pohjalta tunti kokeen alkamisen jälkeen otetuista näytteistä ei havaittu vetyperoksidia. Näin ollen vetyperoksidi ei todennäköisesti ehtinyt reagoida kaiken MTBE:n kanssa, eikä puhdistumistulos siksi ollut odotetun kaltainen. Tämä osoittaa, että reaktion etenemisen kannalta raudan lisääminen katalyytiksi on kannattavaa, mutta todellisessa kunnostustilanteessa lisääminen voi olla haasteellista. Ongelmia tuottavat kiinteän rautasulfaatin jakaminen tasaisesti alueelle sekä vetyperoksidin nopea hajoaminen, jolloin vaikutussäde voi jäädä hyvinkin pieneksi. Lisäksi muodostuva kaasu, jota voi muodostua myös käytettäessä pelkkää vetyperoksidia suurena pitoisuutena (liite 8), voi ulkopuolisen silmin näyttää epäilyttävältä ja herättää huolta esimerkiksi kohteen lähellä asuvissa tai sen ohi liikkuvissa ihmisissä. Raudan lisääminen runsaina määrinä voi myös haitata veden talousvesikäyttöä, sillä se voi aiheuttaa ruostesaostumia sekä väri- ja makuhaittoja. Värin ja maun perusteella juomakelpoisen veden sisältämästä raudasta ei ole terveydellistä haittaa, mutta esteettisten ja teknisten haittojen vuoksi sille on asetettu laatutavoite (200 µg/l). (Valvira 2018). Pilot-kokeiden tulosten perusteella kenttäkokeessa ei käytetty katalyyttiä.

4.3. Kelaattilisäyksen vaikutus

Laboratoriomittakaavan kokeissa havaittiin, ettei kelatoivana aineena käytetyllä trinatriumsitraatilla ollut merkittävää vaikutusta MTBE-pitoisuuksiin kokeen lopussa. Kemiallisessa hapetuksessa kelatoivat aineet voivat tehostaa orgaanisten haitta-aineiden hajoamista muun muassa pitämällä katalysoivan raudan liukoisessa muodossa (Petri ym. 2011). Esimerkiksi Vicente ym. (2011) havaitsivat, että natriumsitraatti, jonka pitoisuus oli sama kuin tässä tutkielmassa (50 mM) tehosti 2,4-dimetyylifenolin muuntumista. Piscitellin ym. (2015) tutkimuksessa EDTA:n (etyleenidiamiditetraetikkahappo) lisääminen pitoisuudella 2 mM puolestaan tehosti MTBE:n hapettumista verrattuna pelkkään Fenton-käsittelyyn. Se, ettei tässä tutkielmassa sitraatilla havaittu selvää vaikutusta, sopisi oletukseen, että kyse olisi haihtumisesta kemiallisen hapetuksen sijaan.

Toisaalta sitraatin lisääminen näytti kuitenkin hidastavan vetyperoksidin hajoamista, mikä näkyi matalampana lämpötilana kokeen aikana. Tämä voi selittyä sillä, että kelatoivat aineet voivat sitoutua maaperän aktiivisille mineraalipinnoille ja hidastaa siten vetyperoksidin hajoamista (Petri ym. 2011). Kelatoivien aineiden stabilointikyvystä on kuitenkin ristiriitaisia tuloksia. Esimerkiksi Watts ym. (2007) sekä Vicente ym. (2011) havaitsivat sitraatin (10 mM – 1 M) stabiloivan vetyperoksidia, kun taas Innocentin ym. (2014) tutkimuksessa kelaatinmuodostajan (natriumsitraatti tai EDTA, 5 mM) lisäämisellä ei ollut merkittävää vaikutusta vetyperoksidin hajoamisaikaan. Kelatoivat aineet voivat myös reagoida epäedullisesti hydroksyyliradikaalien kanssa tai niiden ligandit voivat adsorboitua maaperään (Vicente ym. 2011). Esimerkiksi Pardo ym. (2014) havaitsivat, että trinatriumsitraatti (50 mM) lisäsi vetyperoksidin elinikää maaperässä, mutta heikensi öljyhiilivetyjen poistamistehokkuutta, mikä johtui todennäköisesti siitä, että haitta-aine ja kelaatti kilpailivat vetyperoksidista. Heikomman puhdistumisen selitettiin johtuvan mahdollisesti myös sitraattilisäyksestä aiheutuneesta pH:n noususta, mikä loi kemialliselle hapetukselle epäsuotuisammat olosuhteet. Myös tässä tutkielmassa sitraatin havaittiin puskuroivan pH-muutoksia, mikä saattaa osittain selittää sitraatin melko vaatimatonta vaikutusta lopputulokseen. Tämä puolestaan viittaa siihen, että reaktio olisi pH:sta riippuvainen ja reaktiomekanismissa olisi kyse kemiallisesta hapetuksesta. Muun muassa Wattsin ym. (2007), Vicenten ym. (2011), Innocentin ym. (2014) ja Pardon ym. (2014) tutkimuksissa sekä tässä tutkielmassa tehtyjen havaintojen perusteella voidaan kuitenkin todeta, ettei kelatoivan aineen vaikutuksista voida suoraan päätellä vallitsevaa reaktiomekanismia.

4.4. Käsittelyiden jälkeinen pitoisuuksien nousu

Lysimetrikokeissa MTBE-pitoisuuksien havaittiin nousevan käsittelyiden jälkeen. Tällainen rebound-ilmiö on tavallinen ongelma esimerkiksi ilmastusta käytettäessä. Ilmastuksen aikana pitoisuudet saattavat laskea selvästi, mutta käsittelyn loputtua palata takaisin jopa lähelle alkupitoisuuksia (Bass ym. 2000). Ilmiötä on havaittu myös kemiallisen hapetuksen jälkeen. Mahdollisiksi syiksi on esitetty, etteivät käsittelyt ulotu tarpeeksi tehokkaasti heikosti läpäiseville alueille, maapartikkeleihin pidättyneiden aineisiin tai NAPL-faaseihin. Epätäydellisestä käsittelystä seuraa uusi tasapainotustilanne vesifaasin kanssa, ja haitta-aineita päätyy veteen. (Krembs ym. 2010). Lisäksi orgaaniset haitta-aineet voivat sitoutua vahvasti maaperän orgaaniseen ainekseen. Jopa vähän orgaanista ainesta sisältävässä maaperässä haitta-aineet voivat jäädä loukkuun huokosiin (Vicente ym. 2011), jolloin vetyperoksidin nopeasta hajoamisesta johtuen vetyperoksidi ei välttämättä ehdi reagoida näiden haitta-aineiden kanssa (Petri ym. 2011). Lysimetrikokeessa käytetty hiekka sisälsi vain vähän orgaanista ainesta (8,6 mg/kg kuivapaino), joten MTBE:n sitoutuminen siihen tuskin selittää havaittua rebound-ilmiötä. On kuitenkin mahdollista, että pintamaahan sitoutunut vesi on toiminut MTBE:n lähteenä. Tätä ajatusta tukee se, että hiekkakokeen alussa lysimetrin pohjalta otetusta näytteestä analysoitu MTBE-pitoisuus oli vain kolmasosan laskennallisesta syötetystä pitoisuudesta, joten 2/3 syötetystä MTBE:stä ei ollut näkyvissä missään. Pelkkä haihtuminen ilmaan tuskin selittää näin suurta eroa laskennallisen ja analysoidun pitoisuuden välillä, joten on todennäköistä, ettei kaikki syötetty MTBE ehtinyt kulkeutua lysimetrin pohjalle ennen näytteenottohetkeä.

Lysimetrikokeessa havaittua rebound-ilmiötä voi selittää myös se, että MTBE:ä on tiivistynyt lämpötilan laskiessa huokosilmasta takaisin nestefaasiin. Koska pitoisuus nousi myös kontrollissa, lähteenä on todennäköisesti toiminut maa-aines tai pintamaan sitoma vesi. Toisaalta myös vesifaasissa suoritetussa kokeessa, jossa uutta nestemäistä lähdettä ei ollut, havaittiin lievä nousu vetyperoksidikäsittelyn jälkeen. Kerrostumisvaikutusta voitaneen pitää vähäisenä, sillä vesikokeessa näytteet otettiin pinnalta aina kevyen sekoituksen jälkeen. Pitoisuuden nousu vesikokeessa oli kuitenkin hyvin pieni, joten eroa voi selittää myös mahdollinen epätarkkuus näytteenotossa. Joka tapauksessa rebound-ilmiöstä johtuen kunnostuksen jälkeen on erittäin tärkeää seurata haitta-ainepitoisuuksia pidemmällä aikavälillä, jotta voidaan varmistua kunnostuksen onnistumisesta.

Kenttäkokeessa kuukausi kokeen loputtua otetuista näytteistä MTBE-pitoisuuksien havaittiin nousseen jopa lähtöpitoisuuksia korkeammiksi. Pitoisuuksien nousu ei välttämättä ole pelkästään huono asia, sillä reboundin myötä haitta-aineet voivat siirtyä kunnostuksen kannalta helpommin käsiteltävään vesifaasiin (Krembs ym. 2011). Tässä kenttäkokeessa kohonneet MTBE-pitoisuudet selittynevät kuitenkin sillä, että polttoainesäiliöt, joista MTBE on todennäköisesti peräisin, sijaitsevat yhä maan alla. Vaikka säiliöt ovat jo tyhjennetty, niiden vedellä täyttyminen ja vuotaminen näyttävät aiheuttavan jatkuvan haitta-ainelähteen. Kohteen kokonaisvaltaisen kunnostuksen kannalta ensiarvoista olisikin tyhjentää maanalaiset säiliöt sekä mahdolliset niihin liittyvät muut rakenteet.

4.5. Toimivuus ominaisuuksiltaan erilaisilla VOC-yhdisteillä

Laboratoriokokeissa, joissa käsiteltiin pilaantuneilta alueilta tuotua pohjavettä, kaikkien muiden yhdisteryhmien kuin halogenoitujen hiilivetyjen osalta pitoisuudet vetyperoksidikäsittelyn jälkeen olivat alle määritysrajan. Toisaalta halogenoituja hiilivetyjä edustavan TCE:n alkupitoisuus oli suuri, lähes 30-kertainen muihin VOC-yhdisteisiin verrattuna, ja käytetty vetyperoksidikonsentraatio pienempi (1 M). Todennäköisesti näiden syiden vuoksi loppupitoisuus jäi muita korkeammaksi. Trikloorietyleenin pitoisuus laski kuitenkin lupaavasti yli 99 %. Näiden tulosten perusteella käytetty menetelmä ei ole haitta-aineesta riippuvainen, vaan toimii ominaisuuksiltaan erilaisilla VOC-aineilla. On kuitenkin syytä epäillä, ettei kyse olisi kuplituksesta aiheutuvasta haihtumisesta, sillä kokeessa käytettiin kvartsihiekkaa yhdessä rauta(III)sulfaatin kanssa, minkä jälkeenpäin havaittiin laskevan pH:ta noin kolmeen. Näin ollen olosuhteet olivat otolliset kemialliselle hapetukselle. Vetyperoksidin kuplituksen soveltuvuus esimerkiksi TCE:lle vaatiikin lisätutkimuksia sekä erilaisen koeasetelman.

Kenttäkokeessa käsittelyn havaittiin toimivan MTBE:n lisäksi myös bensiinijakeille sekä BTEX-yhdisteille. Niiden pitoisuudet laskivat muutamassa kuukaudessa jopa 88–97 %, yhdisteestä riippuen. BTEX-yhdisteiden osalta bentseenin pitoisuus lopussa oli 15 µg/l, mikä on yli talousveden laatuvaatimuksen (1 µg/l, YM 2014: 87). Tolueenin loppupitoisuus (87 µg/l) puolestaan alitti kasteluvedelle asetetun enimmäispitoisuuden (600 µg/l, SPI 2011: 78). Etyylibentseenin ja ksyleenien pitoisuudet olivat jo ennen kokeen alkua kasteluveden laatuvaatimusten rajoissa ja niiden pitoisuuksia onnistuttiin laskemaan entisestään. MTBE:n osalta puhdistuminen ei ollut yhtä menestyksekästä todennäköisesti pienten lähtöpitoisuuksien sekä jatkuvan haitta-ainelähteen takia, mutta pitoisuudet olivat kuitenkin koko kokeen ajan alle 200 µg/l, mikä on MTBE:lle asetettu kasteluveden enimmäispitoisuus (SPI 2011: 78). Käsittelyjä jatkamalla ja kohdentamalla vetyperoksidisyöttö niin sanottuihin hot spot -alueisiin pitoisuudet olisivat todennäköisesti olleet vieläkin matalammat. Tulokset ovat kuitenkin erittäin lupaavia ja puoltavat menetelmän käyttöönottoa täyden mittakaavan sovellutuksissa ainakin bensiinillä pilaantuneilla alueilla.

Kenttäkokeessa päätarkoituksena oli todentaa haihtumista, joten kokeessa keskityttiin seuraamaan VOC-pitoisuuksia ilmasta sekä pohjavedestä. Koska pH-muutosten merkitys tulosten tulkinnassa tajuttiin vasta jälkikäteen, pH:n seuranta jäi kokeen aikana turhan vähäiselle huomiolle. Toisaalta kenttäkokeessa ei lisätty katalyyttiä, joten merkittävää muutosta pH:ssa ei ollut edes odotettavissa, etenkään kun laboratoriossa kentältä tuodun maanäytteen havaittiin puskuroivan pH-vaihteluita lysimetrihiekkaa tehokkaammin. Toisaalta esimerkiksi Innocenti ym. (2014) havaitsivat pH:n laskevan noin kuudesta neljään vetyperoksidisyötön seurauksena. Laskun, joka tosin oli vain väliaikainen, selitettiin johtuvan vetyperoksidista, jonka liuos on hapan valmistusprosessissa käytettyjen lisäaineiden takia. Oletettavasti vetyperoksidin levitessä ja hajotessa sen happamoittava vaikutus vähenee, joten matala pH tuskin selittää ainakaan täysin tutkielman kenttäkokeen hyviä tuloksia. On mahdollista, että poistumista on tapahtunut sekä kuplituksen seurauksena haihtumalla että kemiallisesti haihtumalla. Maaperän mineraalit ovat voineet katalysoida kemiallisia hapetusreaktioita myös neutraalissa pH:ssa (Matta ym. 2007).

4.6. Menetelmän siirtäminen täyteen mittakaavaan

Positiivisia tuloksia saatiin laboratorio- ja pilot-mittakaavan kokeissa sekä osittain myös kenttäkokeessa, mikä antaa tukea hypoteesille, että pienessä mittakaavassa saadut tulokset ovat siirrettävissä täyteen mittakaavaan. Mittakaavan kasvattaminen kuitenkin vaikuttanee sekä menetelmän toimivuuteen että lisää kemiallisen hapetuksen osuutta haitta-aineen poistamisessa. Täydessä mittakaavassa vetyperoksidin on levittävä laajemmalle alueelle ja haihtuvan kaasun on läpäistävä pohjaveden pinnantasosta riippuen useamman metrin korkuinen maakerros.

Kenttäkoe osoitti, että vetyperoksidi pystyy leviämään myös tiiviimmässä, siltti- tai silttisessä savimaassa ympäröivälle alueelle, mutta leviäminen on epätasaista. Koealueella seurattiin vetyperoksidi- ja happipitoisuutta sekä lämpötilaa, jotka osoittautuivat hyviksi muuttujiksi vetyperoksidin leviämisen tarkastelussa. Talviaikana suoritetun kokeen aikana havaittu vaikutusalueen laajuus oli noin kolme metriä, tosin käsittely ulottui tehokkaasti vain puolen metrin päähän. Vetyperoksidipitoisuus oli huomattavasti pienempi kauimmaisista havainnointiputkista otetuissa näytteissä. Vaikutusalueen laajuus oli lähes yhtenevä kirjallisuudessa kemialliselle hapetukselle esitettyjen vaikutussäteiden kanssa. Vetyperoksidin on havaittu yleensä kulkeutuvan noin 3–4 m ja usein hajoavan 1–2 m säteellä injektioputkesta (Watts ym. 2007). Esimerkiksi Innocentin ym. (2014) pilot-mittakaavan kokeessa vaikutussäde oli 2–5 metriä. Sen sijaan Krembsin ym.

(2010) julkaisussa, jossa eri kemiallisten in situ -hapetusmenetelmien toimintatehoa kentällä vertailtiin tietokantatietojen perusteella, vetyperoksidikäsittelyn vaikutussäde oli keskimääräisesti edellä mainittuja hieman suurempi, 4,8 m (15 jalkaa).

Tässä kenttäkokeessa suhteellisen heikko vetyperoksidiliuoksen leviäminen muihin havainnointiputkiin selittyy todennäköisesti pohjaveden virtaussuunnalla. Talven viimeisen syöttökerran jälkeisenä päivänä oli havaittavissa, että vetyperoksidi oli vaahdonnut maan pinnalle noin kolmen metrin päähän syöttöputkesta, pohjaveden virtauksen suuntaisesti luoteeseen kohti viereistä jokea ja näin ollen poispäin koealueesta. Pohjaveden virtaussuunnan vaikutusta testattiin keväällä, jolloin syöttö tehtiin myös kunnostettavan alueen kaakkoispuolelta. Vetyperoksidin havaittiin levinneen kevään ja kesän aikana koealueelle, vaikkei vetyperoksidia enää lisätty koealueen pohjavesiputkiin. Tämä antaa tukea oletukselle, että vetyperoksidi leviää tehokkaammin virtaussuunnan mukaisesti. Parhaimmillaan vetyperoksidia havaittiin levinneen kuitenkin koko tutkittavalle alueelle, putkesta PVP3 katsottuna jopa yli 20 metrin päähän PVP2- ja PVP4-putkien alueelle. Vetyperoksidin leviäminen oli kuitenkin epätasaista, joten on oletettavaa, että myös maaperän heikosti läpäisevät alueet heikentävät vetyperoksidin leviämistä. Toisaalta veteen liuenneiden haitta-aineiden voidaan olettaa leviävän samoja reittejä pitkin, joten sikäli vetyperoksidin epätasainen leviäminen ei ole ongelma. Ongelmallisempia ovat vetyperoksidin laimeneminen tai sen hajoaminen, jotka ovat myös voineet heikentää liuoksen leviämistä tutkitulle alueelle.

Käsittelyn aikana VOC-pitoisuudet nousivat selvästi. Tämä selittyy todennäköisesti sillä, että vetyperoksidiliuoksen lisääminen on nostanut pohjaveden pintaa, jolloin maaperään pidättyneet haitta-aineet ovat kulkeutuneet pohjaveteen. Käsittelyn edetessä pitoisuudet kuitenkin laskivat, mikä voidaan tulkita käsittelyn onnistumisena. Esimerkiksi pohjavesiputkessa PVP3 havaittuja BTEX-yhdisteitä ei havaittu alkuperäisellä koealueella, joten voidaan olettaa myös, että käsittely on todella vähentänyt haitta-ainepitoisuuksia, eikä vain mobilisoinut VOC-yhdisteitä. MTBE:n osalta lähtötasoa korkeammat loppupitoisuudet voivat selittyä aiemmin mainitun jatkuvan haitta-ainelähteen lisäksi luonnollisilla vuodenaikaisilla lämpötila- sekä pohjaveden korkeus- ja virtausvaihteluilla.

Vetyperoksidin lisääminen pohjaveteen nosti selvästi veden happipitoisuutta, ja vaikutuksen kesto oli oletettua pidempiaikainen. Mitattu happipitoisuus oli korkeimmillaan 78 mg/l, mikä on huomattavasti enemmän kuin hapen liukoisuus veteen (8–10 mg/l) (Petri ym. 2011), eli vesi oli ylikyllästynyt hapella. On siten mahdollista, että reaktioista vapautuva happi pyrkii kaasufaasiin (Petri ym. 2011), mikä voi edesauttaa VOC-yhdisteiden haihtumista. Kohonneella happipitoisuudella voi olla menetelmässä myös sekundäärinen vaikutus, sillä se voi tehostaa haitta-aineiden aerobista biologista hajotusta. Vetyperoksidin havaittiin myös nostavan lämpötilaa, parhaimmillaan noin 10 asteella, mikä voi kiihdyttää kaasuntuotantoa (Villa ym. 2008). Lämpötilan vaikutusta haitta-aineiden haihtumiseen tai hajoamiseen on kuitenkin hyvin vaikea arvioida, sillä lämpötilan nousu vaikuttaa myös muihin kemiallisiin ja fysikaalisiin prosesseihin (Petri ym. 2011). Kohonnut lämpötila voi myös edesauttaa biologista hajotusta (Leahy & Colwell 1990), mikäli vetyperoksidi ei tapa mikrobeja.

Vetyperoksidin kuplituksen kannalta riskinä on, että lämpötilan laskiessa yhdisteet tiivistyvät kyllästämättömässä kerroksessa ja palautuvat takaisin veteen. Oletuksena menetelmässä kuitenkin on, että kaasun tuotto kunnostettavalla alueella on riittävää ja riittävän pitkäaikaista. Tällöin kaasuvirta ikään kuin huuhtelee myös kuivan kerroksen ja haitta-aineet kulkeutuvat ilmaan saakka ainakin asvaltoimattomalla koealueella. Asvaltoidulla alueella ilmaan kulkeutumisen uskotaan olevan heikompaa ja on mahdollista, että haitta-aineet jäävät loukkuun asvalttipinnan alapuolelle. Myös routainen maakerros ja paksu lumipeite voivat vaikuttaa menetelmän tehokkuuteen. Kenttäsovelluksissa kunnostettavalle alueelle voitaisiin kaivaa vaakasuuntaisia huokoskaasuputkia ja vetyperoksidikäsittely voitaisiin yhdistää huokoskaasuimuun haihtumisen tehostamiseksi.

4.7. Haihtuminen vs. kemiallinen hapettuminen

Tutkielmassa ilmaan haihtuvan MTBE:n pitoisuuksia tarkasteltiin PID-mittarin avulla. PID-mittarilla ei ole mahdollista analysoida yksittäisten yhdisteiden pitoisuuksia, vaan mittari ilmoittaa mitattavien yhdisteiden summapitoisuuden. Näin ollen on mahdollista, etteivät kokeessa mitatut pitoisuudet ole yksinomaan MTBE:ä, vaan esimerkiksi sen muuntumistuotteita tai muita VOC-yhdisteitä. Laboratorio- ja pilot-kokeissa on kuitenkin oletettu, ettei muuntumistuotteiden osuus ole kovin merkittävä MTBE:n osuuteen verrattuna.

VOC-pitoisuuksien perusteella haihtumista tapahtui merkittävästi laboratoriokokeessa sekä pilot-kokeen alkuvaiheessa. Pilot-kokeessa havaittiin, ettei kontrollin ja käsittelyn välillä ollut kovin suuria eroja, kun koe suoritettiin pelkässä vesifaasissa. Alkutilanteessa haihtuminen kontrollista oli PID-tulosten perusteella suurempaa, mutta erot käsittelyiden välillä tasoittuivat kokeen edetessä. Käsittelylysimetrin matalammat alkupitoisuudet selittyvät mahdollisesti sillä, että lysimetrissä on käynnistynyt hapetusreaktioita, jotka ovat hajottaneet MTBE:ä. Vetyperoksidin havaittiinkin alkavan reagoida lähes välittömästi reagenssilisäyksen jälkeen. Kemiallista hapetusta puoltaa myös se, että kokeessa lisättiin katalyytiksi rauta(III)sulfaattia, jonka myöhemmissä tarkasteluissa havaittiin laskevan lähes neutraalin veden pH-arvoa jopa alle kahteen, jolloin olot kemialliselle hapetukselle olivat optimaaliset. Lisäksi käsittelyn seurauksena MTBE-pitoisuudet vedessä laskivat hyvin nopeasti, eivätkä ne heijastelleet ilmasta mitattuja VOC-pitoisuuksia. Mikäli kyse olisi pelkästä kuplituksen seurauksena tapahtuvasta haihtumisesta, olisi kokeen aikana oletettavasti näkynyt selkeä piikki PID-mittauksissa samalla kuin pitoisuudet vedessä vähenivät.

Pilot-vaiheen hiekkakokeissa haihtuminen oli alkutilanteessa suurempaa käsittelylysimetrissä kuin kontrollissa. Lisäksi kontrollilysimetrissä pitoisuus ilmassa oli noin 100 ppm suurempi ensimmäisellä kuin toisella syöttökerralla. Erot kontrollilysimetrissä ensimmäisen ja toisen syöttökerran alkuhetkien välillä saattavat selittyä lisätyn MTBE:n määrällä. Ensimmäisellä kerralla maahan lisättiin lysimetrin sisältämän vesimäärän perusteella MTBE:ä pitoisuudella 1500 mg/l ja toisella kerralla 750 mg/l, joten ilmassa on todennäköisesti ollut syötön jälkeen eri määrä MTBE:ä. Sen sijaan käsittelylysimetrissä kummallakin syöttökerralla pitoisuus oli noin 250 ppm:n tienoilla. Tämä puolestaan voi selittyä sillä, että ensimmäisellä syöttökerralla käytettiin matalampaa vetyperoksidipitoisuutta (1 M), jolloin käsittelyn vaikutus on ollut melko vaatimaton kontrolliin verrattuna. Toisella syöttökerralla käytetty konsentraatio oli 2 M, ja jos tätä konsentraatiota vertaa aiemmin mainittuun Baciocchin ym. (2010) tekemään tutkimukseen, kaasun tuotto on ollut merkittävää, mikä puolestaan on voinut edistää haihtumista. Tämä selittäisi myös, minkä takia käsittelylysimetrissä havaittiin jälkimmäisellä kerralla selkeä piikki kontrolliin verrattuna.

Kenttäkokeessa vetyperoksidin syöttäminen pohjaveteen aiheutti vain väliaikaisen piikin PID-mittauksissa. Vastaavanlainen ilmiö oli havaittavissa Innocentin ym. (2014) tutkimuksessa, jossa lähes kaikissa alueen kahdeksassa pohjavesiputkessa oli havaittavissa piikki VOC-pitoisuuksissa kunnostuksen alkuvaiheessa. Kyseisessä tutkimuksessa haihtumisen merkitys kokonaisuuden kannalta oli kuitenkin vähäinen, sillä laskelmien mukaan vain noin 1 % poistuneesta haitta-aineen määrästä johtui haihtumisesta. Suurimman osan haitta-aineesta arvioitiin mineralisoituneen kemiallisen hapetuksen seurauksena. Suhteellisen vaatimattomien PID-lukemien mutta vesianalyysien perusteella tehokkaan poistumisen perusteella vaikuttaa siltä, että tässäkin kenttäkokeessa on tapahtunut samanaikaisesti kemiallista hapettumista ja haihtumista niin, että kemiallinen hapetus on ollut vallitseva reaktiomekanismi. Vetyperoksidin havaittiin kestävän pohjavedessä oletettua pidempään, joten on mahdollista, että osa vetyperoksidista kuluu aluksi aiheuttaen yhdisteiden haihtumista, mutta jäljelle jäävä pieni osuus jatkaa haitta-aineiden hajottamista kemiallisen hapetuksen kautta.

Tutkielmassa saatujen tulosten perusteella vaikuttaa siltä, että matala pH edistää kemiallista hapetusta, jolloin myös puhdistuminen on tehokkaampaa. Kuplituksen aiheuttaman haihtumisen rooli taas vaikuttaisi kasvavan, kun olot kemialliselle hapetukselle eivät ole yhtä suotuisat. Tämän tutkimuksen puitteissa ei kyetä kuitenkaan perustelemaan, mihin perustuu esimerkiksi se, että käytettäessä pelkkää 5 M vetyperoksidia saadaan kontrollia parempi tulos, kun taas konsentraatiolla 2 M tulos on jo paljon vaatimattomampi. PID-lukemat olivat keskimäärin 60–100 ppm suurempia haihtumiskokeen alkupuolella käytettäessä 5 kuin 2 M vetyperoksidia, mikä viittaisi suurempaan kuplituksen osuuteen. Tälle olisi kuitenkin syytä hakea tukea valvotummista massatasapainokokeista. Hapetuksen ja haihtumisen roolia voitaisiin tarkastella syvällisemmin esimerkiksi seuraamalla hiilidioksidin tuotantoa tai analysoimalla mahdollisia muuntumistuotteita. Esimerkiksi MTBE:n täydellistä mineralisaatiota vedeksi ja hiilidioksidiksi on ollut vaikea saavuttaa (Burbano ym. 2008, Innocenti ym. 2014). Sen sijaan on havaittu väli- ja sivutuotteita, joihin lukeutuvat tert-butyyliformiaatti (TBF), tert-butyylialkoholi (TBA), metyyliasetaatti sekä asetoni (Burbano ym. 2002). Laboratorio- ja pilot-kokeissa näitä sivutuotteita ei kustannussyistä analysoitu. Kenttäkokeessa näytteistä analysoitiin MTBE:n ohella TBA:a, joka on yksi hapetusreaktioiden pääsivutuotteista (Siedlecka ym. 2007, Innocenti ym. 2014). TBA-pitoisuudet olivat jokaisella näytteenottokerralla alle määritysrajan, mikä ei tosin ollut yllättävää MTBE:n pienen osuuden vuoksi.

4.8. Menetelmään liittyvät riskit ja niiden ehkäisy

Koska käytetyt reagenssit ovat samoja kuin kemiallisessa hapetuksessa, liittyy menetelmiin samankaltaisia riskejä. Esimerkiksi reaktioiden seurauksena muodostuvat VOC-höyryt voivat mahdollisesti aiheuttaa räjähdysvaaran tai terveysriskejä (Petri ym. 2011). Muun muassa Villa ym. (2008) havaitsivat, että Fenton-käsittely vetyperoksidikonsentraatiolla 4 M lisäsi DDT:n ja DDE:n haihtumista ilmaan. Tämän uskottiin aiheutuvan lämpötilan noususta sekä mahdollisesti muodostuneista kaasuista (CO, CO_2 ja O_2). Terveysriskien ehkäisemiseksi haihtuvien orgaanisten yhdisteiden monitorointi ja hallinta ovatkin kunnostuksen aikana tärkeässä roolissa. Mahdollisia haihtumisesta aiheutuvia riskejä voidaan ehkäistä yhdistämällä menetelmä huokoskaasukäsittelyyn, etenkin jos haihtuvat yhdisteet ovat haitallisia tai jos odotettavissa olevat pitoisuudet ovat korkeat. On hyvä huomata, että tässä kenttäkokeessa ilman VOC-pitoisuudet eivät nousseet missään vaiheessa kovin suuriksi, eivätkä käsittelyt nostaneet VOC-pitoisuuksia kuin hetkellisesti. Samankaltaisen ilmiön havaitsivat Innocenti ym. (2014) in situ -kenttäkokeessaan.

Vetyperoksidireaktiot voivat myös heikentää maaperän laatua muun muassa hajottamalla maaperän orgaanista ainesta (Bissey ym. 2006), laskemalla kationinvaihtokapasiteettia tai muuttamalla saatavilla olevien ravinteiden määrää (Sirguey ym. 2008). Orgaanisen aineksen liukeneminen puolestaan voi edistää siihen sitoutuneiden haitta-aineiden liukoisuutta, aiheuttaen mahdollisia terveysriskejä. Lisäksi vahvat hapettavat olosuhteet sekä matala pH voivat edistää raudan ohella myös muiden metallien, kuten sinkin ja kuparin liukoisuutta. (Villa ym. 2008)

Vetyperoksidi sekä muodostuvat radikaalit voivat olla toksisia maaperän mikrobeille (Büyüksönmez ym. 1998). Toisaalta vetyperoksidi hajoaa nopeasti vedeksi ja hapeksi (Pignatello ym. 2006), eikä viitteitä pysyvästä haitasta mikrobipopulaatioille ei ole havaittu (Watts & Teel 2005, Krembs ym. 2010). Anaerobisille mikrobeille myös vapautuva happi voi olla toksista. Mahdollisesti heikentynyt mikrobiaktiivisuus on kuitenkin palautettavissa hyödyntämällä kohteen käsittelemättömien osien mikrobikantaa (bioaugmentaatio) sekä biostimulaatiota, jossa biologista aktiivisuutta tehostetaan esimerkiksi lisäämällä maaperään ravinteita.

5. Johtopäätökset

Tämän työn tavoitteena oli selvittää vetyperoksidin kuplitukseen perustuvan menetelmän kykyä poistaa maa- ja pohjavedestä haihtuvia orgaanisia yhdisteitä. Kokeiden aikana saavutettiin lupaavia tuloksia MTBE:llä, BTEX-yhdisteillä sekä muilla bensiinijakeilla. Laboratoriokokeissa sekä pilot-kokeen vesikokeessa saavutettiin lähes 100 %:n puhdistumistulos bensiinin komponenttien osalta. Pilot-vaiheen hiekkakokeessa MTBE:n poistuma oli noin 94 % ja toistetulla käsittelyllä lähes 97 %, mutta seisotuksen myötä pitoisuudet nousivat, jolloin saavutettu poistuma jäi 85 ja 66 prosenttiin. Kenttäkokeessa BTEX- ja bensiinijakeiden pitoisuudet laskivat yhdisteestä riippuen jopa 88–97 % vain muutamassa kuukaudessa. Menetelmää ei kuitenkaan pystytty erottelemaan hypoteesien vastaisesti kemiallisesta hapetuksesta. Tulosten perusteella puhdistuminen johtuu pääasiassa kemiallisesta hapetuksesta, mutta samanaikaisesti voi tapahtua myös haihtumista. Asian varmistamiseksi tullaan suorittamaan monitoroidumpi haihdutuskoe, jossa seurataan massatasapainoa sekä mahdollisia muuntumistuotteita. Esimerkiksi kunnostuslupamenettelyn kannalta on merkitystä, kumman oletetaan olevan ratkaiseva mekanismi, vaikka tehtävät toimenpiteet olisivatkin samoja.

Käsittelyn tehokkuuteen vaikuttivat vetyperoksidin konsentraatio sekä rautakatalyytin lisääminen. Kelatoivana aineena toimivalla sitraatilla ei havaittu olevan selkeää vaikutusta lopputulokseen. Sen sijaan pH osoittautui tutkielman aikana oletettua tärkeämmäksi muuttujaksi, jonka muutoksia on tarpeen seurata kokeiden ja kunnostusten yhteydessä. Vetyperoksidi- ja happipitoisuus sekä lämpötila puolestaan osoittautuivat oleellisiksi muuttujiksi, joiden avulla voidaan helposti arvioida vetyperoksidin vaikutussädettä kunnostustilanteessa.

Tämän tutkielman puitteissa ei ollut mahdollista seurata vetyperoksidireaktioiden vaikutusta raskaampien hiilivetyjakeiden, kuten dieselin ja polttoöljyn esiintymiseen. Esimerkiksi tässäkin tutkielmassa kenttäkohteen alue on pilaantunut bensiinin lisäksi dieselillä ja raskailla hiilivetyjakeilla, joten olisi syytä selvittää, mitä näille jakeille tapahtuu vetyperoksidikäsittelyiden seurauksena. Oletuksena on, ettei raskaampia jakeita pystytä VOC-yhdisteiden tavoin haihduttamaan, jolloin ne voivat aiheuttaa kulkeutumisriskin. Niitä voidaan kuitenkin mahdollisesti hapettaa kemiallisesti (Watts & Dilly 1996), mikä puolestaan voi vähentää mobilisaatioriskiä. Menetelmällä ei myöskään pystytty suoraan ratkaisemaan kaikkia kenttäkohteeseen liittyviä ongelmia, mikä ei tosin ollutkaan tämän tutkielman tavoite. Kohteen kunnostamisessa tärkeä jatkotoimenpide olisi maan alla sijaitsevien öljysäiliöiden poistaminen, sillä säiliöiden täyttyessä vedellä ne toimivat jatkuvana päästölähteenä, saastuttaen mahdollisesti uudelleen maaperää ja pohjavettä. Olennaista koko kohteen kunnostuksen onnistumisen kannalta olisikin myös pilaantuneen maa-aineksen puhdistaminen.

Vaikkei vetyperoksidin kuplitus -menetelmää pystytty erottelemaan kemiallisesta hapetuksesta, tutkielmassa saadut tulokset olivat sikäli menestykselliset, että VOC-pitoisuuksia onnistuttiin laskemaan merkittävästi lyhyessäkin ajassa. Suhteellisen nopean kunnostusajan vuoksi se on kustannustehokas vaihtoehto myös perinteisemmille pump & treat -ja ilmastustekniikoille. Koska aika on usein vaikuttava tekijä kunnostuspäätöksissä, tällaisille nopeille kunnostusmenetelmille on tarvetta ja vetyperoksidin kuplitusta onkin jo suunniteltu käytettävän todellisissa kunnostustilanteissa. Yhden kenttäkohteen perusteella menetelmän yleistettävyydestä ei voida tehdä suuria johtopäätöksiä. Tulevaisuudessa mielenkiintoista olisikin selvittää, miten käsittelyt onnistuvat kohteissa, joiden maaperä on esimerkiksi tutkitun kohteen maaperää savisempi tai hiekkaisempi, tai joissa pilaantuma on aiheutunut esimerkiksi vettä raskaammista VOC-yhdisteistä. Tämä pro gradu -tutkielma luo kuitenkin hyvän pohjan vetyperoksidiperustaisten *in situ* -kunnostustekniikoiden käyttöönotolle ja jatkokehittelylle.

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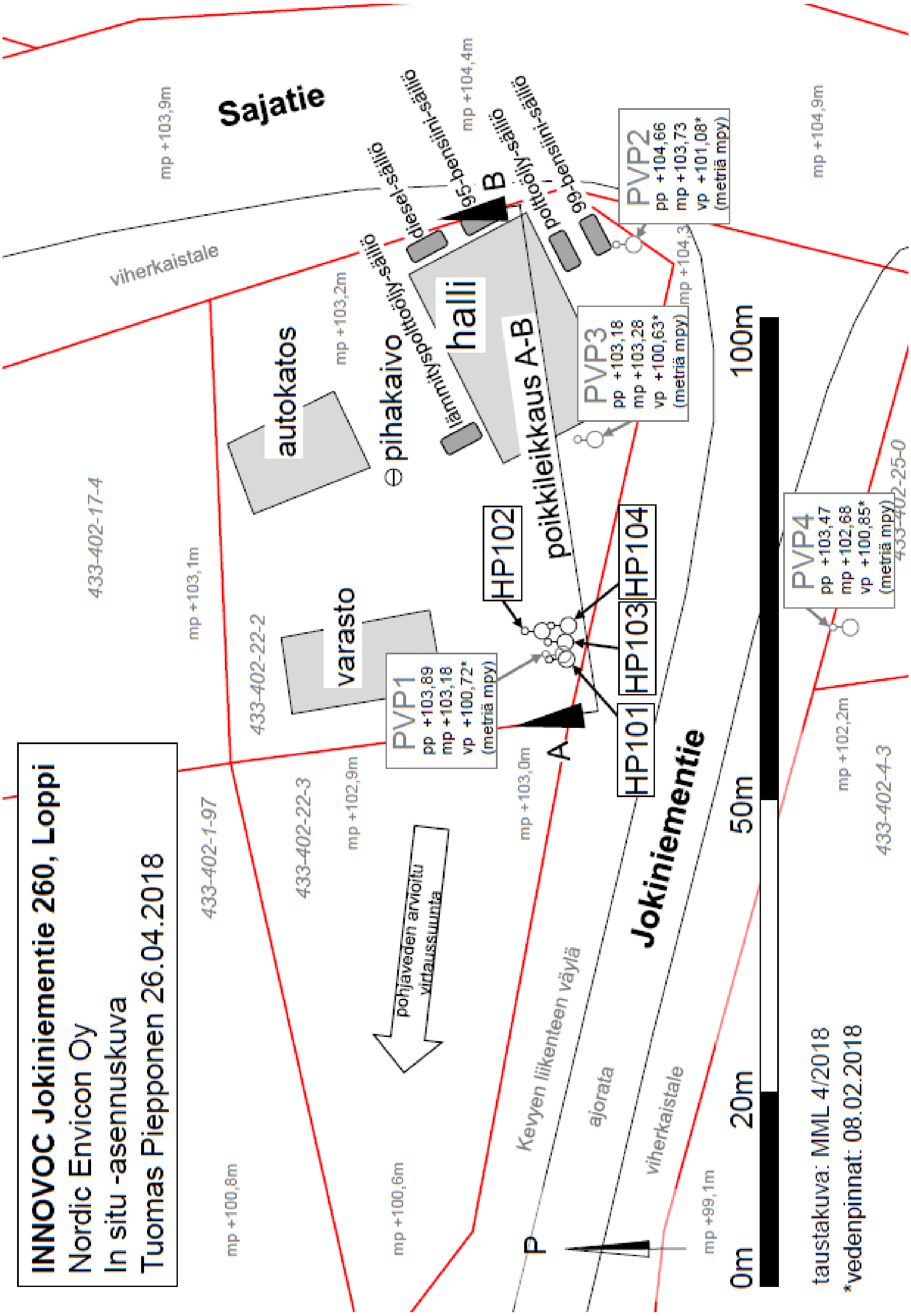
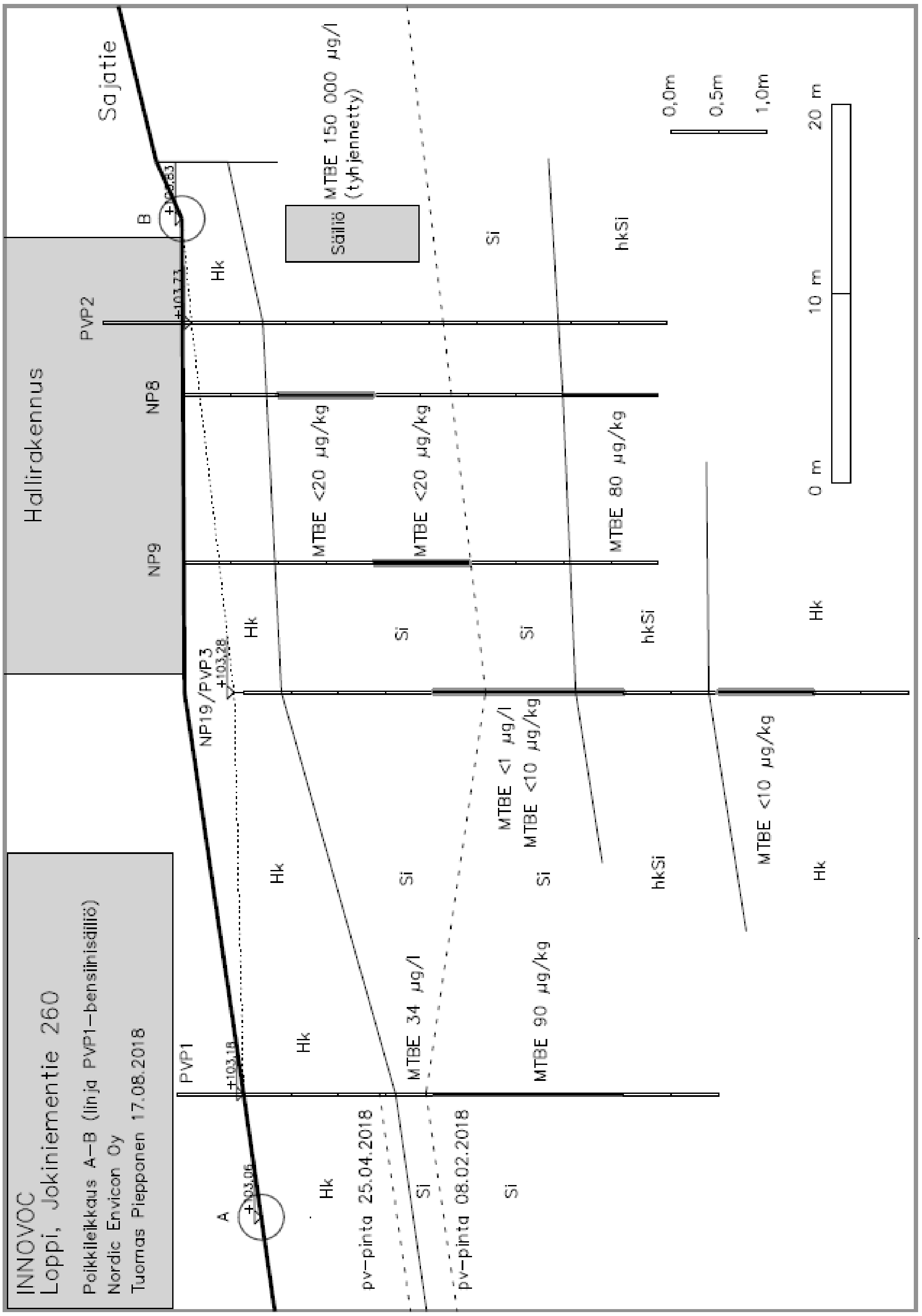
Liitteet



Liite 1. Kohteen Jokiniementie 260, Loppi, asennuskuva (Nordic Envicon oy).



Liite 2. Kohteen Jokiniementie 260, Loppi, poikkileikkauskuva pohjavesiputken PVP1 ja bensiinisäiliön väliltä (Nordic Envicon oy).

Liite 3. Kohteessa Jokiniementie 260, Loppi havaitut haitta-aineiden maksimipitoisuudet sekä pitoisuudet vedellä täyttyneessä 95-bensiinisäiliössä (FCG Suunnittelu ja tekniikka oy sekä Nordic Envicon oy).

	Havaitut maksimipitoisuudet				
	Maaperä		Pohjavesi		Säiliövesi
Haitta-aine	Pitoisuus (mg/kg)	Näytepiste (syvyys)	Pitoisuus (mg/l)	Näytepiste	Pitoisuus (mg/l)
Bensiinijakeet C5-C10	1700	NP4 (3-4 m)	21,0	PVP3	280
Keskitisleet >C10-C21	2400	NP8 (1-2 m)	1,0	PVP2	<0,05
Raskaat öljyjakeet >C21-C40	170	NP8 (1-2 m)	1,3	PVP2	<0,05
Öljyjakeet >C10-C40 (summa)	2570	NP8 (1-2 m)	3,0	PVP3	<0,05
Bentseeni	7	NP7 (1-2 m)	1,0	PVP2	1,2
TEX	351	NP4 (3-4 m)	9,1	PVP3	5,8
Ksyleeni	3000	NP6 (0,5-1 m)	4,1	PVP3	1,5
MTBE-TAME	<0,01	-	0,07	VN1	270
ETBE	<0,01	-	0,29	VN1	0,047
1,2-dikloorietaani	<0,01	-	0,0062	PVP2	<0,5
1,2-dibromietaani	<0,01	-	0,0053	PVP2	<0,5

Liite 4. Valokuva pohjavesiputkesta PVP3, jonne syötettiin sulan maan aikaan vetyperoksidia valuttamalla.

Liite 5. Havainnoiva kuva vaikutusalueiden eroista savimaalla syöttäen ilmaa (ylhäällä) tai vetyperoksidia (alhaalla). Sekä ilma että vetyperoksidi on syötetty maahan samanlaisten injektiokanavien kautta.

Liite 6. Laimennettua vetyperoksidia syötettiin IBC-säiliöstä pohjavesiputkeen käyttäen tavallista puutarhaletkua sekä pilssipumppua.

Liite 7. Talven viimeisen syöttökerran jälkeen vetyperoksidia vaahtosi maan pinnalle n. 3 metrin päähän syöttöputkesta, osittain kuvassa näkyvien parrujen alle. Kulkusuunta oli poispäin koealueesta, oletetun pohjaveden virtaussuunnan mukaisesti.

Liite 8. Keväällä vetyperoksidisyötön jälkeen pintamaassa havaittiin muodostuvan kaasua/vesihöyryä. Tällöin PID-mittarilla mitattu VOC-pitoisuus oli noin 20 ppm. Vaikutus oli hyvin väliaikainen.