4.1 Final publishable summary report

4.1.1. Executive Summary

Due to its long industrial past, the EU has an unfortunate legacy of contaminants in its soils and waters. Accordingly, dealing with soil and groundwater contamination is becoming an integral part of plans for the redevelopment of industrial locations or derelict urban sites not only in the EU but also worldwide. Increased cost and time effectiveness of soil remediation techniques will generate a significant benefit for problem owners and the society as a whole. Additionally, the soil itself is increasingly being considered a valuable natural resource, needed of some degree of protection. Traditional soil clean-up technologies have not taken into account their impact on the soil matrix nor have included the soil natural remediation capacity in their initial designs.

For the first time, **in the UPSOIL project robust technologies (and methodologies)** were developed **for fast, cost-effective, integrated treatment of soil and groundwater that result in both allowable risk levels and maximal use of the natural soil rehabilitation potential at a longer term.** Within this UPSOIL perspective, four lines of research were followed. Although these may seem independent, they are actually interlinked following diverse strategies (use of the same aquifer material for different tasks, use of same technologies from different lines of research in the same field test, etc.):

- Line A – Smart Coupling of Technologies (WP2[1] & WP3): The smart coupling of existing in-situ biochemical remediation technologies is studied, allowing the remediation optimisation and soil functions restoration with respect to the use of the same biochemical technologies in an independent manner.
- Line B – System Driven Injection (WP4): A highly innovative technology where contaminants detection and the in situ treatment are mechanically combined has been developed.
- Line C – Specific Targeting (WP5): A selection and development of new remedial agents that preferably react with the organic contaminants leaving the soil matrix untouched has been carried out.
- Line D – Feedback Driven Remediation (WP6): The feedback driven remediation concept is defined as a crosscutting methodology for all types of in situ remediation, where the in situ treatment is controlled by means of real time monitoring and modelling, allowing the treatment tuning as new information becomes available.

The project core is the Consortium, made up of 15 partners with different professional profiles: 6 RTD institutions, 1 University, 7 small and medium enterprises (SMEs) and 1 contractor, all from 10 different European countries widely distributed. The different partners' backgrounds provide different views and working practices allowing improved project results. Thus, RTD institutions (Tecnalia, VITO-MPT, DELTARES, IETU, ECOIND and SGI) and the University (WUR) safeguard a high scientific and technological quality of the project; whereas the involvement of technological and environmental companies (SMEs) and the contractor ensure practical applicability and the exploitation of results.

[1] WP: Work Package

4.1.2. Summary description of project context and objectives

Project context

Soil degradation is a serious problem in Europe. It is driven or exacerbated by human activity such as inadequate agricultural and forestry practices, industrial activities, tourism, urban and industrial sprawl and construction works. These activities have a negative impact, preventing the soil from performing its broad range of functions and services to humans and ecosystems. In the case of soil (and groundwater) contamination, it poses a threat to the land on its own reducing its fertility and modifying its natural carbon content and biodiversity. Furthermore, it can also impair the health of European citizens, animals and plants and threaten food and feed safety.

According to the European Environment Agency *“soil contamination requiring clean-up is present at approximately 250,000 sites in the EEA member countries, according to recent estimates. And this number is expected to grow. Potentially polluting activities are estimated to have occurred at nearly 3 million sites (including the 250,000 sites already mentioned) and investigation is needed to establish whether remediation is required. If current investigation trends continue, the number of sites needing remediation will increase by 50% by 2025”* (EEA 2007).

In terms of the type of contaminants, organic contaminants such as chlorinated aliphatic hydrocarbons (CAH) and total petroleum hydrocarbons (TPH) form the predominant pollutants in Europe, followed by heavy metals often related to mining and metallurgical industries. Organic contaminants are susceptible to chemical and biochemical (in-situ) degradation treatments although such treatments induce a temporal change of the soil redox equilibrium conditions aimed at degradation of these. The focus of UPSOIL is on chemical and biological remediation technologies for sites with organic contaminants because of the importance of their remediation for economic development throughout Europe. Although metals cannot be degraded by chemical or biological means in-situ remediation strategies aimed at organic contaminants may affect their mobility and bioavailability, primarily through changes in redox or acid buffering conditions. For this reason, in the UPSOIL project the consequences of chemical and (bio)chemical remediation on metal mobility are taken into consideration, to mitigate risks associated with metal pollution on sites with mixed metal and organic pollution.

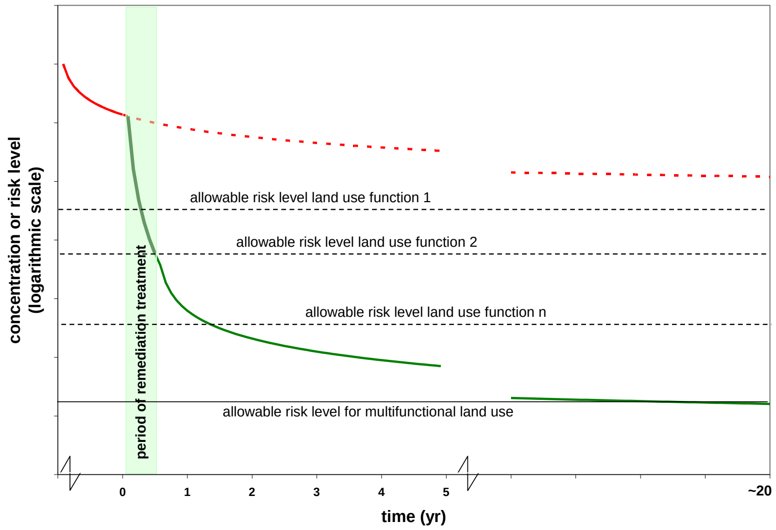
However, current chemical and biological soil remediation techniques are characterized by their cost-inefficiency and inability to recover soil sustainability. Uncertainty about time-scale at which soil remediation can be achieved is an additional frequent factor of these, especially when considering their in situ implementation, i.e. with no soil excavation and/or groundwater pumping.

Project concept and objective

Sustainable soil upgrading, as defined in the UPSOIL project, introduces a new soil and groundwater remediation perspective where, for the first time, **cost, time and environmental impact of chemical and biological remediation technologies are considerably minimized** through a series of specific actions. The remediation project is not only designed from an engineering point of view, but also from its economic and environmental one. This will be achieved by the **smart coupling of existing**

technologies and the development of new frontier technologies. The general approach for the aimed technologies is shown schematically in the next figure:

Figure 1.1. General approach for aimed remediation technologies. De red line shows the development of the concentration or risk level without active remediation. Active remediation is achieved within a set timeframe (here six months). This results in lowering the risk level to what is allowable for the intended land use function (here land use function 2). Also, soil biodiversity and environmental conditions are brought to a state where the natural degradation processes will lead to allowable risk levels for more sensitive land use functions within the foreseeable time of the normal land use cycle of about 20 years.



First of all, <u>**active remediation**</u> **is aimed at reducing risk levels down to the acceptable limit for the intended land use** (in the previous graph land use function 2). The time dimension here is set by the requirements of the redevelopment processes and is in the order of months. Optimisation is foremost on costs. This basically means reducing the amount of reactant(s) for which the following biochemical approaches are adopted (each of them has been further investigated in the associated WP):

- taking into account soil structure and properties in selecting the type of chemical treatment (WP2);
- developing reactant species that are more selective towards the contaminant (WP5);
- developing new optimized injection systems (WP4);
- following feedback driven remediation methodologies (WP6).

The cost optimisation already ensures that degradation of the soil matrix is reduced as compared to current technologies.

In addition, the UPSOIL concept aims to ensure that at no or limited additional costs, and still within a finite time period, **risk levels are further reduced down to multifunctional land use (<u>passive remediation</u>)**. The time frame here is in the order of decades, in line with the period of the land use cycle. For this, it is necessary that at the end of intensive remediation not only risk levels have been adequately reduced for the functional use, but also that viable microbial soil populations are present and environmental soil conditions are such that the natural attenuation capacity of the soil is restored (WP3). This means that the bioremediation and NA prerequisites are fulfilled and that these processes will undoubtedly lead to further reduction of the risk level. This of course greatly contributes to soil sustainability, but also means that the value of the property involved increases with time, as a more sensitive type of land use becomes possible.

The results of the project are a set of well-documented and tested in-situ (bio)chemical remediation technologies. More specifically, the products include:

- ✓ methods and procedures for cost-effective coupling of existing soil remediation technologies,
- ✓ improved remediation technologies that take into account soil properties and functions,
- ✓ methodologies for assessing the overall effect of remediation on soil sustainability,
- ✓ methodologies and indicators for assessing the viability of soil microbial populations and natural attenuation capacity after remediation,
- ✓ methods for targeted injection of remedial agents,
- ✓ contaminant selective remedial agents,
- ✓ methods for predicting the collateral effects of organics remediation on heavy metals leachability,
- ✓ methods and procedures for the use of feed-back driven monitoring technologies for the control of remediation works development,
- ✓ several SME involvements in various European countries/regions that have gained experience with one or more of these technologies,
- ✓ a market application plan will be made in close cooperation between partners and UPSOIL associated SME's, for UPSOIL approaches and the patented technologies.

<u>Project conception</u>

Funded by the EC, under the Seventh Framework programme (FP7), Collaborative funding scheme and theme 6 "Environment (Including climate change)" (Activity: FP7 ENV 2008.3.1.2.1. "Recovery of degraded soil resources") - year 2008, The UPSOIL project started the 1st of October 2009 with the Kick-off meeting being held in Bilbao (Spain) and following 3 years of intensive research work finalized on the 30th September 2012 in the final meeting in Barcelona (Spain).

The project is divided into a total of 7 work pakages (WPs), from which 5 are technical and 2 organisational (WP1 management and coordination and WP7 dissemination and end user consultation).

<u>Consortium</u>

The UPSOIL core is the Consortium. A total of **15 partners**, whose geographical distribution is shown in Figure 1.2. The UPSOIL participants constitute a well-balanced, multidisciplinary, and competent Consortium capable of the conception and consecution of the project objectives.

The six RTD Institutions (Tecnalia, VITO, Deltares-TNO, IETU, ECOIND, SGI) and one University (Wageningen University) safeguard a high scientific and technological quality of the project. The involvement of seven Technological and Environmental Companies (seven SMEs) and one Construction and Environmental Company ensure practical applicability and exploitation of results.

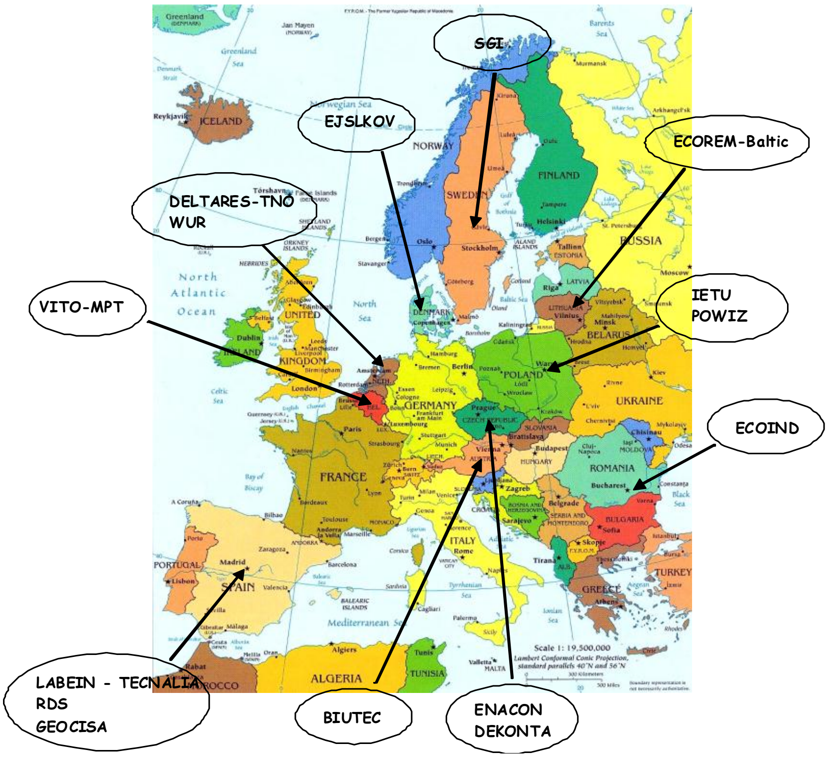


Figure 1.2. Partners geographical distribution

4.1.3. A description of the main S&T results/foregrounds

Following the objectives of the UPSOIL project as related above, the work progress and main achievements during these 3 years of project duration are detailed for each of the work packages:

Table 3.1 - Work packages list according to the Annex I of the Grant Agreement

WP Nº	Work package title	Type of activity[1]	Lead participant short name	Start month	End month
WP1	Management & Coordination	MGT	TECNALIA	1	36
WP2	Smart coupling: System based process technology	RTD	DELTARES	1	30
WP3	Smart coupling: Soil function sustainability	RTD	WUR	1	36
WP4	System Driven Injection	RTD	SGI	1	30
WP5	Specific Targeting	RTD	VITO	1	36
WP6	Feedback Driven Remediation	RTD	TECNALIA	1	36
WP7	End user consultation & Dissemination	OTHER	IETU	1	36

According to the Annex I of the Grant Agreement, all work packages start in month 1 and finish in the very last months of the project life (month 30-36). From the beginning of the project all work packages have run in parallel. This situation has been consolidated by existing interactions between all of them: use of the same field sites for several WPs testing, same samples for several WPs, one WP developed knowledge in another one, etc. Special attention is to be paid to the interconnectivity between WP2 and WP3 as both work packages are based on the smart coupling of existing technologies. Thus, whereas WP2 is focused on the active remediation phase, i.e. the stage in which remediation treatments are actively applied with the goal of a rapid and significant reduction in the contaminants concentration with a minimum soil matrix disturbance, WP3 starts when the active treatment finishes, namely the following passive remediation stage. Here the best conditions are set for long-term passive remediation (natural attenuation), ensuring that all potential redevelopment plans are possible.

WP2 Smart coupling: system based process technology

Leader: DELTARES
Participants: VITO, WUR, IETU, POWIZ, DEKONTA, ECOIND, BIUTEC

In-situ remediation technologies have progressed mainly along a "single-technology" track without taking into account the potential benefits form combining technological approaches. Advantages are to be gained from combining existing technologies either in space or time (treatment trains). With that, it is realized that a successful "smart coupling" approach to any in situ remediation of contaminated sites should take into account the geohydrology, geochemistry and contaminant distribution at a site, as well as the contaminant type(s). Insight in these factors allows an optimal application of one or multiple technologies from the wide range available in the in-situ remediation toolbox.

The aim of WP2 is to be able to define the most cost-effective remediation approach by integrating a balanced use of multiple technologies, based on the integrated system of contaminant conditions, soil system characteristics and functions. This smart coupling of technologies aims:

1. to maximize contaminant degradation;
2. to minimize disruption or depletion of soil chemical, physical and biological functions;
3. to minimize energy and material use and;
4. to optimize cost.

Within this WP, four tasks are identified that focus on a specific balancing approach. The third task 2.3 is focused on studying the effect of active treatments (biological and chemical) on the geochemical and microbial properties of the soil. For this reason, this task follows and supports previous tasks 2.1 and 2.2:

Task 2.1. Balancing Chemical and Enhanced Biological Oxidation technologies for the Remediation of Total Petroleum Hydrocarbons (TPHs) & Task 2.3. Minimizing the (side) effects of redox treatments on natural soil composition and functions.

This research area focuses on the smart coupling between chemical and enhanced biological oxidation of TPH contaminants based on soil system characteristics. The task started by finding a suitable TPH contaminated site: the Wegleniec site (Poland). Soil and groundwater sampling at the site selected in Poland, Wegleniec, a railway refuelling station which was contaminated with diesel from 1970-2000, took place in March 2010. A team of Deltares, WUR, IETU and POWIZ hand augered at ten locations, including a non-contaminated control location, for soil and groundwater samples collection. The experiment design was worked out by WP leader Deltares, in consultation with WUR, Dekonta and Ecoind. It included dissolution experiments with the LNAPL diesel samples, and oxidation experiments of LNAPL and soil samples with three types of oxidants: potassium permanganate, sodium persulphate and activated persulphate.

Potassium permanganate results

Results indicated that the effectiveness and efficiency of oxidative treatment with potassium permanganate are strongly dependent on soil type. In the peat samples and sand sample, permanganate was always fully consumed, primarily by oxidation of the soil organic matter (SOM), with minor degradation of the diesel contamination (TPH). In sand sample hardly any oxidisable SOM appears to be present. SOM is generally less affected in the fill and especially the clay samples, as evidenced by remaining permanganate at the end of the experiment and more effective diesel degradation. Interpretation of the results is hampered by the heterogeneity of the samples, both with respect to SOM as to TPH contents.

Sodium persulphate results

Once sodium persulphate oxidation is carried out, as expected, peat samples are much more reactive than other types of soils treated, especially when using permanganate as the oxidant. In general, with equivalent oxidant concentrations, oxidant consumption is slightly faster or equally fast (fill sample) for permanganate than for persulphate. However, the overall degradation of diesel contaminant and soil organic matter seems similar for both oxidants in all sample types. The opposite effect that these two oxidants have on soil pH is evident: more alkaline conditions arise from permanganate treatment, while persulphate leads to soil acidification. Permanganate treatment further leads to accumulation of manganese oxide, creating a long-term buffer for maintaining a high oxidation-reduction potential (ORP) in the soil. The reaction products of persulphate treatment are dissolved Na or K, and dissolved sulphate, that will usually be transported away from the treated site with water flow.

Ca-peroxide and activated persulphate results

Chemical oxidation experiments with Ca-peroxide and pH adjusted activated persulphate were also performed, both on a freshly sampled contaminated soil (more than 100 g/kg d.m. TPH) and on the same soil after 2-month Natural Attenuation (NA). A reduction of 60% was achieved over a period of 3 days for the freshly sampled soil. This required a large oxidant dose, however. For the soil that had first been subjected to NA, during which a 50% TPH reduction was achieved, the TPH reduction by the activated persulphate treatment was lower (28% after 3 days).

Polish field test

Based on the results of the laboratory experiments and considering other boundary conditions, it was decided to push these along onto a field-scale test (IETU, POWIZ, Deltares). This field test was conducted in the period between May and August 2012, comprising two separate injections of non-activated persulphate as an active phase of an in-situ remediation. After the second injection of persulphate nutrients were injected to stimulate the biological degradation to further answer WP3 research questions.The effect of the injection is only observed after 10 to 15 days into the monitoring and shows an increase in TPH-concentrations, which is as mobilization of TPH due to the oxidation of the organic matter by the persulphate. After the second injection of persulphate the mobilization of TPH is again observed both in the immediate vicinity of the injector as further downstream. However the amount of TPH measured in the groundwater after the second injection is far higher, in excess of 110 $mg \cdot l^{-1}$, compared to 15 $mg \cdot l^{-1}$ measured after the first injection. Furthermore, TPH concentrations increased in more monitoring wells after the second injection than it did after the first injection. Subsequent injections of the oxidant will oxidise more of the SOM resulting in an increased mobilisation of the contaminant of concern. The mobilisation of the TPH also indicates that the contaminant is readily available and may also be available for biodegradation.

Task 2.2. Balancing Chemical Oxidation and Enhanced Biological Reduction technologies for the Remediation of Chlorinated Hydrocarbons-(CAHs) & Task 2.3. Minimizing the (side) effects of redox treatments on natural soil composition and functions.

As in previous task, Task 2.2 was initiated by finding a suitable CAHs contaminated site. The site finally selected, the Brückl site in Austria, was a production facility of chlorinated aliphatic hydrocarbons (CAH) that was operational during the period 1930-1992, resulting in severe contamination of the subsurface down to 50 m and more. UPSOIL resources allowed for a drilling down to 20 m, above the main DNAPL (dense non-aqueous phase liquid) source zone, which was organised by Biutec and performed in February 2011. A team of Deltares, WUR and Biutec were present on the site to collect sediment material from the drilling. This was complemented by the collection of contaminated groundwater from already existing observation and/or remediation wells, and of pure phase DNAPL retrieved from the regeneration of active carbon columns currently used in the remediation process. The laboratory experimental design was worked out by WP leader Deltares, in consultation with WUR, Dekonta and Ecoind, and VITO. In analogy with the work in Task 2.1, laboratory experiments were performed with permanganate and persulphate (Deltares, Dekonta and Ecoind) and reductive dehalogenation (VITO).

<u>Potassium permanganate and sodium persulphate results</u>
Permanganate showed to be an effective oxidant for TCE and PCE, also when present in a complex NAPL mixture. The capability of persulphate to oxidize TCE is comparable to that of permanganate, while oxidation of PCE (and HCB) is less effective. The above-groundwater (AGW) sample collected from the Brückl site appeared more reactive with permanganate than the below-groundwater (BGW) sample: more oxidant was consumed and the soil organic carbon content was more strongly affected by the oxidation, being reduced to about 50% in the AGW sample compared to more than 60% remaining in the BGW sample. This suggested that the organic matter in the saturated zone is more chemically inert or otherwise more physically protected within organo-mineral complexes.

<u>Biological reductive dehalogenation results</u>
Moreover, reductive degradation experiments were performed by VITO. In March 2011, the degradation experiment was worked out, focussing on biodegradation of CAHs and chemical reduction (nano-iron and micro-iron). The experiment was set-up in October 2011 under anaerobic conditions with groundwater and aquifer material of the Austrian site delivered by BIUTEC. In the test set-up with sorbed DNAPL concentrations (very high CAH concentrations), significant reductions were observed in the poisoned control due to abiotic processes. When evaluating the data relative to the

poisoned control after 100 days of reaction time, the best CAH removal was obtained with nano-iron, followed by micro-iron. Biodegradation was limited or not existing within the first 100 days.

Lysimeter experiments

At the Brückl site, contaminated with CAHs, a different approach was chosen to that of the previous Polish site. As the contamination is situated at 30 to 50 m below ground, soil collected during the installation of monitoring wells was used for large scale column experiments to test the potential of various treatment options. Two columns were setup using aquifer material, site groundwater, and spiked with pure product regenerated from the activated carbon remediation setup currently used at the site (see Figure 1.3). In one column the natural attenuation capacity of the location was tested by creating optimum conditions through the addition of electron donor and nutrient media. The second column received identical amendments, with the addition of a dechlorinating culture to test the potential of bioaugmentation. Finally, nano zero valent iron was added to test the potential for chemical reduction. Measurements of the chemical and physical parameters (pH-value, conductibility, temperature and redox potential) were made continuously after flow through the soil columns. In addition, the CAH-concentration of the groundwater was analysed by GC/MS at least once per week.

The pilot application of zero-valent iron nanoparticles (NANOFER 25S) for the mix of chlorinated hydrocarbons present, confirmed the results of laboratory experiments and the high efficiency and safety of this method. However, the results indicate that while nZVI reacts with the contaminants, it also destroys the bacteria, as no bioremediation was observed after addition of nano iron.

Figure 1.3. Picture of the soil column experiments for Brückl site

Task 2.4. Minimizing active treatment, allowing maximal utilization of the intrinsic contamination degradation capacity of soil

Aquifer material from undisturbed aquifer cores and groundwater both taken at the Antwerp site, were used to performed a lab scale degradation experiment to evaluate the impact of chemical oxidants and reductants on the pollutants, microbial community, CAH-biodegradation capacity and soil OM. The results showed that, for the tested aquifer, chemical reduction had a much higher impact on the chlorinated contaminant concentration than chemical oxidants. This emphasizes the importance of considering the redox state of the aquifer during the selection of the chemical reagent. An important observation, with implications for the subsequent biological phase, is the impact on the

ORP, especially after chemical oxidation. The ORP was shown to increase significantly with the number of oxidant additions.

Applicability from legal and organisational perspectives

An overview of the soil pollution and remediation landscape in selected European countries was produced, to provide insight in the application potential of ISCO in Europe. The information was gathered by means of a general questionnaire that was completed by most partners engaged in the UPSOIL project, with input from national experts of the given countries who have access of the relevant data necessary for filling in the questionnaire.

General recommendations: new selection tools

Based on the experiments and pilots a number of selection tools were derived for environmental practitioners that will help to select the suitable chemical oxidation technology for the active phase. These selection tools take into account the type of contaminant of concern and the natural soil conditions affecting the oxidant consumption. Also, the effect of the active phase on the natural geochemical conditions is considered. Additionally, selection tools for the coupling of remediation technologies were also derived. An example of a selection tool is shown in Figure 1.4. Some of the lessons learned during the project or results could not be captured in selection tools.

These do's and don'ts were laid down in rules which can help guide the environmental practitioner in selecting the proper technology but also applying it in a cost-effective, timely and sustainable manner. One of the key messages is that laboratory testing and pilot testing prior to a full-scale application of any given remediation technology will save time and will turn a remediation more cost-effective in the long run.

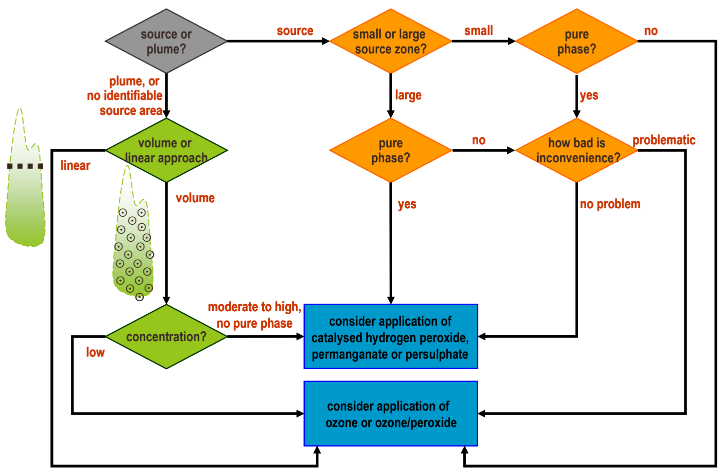


Figure 1.4. Selection tool of the appropriate chemical oxidation technology to apply depending on the type of appearance of the contaminant in the soil-groundwater system.

All the information here indicated is provided and extended on the following external deliverables available in the UPSOIL web page:

PUBLIC DELIVERABLES
D2.1→ divided into Part A and Part B: **D2.1A** External report: Definition of the conceptual modelling approach based on soil contaminant characteristics that provide the soil and groundwater samples required for

geochemical and contaminant content – Part A: Wegleniec site
D2.1B External report: Definition of the conceptual modelling approach based on soil contaminant characteristics that provide the soil and groundwater samples required for geochemical and contaminant content – Part B: Bruckl site
D2.3. External report: Present a methodology of parameters that determine effectiveness, efficiency and rates of contaminant remediation.
D2.5 and D2.8→combined into D2.8 **D2.8.** External report/journal paper: Conceptual methodology for determining a-priori screening for smart-coupling approaches based on biogeochemical analysis of soil-contaminant system.
D2.6. External report/journal paper: Methodology to identify subzones in the soils from contaminated field sites where the (lower) contamination levels are such that the natural intrinsic remediation capacity to timely achieve remediation target level is sufficient
D2.7. External report: An evaluation of most common European contaminant and geochemical site conditions to produce an overview for end-users of probable smart-coupling approaches.

WP3 Smart coupling: soil function sustainability

Leader: WUR

Participants: TECNALIA, DELTARES, VITO, IETU, ENACON, POWIZ, BIUTEC

The aim of WP3 is to use the assessment of the most cost-effective remediation approach as presented by WP2, in order to be able to assess process technology conditions that meet sustainability criteria for a lively soil and optimal soil matrix. Within WP3, the effect of selected degradation treatments is defined less in terms of the degradation of the contaminant. Rather, focus is placed on the impact of a treatment on subsequent bioremediation during the passive phase.

Although the applied remediation aims to reduce risk, remedial techniques could result in new conditions, which change the risk assessment. Therefore, another goal of WP3 will be to incorporate a tool for modelling and predicting the risks for ecosystems and human health associated to the presence of mixed contaminants (organic compounds and heavy metals) in the system before the active treatment takes place. WP3 objectives were listed in five tasks:

Task 3.1 Study of effects of selected degradation treatments

Using TPH contaminated samples (Wegliniec, Poland) the effect of chemical oxidation with (Modified) Fenton's Reagent at pH 3 or 7 with hydrogen peroxide added at one time (1x) or sequentially over the course of three days (3x) on bioavailability of the residual contaminant was studied. Results indicated that chemical oxidation increases bioavailability of the residual contaminant as opposed to no chemical treatment. Additionally it was found that the efficiency of the treatment was not only dependent on the type of chemical treatment, but also on the type of soil. Good regeneration of microbial degradation capacity was observed following chemical oxidation with Fenton's and Modified Fenton's reagent. No biodegradation occurred after permanganate and persulfate oxidation.

Additionally, batches were setup with two soil types (Loam with 10% organic matter and Sand with 1% organic matter), nutrient rich media, 1.9 g/L PCE, and 10% (v/v) of an active dehalogenating culture. Permanganate was added at low concentrations (0.5, 1, 2, 3, 4 g/L) to simulate edge of ISCO injection. Following oxidation, headspace analyses for residual PCE and CO_2 concentration were performed. Results show the impact of additional organic material in the loam sample on the efficiency of chemical oxidation (see next figure 1.5.)

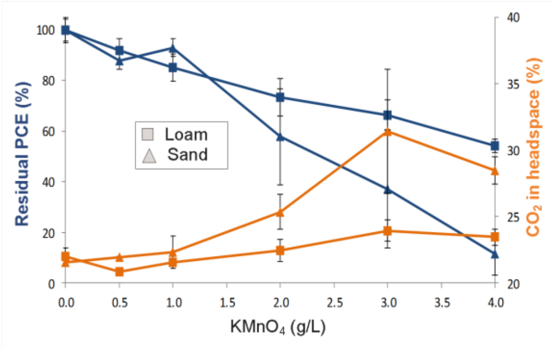


Figure 1.5. Results testing the degradation of PCE with permanganate treatment at different oxidant concentrations.

Task 3.2 Analysis of role of environmental conditions on presence and activity of biodegrading organisms

<u>Wegleniec site (Poland) – Lab tests</u>

Three diesel (measured as total petroleum hydrocarbons or TPH) contaminated soil samples collected at Wegliniec, Poland (W2-A, W2-B, and W3-B) were used for experiments where chemical oxidation was coupled to a biological phase. Chemical oxidants were permanganate, persulphate, Fenton's Reagent, and Modified Fenton's Reagent. Following the chemical phase, biodegradation was performed under fully oxidizing conditions with the addition of supplemental nutrients, in some cases. Measurement of dissolved constituents indicates that significant degradation of soil organic matter occurs. This yields increased concentrations of dissolved organic carbon (DOC) as well as macro-nutrients such as nitrate, nitrite, ammonium, and phosphate. In the case of microcosms where no nutrient amendment was performed, the mobilization of these dissolved constituents served as an important source of macro-nutrients for microbial growth. However, DOC also serves as an alternative substrate to TPH for microbial growth. Thus, the presence of DOC reduces microbial degradation of TPH. Experiments with and without nutrient amendment on sample W2-B indicated the necessity of nutrient addition for biodegradation. In microcosms without amendment, nutrient limitation appears to hinder biodegradation and respiration rates. Only minor degradation is observed in microcosms where the harshest chemical oxidation treatment degraded organic matter, mobilizing nutrients into the dissolved phase.

<u>Brückl site (Austria) – Lab tests (lysimeter tests)</u>

The lysimeter experiment, used in conjunction with WP2, is described in Task 2.2. Results indicate a significant reduction in the concentration of CAHs due to biological degradation. However, in the bioaugmented column, more biodegradation was observed, especially when spiking with higher concentrations of CAHs. Although these results were specific for the Bruckl location, the methodology developed is useful for the assessment of treatment technologies at a large range of sites.

<u>Wegleniec site (Poland) – Field test in conjunction with WP2</u>

Field test in Węgliniec site (Poland) was planned together with WP2 activities (see Task 2.1). Soil samples were taken from four wells during drilling of the wells and stored as archives. Sampling on the site performed during two sampling campaigns and field work. Five biological sampling campaigns took place in May, June and August. Groundwater samples were filtered either in the field or in IETU laboratory and the filtered material was frozen and sent to WUR for analysis. Microbial analysed were performed in WUR (see Task 3.3). Third injection in Węgliniec (in conjunction with WP2) was performed with nutrients intended for bacteria growth stimulation. Samples of groundwater from wells were taken in the area impacted by the injection on a week basis.

Task 3.3 Application of molecular techniques

Wegleniec site (Poland) – Lab tests

Initial molecular work focused on obtaining an understanding of the microbial diversity present at the Wegliniec site, Poland. The goal was to ascertain which portion of this community is associated with TPH contamination and therefore maybe responsible for bioremediation. Phylum level analysis performed thus far indicated a shift in diversity based on the contaminant concentration and indicated a number of phylum that could be associated with bioremediation. Additionally, in order to better implement coupled ISCO with bioremediation treatments, this study systematically analysed the impact of selected chemical oxidants on the TPH removal and the subsequent regeneration of microbial activity and diversity in two different diesel contaminated soils. During biological incubation, microbial activity and diversity were estimated by measuring respiration, the abundance of bacteria and the alkane monooxygenase gene *alkB*, and using denaturing gradient gel electrophoresis (DGGE). Through linking observed impacts of chemical oxidation and TPH (bio)degradation to changes in the microbial population, this study provides a systematic understanding of the overall processes behind coupling ISCO with bioremediation. Finally, in order to understand the impact of chemical oxidation on dehalogenation potential, molecular analyses were performed on batches from the Polish site described in task 3.1. Following chemical oxidation with permanganate on PCE contaminated batches with active dechlorinating microbial populations, an array of targets important for dehalogenation were analysed. Results indicate that dehalogenation potential is reduced due to ISCO, which was more prominent in Loam soil. Yet, although ISCO affects microbial community, bioremediation potential remains present, which could prove essential to a subsequent bioremediation step.

Wegleniec site (Poland) – Field test in conjunction with WP2

ISCO treatment with persulfate and biostimulation with nutrients were performed on a pilot scale at the diesel contaminated railway site at Wegliniec, Poland. Previous work with site material had investigated the effect of ISCO treatment on soil and contaminant properties, parameters essential to bioremediation, and microbial population diversity and biodegradation capacity. The pilot experiment incorporated the knowledge gained from microcosm experiments in the lab to field application, where heterogeneity and groundwater flow are present in a much larger system.

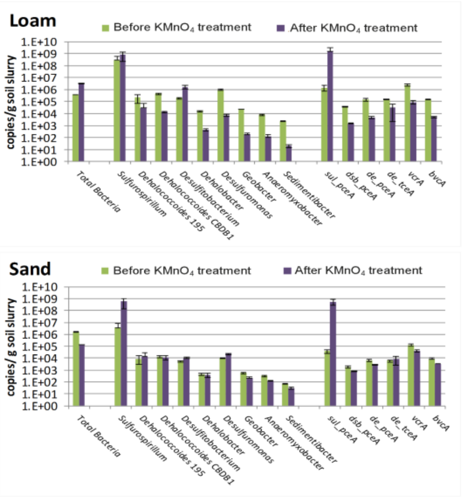


Figure 1.6. Comparison of microbial dehalogenation potential prior to and following permanganate treatment in loam (above) and sand (below).

Laboratory experiments gave a basic idea of parameters essential for the success of conversion from rapid chemical treatment to slower biological degradation. In addition to closely monitoring those groundwater physical and chemical parameters of importance, the size and biodegradation potential of the soil microbial community was monitored. Through investigating coupled ISCO and bioremediation at the field scale, an understanding of the impact of the treatment train on the microbial population in a heterogeneous open-system was gained.

Task 3.4 Biochemical treatment & heavy metal leachability

Chemical treatment of soil to degrade organic contaminants can impact the mobility of heavy metals when present. To determine both the extent of heavy metal mobility and the associated risk, WP3 aimed to develop procedures that predict the impact of biochemical treatment on inorganic contaminants. Samples both naturally occurring or at complex contaminated sites with mixed contamination of organic compounds and heavy metals from at least two locations were chosen. From lab tests following results and conclusions were obtained.

<u>Metals leaching/mobilization from oxidative protocols:</u>

- High leaching of heavy metals in persulfate treatments, related mainly to low pH (around 2-3)
- Cd, Cu and Zn are almost 100% mobilized with persulfate treatment

<u>Sequential extraction post-treatment:</u>

- Total concentrations of metals for pre-treated samples are higher than post-treated samples. This difference could be mainly related to metals released during the oxidation test.
- Higher content of the metals (e.g.Pb, Cu, Cr) can be found in the reductive fractions for the permanganate treatment rather than for the persulphate, probably as a consequence of the manganese oxides produced from the added permanganate during the oxidation process.
- High concentrations of Pb are extracted in phase 1 (exchangeable fraction) and 2 (related to carbonated species). However Pb is generally a very low mobile metal and these fractions could be the result of a washing-off process from the previous oxidative treatment.

Chromium behaviour:

- Original Cr(III) in the soil are significantly affected by oxidative treatments, changing partially into Cr(VI).
- 50% of total Cr mobilizes into water, appearing with a ratio of 1:1 for Cr(III):Cr(VI). Generally Cr(III) species are highly insoluble, so they likely exist as Cr^{3+} at low pH for PS treatment and as soluble complexes with low molecular weight organic acid (citric, fulvic,…) for PM treatment.
- 50% of total Cr remains in soil, as insoluble species ($Cr(OH)_3$). Low fractions of Cr(VI) can be found also in the soil, probably adsorbed to soil particles.
- Oxidative effect of PM seems to be higher, leading to higher rates of Cr(VI) both in soil and water. This could be related to a non-activated performance of PS.

General conclusions:

- Main problem was the inconsistency in total contents of metals from different analyses methods (maybe due to sample heterogeneity), which makes difficult comparison in terms of total contents
- Chromium can be transformed into harmful species Cr(VI), at least when high contents of Cr is present in the site.
- pH is a critical geochemical factor to be carefully monitored and controlled, since most of the metals become into more soluble (and leachable) species when the environment is acidified
- Methods
  - Simple batch leaching tests based on selected oxidant: easy and non-expensive, but the oxidant to be used should be known
  - Sequential extraction tests: prediction of metals behaviour under different conditions (activation of oxidant, acidic reagents, etc). It is more complex and time consuming.

Task 3.5 Environmental – Human health risk management

Toxicity of soil samples before and after their treatment by selected oxidant(s) were assessed by bioluminescent test using bacteria *Vibrio fischeri* according to European Standard EN ISO 11348-3 Determination of the inhibitory effect of water samples on the light emission of *Vibrio fischeri*. Set of ecotoxicity tests on selected samples at the end of their active chemical treatment was conducted. In addition, samples after biostimulation following chemical treatment were also performed. Performed ecotoxicity tests indicated significant inhibition of luminescence after the ISCO treatment. However, the expected main stressor comprised of mobilized heavy metals was not proved. The increase of ecotoxicity was detected also in case of samples with low heavy metals content where no metals mobilization occurred. The potential stressors inhibiting bacteria luminescence could increase bioavailable TPH and/or other aspects (e.g. various by-products of chemical treatment, ionic stress etc.). The effect of the increase of absolute concentration of bioavailable total petroleum hydrocarbons could stress bacteria with low heavy metals content. Furthermore, smart-coupling of chemical and biological treatments leads to the reduction of ecotoxicity probably due to further decrease of target contaminants concentrations and also due to the redevelopment of the initial conditions. The fact that risks due to chemical oxidation are mitigated by biological treatment supports the concept of smart-coupling of chemical and biological remediation techniques.

All the information here indicated is provided and extended on the following external deliverables available in the UPSOIL web page:

PUBLIC DELIVERABLES
D3.6: Development of a protocol that resembles the effect of (bio)chemical treatment on the heavy metal leaching and key factors that will be determined to minimize the risk of chemical treatment.

WP4 System driven injection

Leader: SGI

Participants: TECNALIA, VITO, IETU, ENACON, ECOREM-Baltic, DEKONTA, EJLSKOV

The objective of WP4 “System driven injection” is to take forward, design, pilot testing and test/demonstrate in full-scale an innovative detection-injection system, called MIP-IN. It can be used for in-situ remediation of sites contaminated with substances that are detectable in situ with a MIP-devise (Membrane Interphase Probe) and at the same time be remediated by pumpable/injectable degradative agents. The principle is given in Figure 1.7. The initial idea from SGI to combine simultaneous in situ detection and injection into one unit system was developed, designed and pilot tested in Denmark by Ejlskov A/S. This innovative system was then tested in full-scale at a site in Flanders by Ejlskov A/S with support by WP4 members and supervised by SGI and results compiled and evaluated in supporting deliverables. Objectives of WP4 were initially listed in four tasks, three deliverables, and one milestone.

Task 4.1: Selection of chemical oxidant, including evaluation of possible risks

Initially, the full scale implementation was planned to be performed at a site, pre-selected by Ecorem, in Klaipeda harbour, Lithuania. Initially a conceptual model of the Klaipeda site was presented by VITO. It showed that contamination, geology and hydrology were in general very complex, and to some degree not well known, which made the site not suitable for the test. Finally a complementary site was found in Flanders with separate vertical layers of DNAPL and LNAPL. The full-scale test was thereafter designed for the Flanders site. To select optimal site-specific chemical oxidant, lab tests were performed by VITO to measure the matrix demand and the degradation of the contaminants. The matrix demand was found very high, i.e. 20 g oxidant/kg soil (wet) for both permanganate and persulphate. Based on results from the degradation test permanganate was the best oxidant for degradation of all pollutants, except dichloromethane. $NaMnO_4$ was chosen for the full-scale test. Possible risks coupled to full-scale in-situ chemical oxidation (ISCO) at the Flanders site were described by Enacon in a risk assessment report. Site settings, contamination extent and potential side-effects of the chemical oxidation technology were taken into account in the risk assessment.

Task 4.2: Development and design of injection system, including pilot test, evaluation

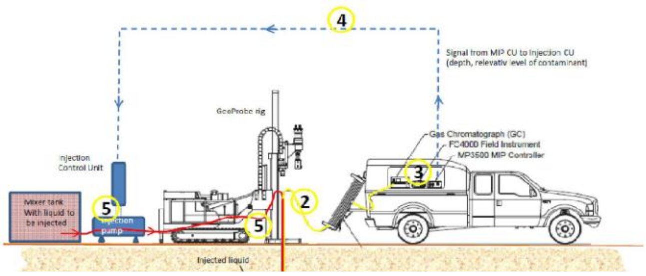
A new innovative designed system, called “MIP-IN”, has been developed by Ejlskov. It is based on system driven injection with integration between Membrane Interphase Probe (MIP) and injection delivery system. This system combines the function of MIP and injection making it possible to do detailed detection and targeted mitigation of contaminant in one operation. A patent application for the innovative probe was thereafter taken forward (Ejlskov, VITO), sent in to, and accepted as a valid application by the patent authority.

Figure 1.7. - Description with illustration/flow chart of the MIP-IN process.

The operational step 1 to 6 is an "injection process cycle" that occurs for each 0,3 m depth interval during the *vertical top down penetration of the MIP-IN probe into the soil.*

1) Volatile contaminants enters the MIP device and the volatile contaminants are detected over 0,3 m vertical soil column.
2) App. 25 measurements/samples from each 0,3 m depth interval are transported by the carrier gas to the field GC (giving a very high data resolution for detecting volatile contaminants).
3) The field GC signal from the 0.3 m interval and correlating depth interval is shown on the interface. The MIP signal response is logged automatically.
4) When contamination is detected the operator has to define a corresponding volume of solution to be injected at the given 0,3 m interval. The volume is entered on the interface (the lap top) and the program gives a signal to inject this volume when the injection part of the probe is at the same depth as the corresponding MIP signal.
5) Under pressure the injection pump delivers the volume of solution defined for a given depth interval. Pressure, flow rate and volume delivered are logged for each depth interval.
6) The solution is entering the soil under pressure.

If wanted the injection process can be stopped at any time and only the actual injected volume is logged or more solution may be injected by adding a second volume of oxidant to the first volume entered.
When injection is finished the probe is pressed down to the next 0.3 m (1 foot) depth interval.



Task 4.3: Implementation of full scale with successful delivery of selected chemical

The full scale test of the MIP-IN probe was performed by Ejlskov A/S, with assistance and over viewing by majority of the WP4 members, in the period 15th-18th of March 2011 in the Flanders site. Totally 14 ground-water/monitoring wells were constructed during which soil samples, both undisturbed and disturbed, were taken for further tests and 3.8 m^3 of a water solution containing 83 kg $NaMnO_4$/m^3 was injected in three different injection spots with injection levels varying between 2-7 m below surface level (Figure 1.8):

1. The main objective of MIP-IN 1 spot was to achieve site specific injection knowledge about formation "absorption" capacity, formation counter pressure and radius of influence (ROI). Visual response was detected in the 2-3 closest monitoring wells.
2. Injection in MIP-IN 2 was conducted 5.4-6.9 m below ground level. Multi-loggers, placed in all monitoring wells around MIP-IN 2, monitored the outcome of the injection.
3. MIP-IN 3 was mainly conducted to assure the bio-trap/bio-socks (WP5) in MW6 were affected by permanganate.

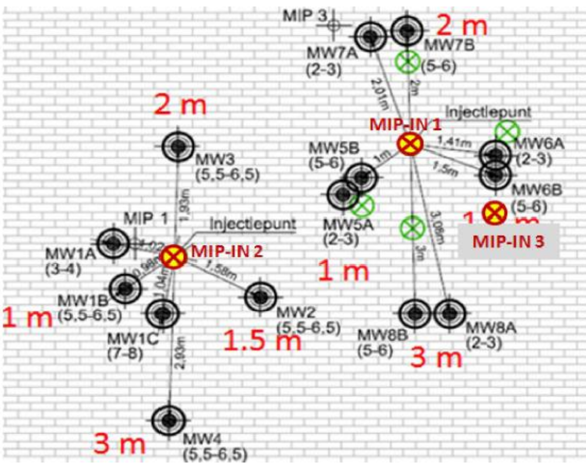
During the full scale injection, and parallel to automatic logging (Task 4.4), manual monitoring of basic field parameters (pH, electric conductivity, redox, soluble oxygen, and temperature) were performed in selected wells just before, and during injection. The full-scale test of the innovative detection-injection probe (MIP-IN) was successful. After the test, Ecorem reported the progress of the project to OVAM.

Task 4.4 Monitoring the outcome of the full-scale treatment

In order to be able to study the variation of chemical properties before and after oxidant injection a sampling/analysis/monitoring plan was taken forward. Totally six sampling events were performed: two sampling events before the injection and four sampling and analysis events following the full-scale test (1, 3, 8 and 16 weeks after the test). Field parameters (pH, electric conductivity, soluble oxygen, and redox) were manually measured before and during injection by VITO and SGI. Additionally, before, during and after injection field parameters were measured by automatic logger systems taken forward and evaluated by Tecnalia. The outcome, evaluated based on manual comparison of data and on the outcome from a computerised visualization program (the latter performed by IETU), showed temporary and limited reduction of some CAH and BTEX in some wells. This was in line with organoleptic observation of oxidant in these wells, but with no consistent trend throughout the four events after the test. This was in accordance with expectation due to the fact that the full scale field test was not designed for remediation of the site. However, spikes in chloride concentrations were found directly after injection in some wells, possibly indicating CAH degradation by the injected oxidant.

For further proofing successful delivery of oxidant, background information and the outcome of the test were continuously registered by Tecnalia in cooperation with WP6 via six stationary multi-parametric loggers (MIP-IN2 area, Figure 1.8) and four small temperature loggers (part of MIP-IN1 area, Figure 1.8), all placed in different levels. In addition, and in cooperation with WP6, a computerised system was developed (IETU, Tecnalia), based on data from these loggers, as wells as on the chemical data obtained within WP4 from the site. The automatic monitoring/logging helped tracking the injected oxidant for the WP6 modelling of flux speed, depth, ROI, etc. In addition, two types of changes, flashy and long term, were found in the logger data. The former may be linked to oxidant arrival and the latter to changes in environment/background and probable contaminant degradation.

Figure 1.8. - Placement of monitoring wells (black spots; well label and filter level given beside each well) and injection points (red-yellow rings). MIP1 and MIP3 correspond to some of the points where the initial MIP-investigations were performed



<u>Final conclusions</u>

The MIP-IN system has several clear advantages compared conventional injection systems. Present version of the MIP-IN system is a flexible, operational and solid system that can be further tested in other in-situ remediation projects. Impact indicators to be used to verify the gains of the MIP-IN system are:

1) **Reduction in total project time**: the total project time will be reduced due to targeted injection deliver more effectively a balanced volume of the degradation agent to the contaminant where situated (volume equivalent to the total need including detected level of contaminant). The project time will be reduced further as the investigations prior to injection can be reduced as well as the delineation investigations needed between the first and a second injection campaign.
2) **Reduction of volume to be injected**: the volume of remediation products can be significantly reduced as the liquids only are injected at the levels where contaminants are present.
3) **Reduction in injection time**: as the required volume of product is reduced, the time needed for injection will as function hereof also be reduced. Reduced total time span of the project is obtained due to less consumption of hours during the project and due to increased efficiency. Possibly also less number of injection campaigns is required.
4) **Reduction in total remediation costs**: reduction in volume of (often costly) remediation liquids to be consumed is obtained. Required investigations prior to the first injection are minimised as well as additional delineation between a first and second injection campaign. Time consumption in the field during injections, in general and number of mobilizations, is significantly reduced.
5) **Increased sustainability**: by targeting the reagent towards only the contaminant, non-polluted soil is less subjected to the reagent. Additionally, the technology may give reduced risk of negative environmental impacts as smaller volumes of product are injected. Hereby, use of less amount of reagent contributes to an increased sustainability of the technology, as well as reduction in transport energy and CO2 exhausts by reduction in mobilisation/demobilisation events at the site. Investigation and remediation is done at the same time and target injection may reduce number of separate injection events in order to reach remediation goals. Further, optimized effect of the remediation produc injected is obtained due to high flexibility of the system e.g. different products, “mixtures”, flow rate / pressure, and concentration variability.

Whereas the <u>main disadvantages</u> of the system are:

- Limited injection depth due to relatively wide injection probe, compared to a regular direct push probe.
- MIP equipment can be sensitive to injection fluids (e.g. chemical oxidants).
- Highly trained staff has to be present on site with negative impact on project cost.

<u>Evaluation of risks</u> was done during this period by Enacon based on the significant change in groundwater composition occurred only in wells where sodium permanganate was visually observed. The main observed changes were:

- increase in sodium (Na) concentration;
- increase in chloride (Cl) concentration;
- generic drop of concentrations of organic compounds during the initial sampling event(s) (with exceptions);
- gradual recovery to the conditions observed before the MIP-IN test;
- temporary increase in chromium (Cr) concentration. In general, it could result from introduction of Cr to an aquifer as impurity in oxidant solution, and/or Cr

mobilization due to change of redox conditions and/or Cr mobilization due to oxidation of organic matter that absorbs metals. In this particular case, it seems Cr mobilization occurred temporary and due to the oxidation of organic matter that absorbed metals (probably local soil contamination by Cr not discovered by the previous investigations).

All the information here indicated is provided and extended on the following external deliverables available in the UPSOIL web page:

PUBLIC DELIVERABLES
D4.3 Demonstrator/Public: Successful delivery of the chemical

WP5 Specific targeting

Leader: VITO

Participants: TECNALIA, DELTARES, WUR, IETU, ECOIND, ENACON, POWIZ, RDS, BIUTEC, GEOCISA

The aim of WP5 is to develop targeting oxidants/reductants, which implies:

- As less as possible interaction with the soil matrix (1) for not losing expensive reagents (Cost_Efficiency) and (2) for not effecting the soil matrix (Sustainability)
- Reactants can be 'attracted' to the NAPL, meaning preferential reaction with the pollutants

In order to achieve WP5 objectives, five different lines of research (concepts) were initially planned, although works finally started in four of them: the first focused on the soil protection, the remaining three on the improvement of the reactants (oxidants/reductants). Approach 5 (activators) was only theoretically considered at the start of the project, but no resources were available within UPSOIL to elaborate this idea further so it was initially invalidated.

Four potential concepts for specific targeting have been explored practically within the UPSOIL (see Task 5.1) towards (1) packing of oxidants/reductants in selected coatings (WP5.2/WP5.3) and (2) Delivery of the oxidant/reductant in NAPL/aquifer (WP5.4 & WP5.5). A field trial with a selected product (WP5.5) was also considered but not found feasible within the UPSOIL time and resource frame. Not all approaches reached final stages in WP5. Indeed, only 3 out the initial 10 approaches were finally delivered as defined in Task 5.4 and 5.5 (see table 1.2).

Concept	Approach	Partner	Results Task 5.1	Results Task 5.2/5.3	Further research lab scale Task 5.4/5.5
1 Protection soil	1a Temperature (ox)	Deltares	More tests needed	OK	PM & PCE
	1b Phosphate (red)	Deltares	Effect observed	Not considered due to available time	No
2 Hydrophilic packed particles	2a Cyclodextrines (red)	VITO	More tests needed	Not very promising	No
	2b Dithiothreitol (red)	VITO	More tests needed	Precipitates, pH issue	Optimize conditions
	2bb Thioglycolate (red)	VITO	Starting!	Precipitates, pH-issue	No
	2c Caprolactone packed particles (red)	Tecnalia & VITO	Starting!	Results are promising, More research needed	Additional characterization Reactivity test
3 Hydrophobic particles	3a Paraffin wax oxidant (ox)	Ecoind	Promising	Not stable in water	Improve particle - more stable in water
	3b Carnauba wax packed oxidans (ox)	Ecoind	More tests needed	Not stable in water	Improve particle - reactivity
	3c Carnauba wax packed FeS (red)	VITO	More tests needed	Not considered	No
4 Emulsions	4 Emulsified ZVI (red)	VITO	Promising	OK	Extra column tests

Table 1.2. WP5 approaches progress

Task 5.1 Selection of coating materials/approaches (level 1)

Concept 1 - Protection of soil: aims at targeting via protection of the soil against reactants by using something that protects organic matter & minerals in the soil. Selected 'coating materials' (the term 'coating material' was allowed to be quite broad):

- <u>Approach 1a:</u> Temperature (applicable for chemical oxidants): Decreasing temperature is expected to lower degradation rates of the soil organic matter more than the degradation rates of pollutants; As such lowering of temperature can lead to more selective
- <u>Approach 1b:</u> Phosphates (applicable for reductants): Phosphate is known to adsorb well to iron oxide mineral surfaces, and can as such potentially protect oxides form reductive dissolution.

Concept 2 - Hydrophilic packed particles: focuses on particles 'packed' with a hydrophylic coating that migrate well in the groundwater, but that can have a 'chemical lock' to interaction with NAPL/pollutants and to be active near water-NAPL interphase. The following hydrophilic coating materials were selected:

- <u>Approach 2a:</u> Cyclodextrines are large molecules that possess a cavity that can host more hydrophobic molecules like reduced iron particles, which are in that case expected to have a reduced tendency to aggregate and an imporved transport in the groundwater.
- <u>Approach 2b:</u> VITO decided to make a complex of ferrous iron with DiThioThreitol (DTT).
- <u>Approach 2bb:</u>similarly to the previous approach VITO decided to make a complex of ferrous iron with Thioglycolate (TGA),
- <u>Approach 2c:</u> Polymers (rosins and polycaprolactone) are rather hydrophilic for complete coating of the reductants/oxidant. Coating dissolves in NAPL.

Concept 3 – Hydrophobic particles: aims at developing hydrophobic transportable particles that can enter in NAPLs. A large number of polymeric coatings were listed and evaluated theoretically; The following coatings, soluble in NAPL, were selected for labscale work:

- <u>Approach 3a:</u> Carnauba wax, polyethylene wax
- <u>Approach 3b:</u> Palm wax, Palm oil

Concept 4 – Emulsions: micelle-like particles, oil was selected as coating for production of emulsified reductants.

- <u>Approach 4a</u>: CAH present as NAPL in source areas may be taken up in iron containing vegetable oil micelles, allowing for a more targeted reaction of ZVI with the pollutants.

Task 5.2 & 5.3: Packing of oxidants & reductants in coatings (level 2)

<u>Approach 1a: Temperature – Oxidants</u>

The effect of temperature on relative oxidation rates, i.e. of contaminant versus soil organic matter was investigated, through a series of permanganate oxidation tests on isolated organic materials like cellulose, anthracite, reed and forest peat, and oak wood. This was complemented with persulphate tests in the second period, and with tests on pure pyrite and clay mineral samples. Permanganate was consumed by most of the OM-types, except for anthracite, indicating oxidation of the OM, whereas persulphate was hardly consumed, indicating no oxidation. The oxidation rate between the types of OM and permanganate differed, with the fastest oxidation of reed. The test with Pyrite learned that $KMnO_4$ oxidant consumption increased when the pH decreased. With $Na_2S_2O_8$, less oxidant was consumed at 4°C as compared with at 16°C

Appraoch 1b: Phosphates

It was not further elaborated as choices needed to be made with the limited remaining budget. In addition, it appeared that a patent is already existing describing this approach.

Approach 2a: hydrophilic coatings – cyclodextrins surrounding FeS

Cyclodextrines are large molecules that are oligomer derivatives of glucose with a cavity which can host hydrophobic molecules. Attempts were made to incorporate small iron sulphide particles in the cavity, which are powerful reducing agents used for in-situ dechlorination of chlorinated hydrocarbons such as chlorinated ethenes or ethanes. Reduced iron particles which are coated with polar molecules are expected to have less tendency to aggregate which will facilitate their transport in groundwater. VITO did tests with α- and β- cyclodextrins by equilibrating a solution of the cyclodextrine at first with ferrous iron and in a second step sodium sulphide was added under nitrogen atmosphere. Three consecutive tests were performed in which the ratios between cyclodextrin, iron, base and CAH were varied. Further investigations revealed that the activity that was observed was mostly linked to the precipitate fraction, which is not incorporated in the cyclodextrines. It was concluded that this approach was not promising.

Approach 2b: hydrophilic coatings – dithiotreitol–FeS-compounds

Inorganic iron sulphides are known to promote chemical dehalogenation of VOCL. Iron sulphide complexes also exist in biological systems that perform biochemical reductions. In these systems, iron is typically complexed by organic ligands. This may be an approach which may also be useful to create catalytic iron sulphide based molecules which are soluble and mobile in the subsurface. VITO pursued complexes of ferrous iron with DiThioThreitol (DTT). The latter is a small molecule that has two sulphur atoms that can form a catalytic complex with iron, while it also has two hydroxyl groups that are expected to provide a polar surrounding to the complex which may facilitate its transport in groundwater. Different ratio's between dithiothreitol and ferrous iron and different pH-conditions were investigated by VITO. Only the lower ratio DTT/Fe of ½ showed significant removal of PCE at a pH of 8 as compared to negative controls, but the reaction was incomplete. When the pH was increased to 11, a fast degradation of TCE was observed. Addition of extra dithionite also activated the 1:1 complex at pH 9. The concept was considered to have potential after further optimisation.

Approach 2bb: hydrophilic coatings – Thioglycolate–FeS-compounds

Following a similar principle as with DTT-iron complexes, it was evaluated complexes of ferrous iron with thioglycolate (TGA). The latter is a small molecule that has one sulphur atom that might form a catalytic complex with iron, while it also has a carboxylic group that is expected to provide a polar surrounding to the complex which may facilitate its transport in groundwater. Three molar ratios between TGA and Fe were tested, each at 3 pH values. At the beginning all test conditions showed clear solutions, without any precipitates. However, after addition of dithionite, all test conditions with TGA showed precipitates (to varying extent). There were no significant differences in the rates of decline of PCE for any of the test conditions, which all were similar to the negative controls. The addition of dithionite as an electron donor did not activate any of the TGA + ferrous iron conditions. No significant amounts of degradation products were observed. Because any evidence was found for enhanced catalytic activity of combinations of ferrous chloride with TGA in a number of different conditions as compared to ferrous chloride alone, this route was not pursued.

Approach 2c: hydrophilic coatings – rosin & polycaprolactone approach

New attempts for using polycaprolactone as coating were made by Tecnalia supported by VITO, following 2 ideas:

Polycaprolactone packed ZVI:

- Batch test in aqueous medium unsuccessful due to poor water solubility
- Batch test in organic medium unsuccessful: once PCL get in contact with water it becomes insoluble!

PCL-POE packed ZVI:

- TEM images of the POE-PCL micelles show a great hetereogenity in terms of size and morphology of particle. It is not possible to ensure if the iron is really inside
- The solubility in DNAPL (TCE) is not good (not clear if it is completely dissolved)
- The prepared suspensions show better stability than bare nanoparticle suspensions

A reactivity test with particles prepared by Tecnalia was performed at VITO, but the nano-ZVI-particles were not found reactive. Ecoind also performed test with Polycaprolacton as coating for chemical oxidants. Spherical and chemically stable micro-capsules were obtained when Polycaprolactone was the packing material.

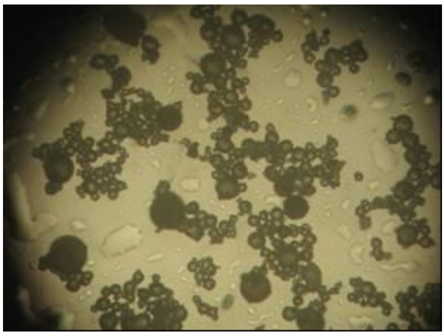


Figure 1.9. KMnO4 packed in melt PCL (21.5%)

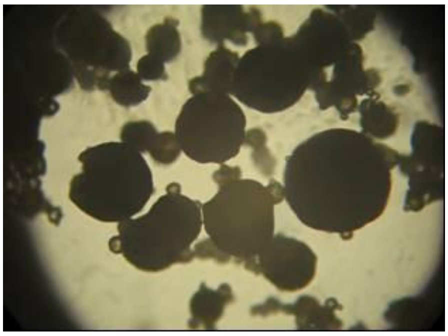


Figure 1.10. KMnO4 packed in melt PCL+Stearic acid – double layer

Approach 3a: Carnauba wax packed oxidants (Ecoind)

Starting from the previous results, packing in wax blends targeted to increase wax solubility, in case of Carnauba, and increasing the melting and degradation point, together with reducing the adherence, in case of Paraffin. Many blends were tried and the selected ones allowed preparation of spherical micro-particles. Testing the microcapsules for the permanganate release showed that:

- burst started rapidly (about one hour) and evolved quite slowly, along 2 or 3 days;
- after the burst period the permanganate concentration stayed constant.

Reactivity of KMnO4 microparticles packed in Carnauba-Paraffin wax blends

The newly produced micro-particles well reproduced the size of those obtained when one, pure wax was used as packing material. Reactivity was checked in mono-component, three-phase DNAPL (PCE – water – microcapsules) and tri-component, three phase NAPL (PCE – TCE – Diesel – water) systems. For the monocomponent system the results showed that: about 50% of PP ($KMnO_4$) is released from packed PP (PPP) in between 1 - 24 h and this is in good correlation with the quick „burst" established in release tests, the burst phase was followed by slow release, up to 91%, for the rest of 30 day testing period and PCE degradation still followed a different pattern and its reduction yield increased from 33% (day 1) to 93% (day 30), this indicating that the released PP, in presence of PPP remained reactive. In case of tri-component system, a competition was noticed between PCE and TCE degradation: TCE was much faster degraded, for PCE quite similar decrease profile was noticed, but the overall DNAPL reduction was lower than in the mono-component case (58% after 30 days).

Experimenting other techniques for encapsulating Potassium Permanganate
The feasibility of preparation techniques, other than spray congealing/drying or spray coating was investigated. Laboratory research was carried for obtaining microcapsules of $KMnO_4$, using biodegradable polymers. The experienced methods were:

- Insitu polymerization
- Coacervation by thermal change, melt encapsulation and solvent evaporation
- Double-layer coating.

Among the experimented techniques, double-layer microcapsules seems the most promising, at least from the perspective that the oxidants is reactive in presence of water, but it should be released mainly in contact with organics. Working on the preparation working parameters when applying a stearic acid (AS) as second layer on the CW-permanganate, a sigmoidal release curve can be obtained, delaying the release up to 24 h. Improvements are still necessary to: further delay release and increase the active (permanganate in our case) concentration in the initial micro-capsules.

Task 5.4 &5.5: Delivery of oxidants & reductants (Level 3)

Approach 1a: Temperature – Oxidants
Futher tests were performed at 24°C and 16°C with persulphate and PCE contaminated aquifer from the Brückl site as well as with toluene contaminated aquifer from the Wegliniec site. Oxidation of aquifer material of the Wegliniec site with $KMnO_4$ shows an effect with temperature. Lower temperature gives lower oxidant consumption. This indicates that applying lower temperatures when injecting $KMnO_4$ can decrease the oxidant demand of the soil matrix. Oxidation of the aquifer material with $Na_2S_2O_8$ did not show an obvious oxidant consumption or difference at both temperatures. Oxidation of the Brückl product with $KMnO_4$ showed partly the same effect as oxidation of DNAPL PCE with $KMnO_4$. In the first part of the experiment where the oxidation of PCE and TCE takes place, no effect of temperature is observed. The dissolution rate is rate limiting. As soon as HCB is left, the temperature starts to play a role. Applying lower temperatures when injecting $KMnO_4$ at a site with PCE and TCE, but also compound that oxidizes much slower less consumption will have a positive effect on the oxidant demand of the soil as long as PCE and TCE are oxidized. As soon as they are finished and the slower oxidizing compounds are left, a lower temperature will not have a positive effect anymore.

Approach 4: Micelles – emulsified ZVI & FeS
Based on a review of the scientific literature and experience of earlier experiments by VITO, three formulae for preparing emulsified particles of zerovalent iron (ZVI) were prepared and characterized. One was the original and patented method for preparing

EZVI which was used as a reference (EQ), another one was published by Berghe et al (EB) and a third one was a recipe made by VITO (EV). In terms of emulsion stability, the original formula EQ was the least stable when it was used without addition of reduced metal particles. However, in the presence of reduced metal particles, it yielded the most stable suspensions, which also contained the highest concentrations of metallic particles. The other two emulsions both showed some settling of metallic particles which were not included in oil droplets. Emulsion type EV apparently had more reduced iron particles in suspension than emulsion type EB.

When combined with nano-ZVI, emulsion type EV had the highest rate of TCE-reduction and of production of C2-alkanes, followed by emulsion type EQ and emulsion type EB which had the lowest rates. Emulsions that were made based on the same three recipes with iron sulphide and microscale ZVI were not active (while microscale ZVI alone degraded TCE completely).

Column tests were performed by VITO to investigate the mobility in soil and effectiveness for reductive dechlorination. The column test setup is shown in the picture below which was taken after percolation of the columns with 20 pore volumes of groundwater. It can be seen that significant migration of ZVI was only observed with straight nano-iron (columns 3 and 4) and with the emulsified nZVI type EV (columns 5 and 6). The emulsified iron type EQ dit not move through the columns (C7 and C8), which was probably caused by the disintegration of the emulsion upon its dilution by groundwater. Emulsified nZVI EV showed improved mobility as compared to unmodified nZVI. The effluents of columns with pure nZVI and with emulsified nZVi type EV had significant amounts of degradation products of TCE. The chlorinated daughter products cDCE and VC were formed in higher quantities for the emulsified nZVI than for the straight nZVI. The final degradation products which are free of chlorine (ethane and ethane) were formed in comparable quantities for both test conditions. The effluents of the control columns and the columns with emulsified ZVI type EQ showed no reaction products.

Figure 1.11. Column experiments in VITO for nZVI and emulsified nZVI testing

All the information here indicated is provided and extended on the following external deliverables available in the UPSOIL web page:

PUBLIC DELIVERABLES
D5.3→ divided into Part A and Part B
D5.3A field site efforts & labscale tests
D5.3B Report on additional labscale testing

WP6 Feedback driven remediation

Leader: TECNALIA
Participants: IETU, VITO, DELTARES, ECOREM-Baltic

Following UPSOIL's aim, WP6 main purpose is to significantly optimise the process performance by following a feed-back driven remediation approach, thus improving the cost-effectiveness and reducing the time frame of the active restoration measures.

In order to achieve this, a dynamic work approach is followed, with enough flexibility to adapt the in situ process control in real time as new monitoring information becomes available. This is done by means of a combined real time monitoring and numerical modelling system. Partial objectives of WP6 were initially listed in five tasks as follows.

Task 6.1.- Setting of site-specific remediation objectives and analysis of the application domain – reminder from previous first reporting period

The objective of Task 6.1 was to set remediation technologies operational factors and key monitoring parameters as an internal shared database between the participants of the work package, and to describe the domain or monitoring system including relevant physical and technological constraints. Yet, before carrying out any particular activity in task 6.1, the approach for WP6 as well as the work plan was defined in detail by TECNALIA, IETU, VITO and DELTARES. An extensive literature study on the use of modelling for different remediation technologies, and more in detail for ISCO treatments, was carried out. As a result, a selection of key monitoring parameters and their variations according to some of the different oxidants/reductants used in ISCO treatments was also done.

The application domain was described as a combination of a data compilation and analysis system (or real time monitoring and modelling system). The combined tool was broadly defined as a data collecting loop as follows (see Figure 1.12): remediation operations start on site (ex. injection of reactants associated to an ISCO treatment). Loggers placed in monitoring wells around the treatment area collect continuously basic chemical data. A wireless communication system sends real-time data from the loggers to a nearby field PC. In the PC there is the data-management software that collects and stores all the data. The PC is connected to Internet so that the data-management software is accessible for the Consortium. The modelling tool developed within WP6 is then fed with the online data as well as additional field parameters measured during previous site investigation works. A newly developed modelling tool (or data management software) is then able to translate measured parameters into the presence of a particular reactant and contaminant degradation rates. These will then be checked against previously established goals and following feedback remediation instructions, further decisions will be made (ex. re-injection, increasing the quantity of reactants).

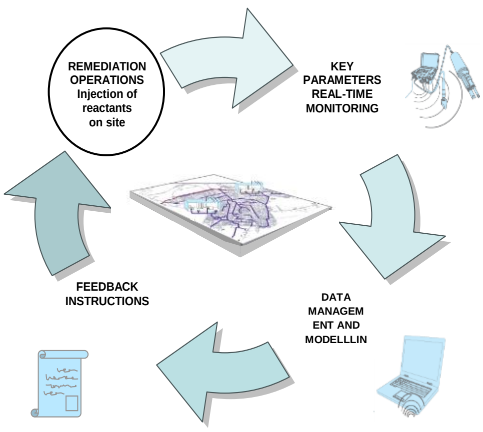


Figure 1.12. Feed-back remediation conceptual scheme

Task 6.2.- Computational characterisation of the defined model and Task 6.3.- Design of a monitoring and data analysis system

These two tasks have been grouped into a single task where the new full-featured software toolkit was thoroughly described both in terms of the mathematical model that lies behind it and its architectural and component structure. The numerical model objective is to fully or partially define the behaviour of the soil recovery process, including an outline of one or more possible computational approaches. It was exclusively developed by IETU. The model developed in UPSOIL project has a form of Microsoft Excel spread sheet coupled with monitoring data and is composed of two main calculation parts. The first one is designed for the summarisation and estimation of initial physical and chemical conditions. These conditions are calculated for each monitoring point and are distance averaged for the injection point. Detailed list of calculated parameters can be found in the table below. Results of these calculations are used partially as an input to the second model part: the hydrogeochemical model (PhreeqC), which calculates the future status of groundwater along the flowpath between the injection point and each monitoring well. Subsequently, outcomes from the PhreeqC model can be imported to the spreadsheet as:

- Tables,
- charts presenting changes of physical and chemical parameters,
- maps of the monitored area with the interpolation of simulated parameters.

Task 6.4.- Implementation of the system – Field testing and Task 6.5.- Validation and final conclusions

These two tasks were grouped into a single task where all tests sites where the feedback driven remediation has been put into practice are described in detail and final conclusions and recommendations are presented. The feedback driven remediation has been tested in three different sites, with different geological and chemical backgrounds as well as associated treatment: The Flanders, Poland (Wegleniec) and Spain sites.

<u>Flanders test site</u>
During the Flanders test site, both WP6 and WP4 technologies and practices were put in practice, as part of the interconnectivity strategy defined in the initial stages of the UPSOIL project. Totally 14 ground-water/monitoring wells were constructed during which soil samples, both undisturbed and disturbed, were taken for further tests. Totally 3.8 m^3 of a water solution containing 83 kg $NaMnO_4/m^3$ was injected in three different injection spots (MIP-IN 1, MIP-IN 2 and MIP-IN 3) with injection levels varying between 2-7 m below surface level. (The site is described in detail in Task 4.3).

Real time monitoring
A total of six stationary multi-parametric loggers (pH, EC, ORP, Tre, pressure) and four Tre were placed in different monitoring wells at different levels around the two injection areas. In general, based on outcome of the multiloggers, two types of changes during the monitoring could be noticed: 1/ flashy change and 2/ long term change. The first one (flashy or a sudden change) may in most cases be linked to the oxidant arrival and its effects, in few minutes or maximum hours. The second one can be linked to larger time frames, related to changes in the environment and pollutants degradation.

Numerical modeling

The numerical modeling simulation was performed for 6 observation boreholes: MW1A, MW1B, MW1C, MW2, MW3 and MW4 situated as it is shown on Fig. 3.6.4. The injection started on 17th March 2011 at 10.30 AM, thus this point of time has been set up as the beginning of the simulation. In the following table one might find the detailed information concerning the performed injection. The results were calculated for a feedback case scenario, it means that the flow velocity was estimated on the basis of the oxidant arrival to the monitoring well, in addition, it should be kept in mind that the input values for the model were averaged.

In the monitoring well MW1, i.e. 1 m from the injection point, the analysis of pH changes during the injection of permanganate brought that the influx of the oxidant causes an imminent increase of pH followed by a rapid decrease both for predicted and measured values.

Hence, in the considered study case modeled value of pH reached value of 9.2. On the contrary, in MW4, i.e. 3 m from the injection point, similar behavior is noted in the modeled version, whereas no variation occurs in the measured one, which may be indicative of some preferential oxidant flow pathway. For the modeled pH value, within both distances, i.e. 1 and 3 m from the injection point, the decreasing tendency has been observed from 19th March, i.e. 4 days after the injection; however in more distant borehole values of pH showed some fluctuations. In turn from 25th May, within this distance of 3 m, the drop in values of pH is very noticeable, which might indicate that the extent of reaction between oxidant and COCs is totally reduced. Moreover, within the distance of 1 m from the injection point, pH is also decreasing but there is no very visible drop which might be interpreted as the partial consumption of the oxidant.

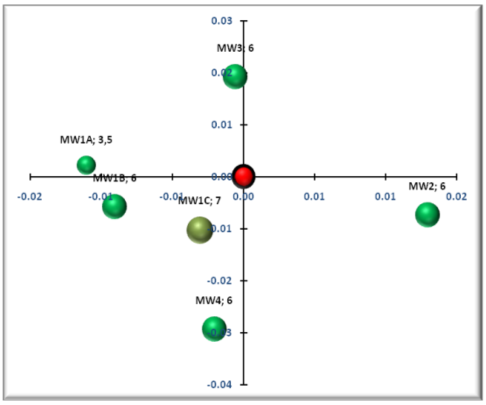


Figure 1.13. Monitoring wells and injection point location in the numerical model

Polish test site - Wegleniec

Analogously as the Flanders test site, the Polish site was used for the field testing of several WPs: WP2, WP3 and WP6. The test site is located in Western part of Poland, approximately 15 km from the Polish-German border between Bolesławiec (Poland) and Görlitz (Germany), in Węgliniec town. The site is located in a railroad yard and comprises a railway refuelling station and locomotives cleaning area which was contaminated with TPH, mainly diesel oil (see Task 2.1 and Task 3.2 for more information on the site). Finally 10% persuphate solution was determined as the optimal oxidant concentration for the field test. The testing field has regular form of a 5x5m square. The field test consisted basically on two separate persulphate injection campaigns followed by some nutrient injection after the chemical oxidation phase. The injection of the oxidant was done by gravity with no added pressure.

Real time monitoring

Since the beginning continuous data logging had been carried, with loggers automatically recording temperature, pH, electrical conductivity (EC) and ORP. Other monitoring wells were controlled manually for the same parameters on the basis of an individual monitoring scheme. Groundwater within the pilot area was also monitored for TPH to enable an assessment of the effect of the oxidant injection. Both during the first and second injection campaigns, the propagation of the injected chemical oxidant was clearly observed in wells with in-situ loggers. Finally, 50 days after the second injection the pH had risen to levels suitable for the injection of nutrients with visible lowering of the ORP indicating the end of the chemical phase. All field activities were adjusted basing on the continuous automatic data logging, which gave feedback about remediation performance and a basis for further on site decisions.

Numerical modelling

In terms of numerical modelling, a set of 2D maps were prepared using the visualization tool developed in the framework of the Upsoil project. Maps had been prepared at 4 hours intervals at the day before the injection and in the first phase after each injection campaigns. Less frequent maps were prepared in the post-injection phase, when the groundwater status change was assumed to be much slower. For instance, the conductivity, just before the first injection of persulphate, was in a range of 300-600 µS/cm. The highest values were observed in wells C6, C7 and C8. After the injection the conductivity increased rapidly within a radius of approximately 1 m diameter with the highest influence in wells C6, C7 and C8. The lower change in well C9 suggests the lower hydraulic conductivity to the East of the injection area. Lower increase in the well C10 indicates that the radius of influence is less than 2 m in the direction of natural groundwater flow (Figures 1.14 and 1.15). The radius of influence after the first injection was confirmed by the pH changes.

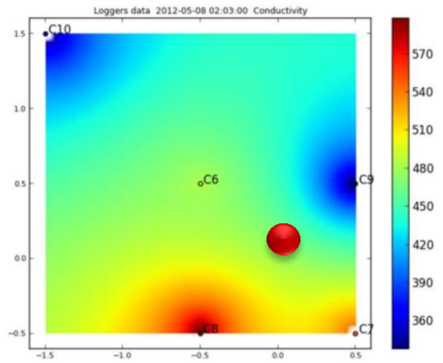


Figure 1.14. Loggers data before the injection works (conductivity) Injection point:

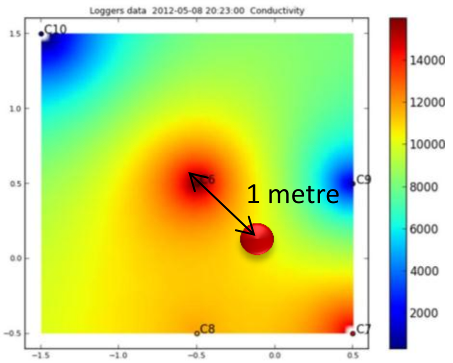


Figure 1.15. Loggers data after the injection works (conductivity). Injection point:

<u>Spanish test site</u>

The facility where this investigation has been carried out is located in a coastal area to the South of the Iberian Peninsula, and has been operational for over 40 years using some chemical products, developing several chlorinated compounds, including Dichloromethane, Trichloromethane and 1,2-Dichloroethane. It might be occurring natural attenuation of existing compounds, because complete chains of Chloromethanes (Tetrachloromethane, Trichloromethane and Dichloromethane) & Chloroethanes (Tetrachloroethane, Trichloroethane, Dichloroethane and Vinyl Chloride have been detected in groundwater. Following batch degradation tests, only activated persulphate was found to have a significant impact on all mentioned pollutants. Several tests developed in different piezometers allowed setting some parameters, such as GW flow velocity and direction, hydraulic conductivity, porosity, density, transmissivity and permeability. This data from study area has been used to define a representative physical model necessary before the injection works.

Real time monitoring
On 12 July 2012 a total of three sets of multiloggers were installed for the real time monitoring system allowing the measurement in continuous of several parameters in GW, such as electrical conductivity, pH, ORP, pressure and temperature. All loggers were connected to a wireless communication card. Loggers have to be placed in wells' saturated zone. In the Spanish site, all sensors were located 7 meters below the surface. This depth ensured all sensors contact with the GW and allowed GW sampling. The system installed allowed data transferring from loggers to a nearby PC. This PC had to be connected to internet. Once all the devices were connected, the SCADA software is the data gathering tool where all the data from loggers are recorded.

Numerical modelling
Regarding the numerical modelling, the use of the model was centred on the calculation of the oxidant movement between the injection point and monitoring wells, as well as the monitoring data visualisation and the alarm system setting. The model included 6 monitoring wells: MW-1, MW-2, MW-3, MW-4, MW-5, MW-6. From all, three of them were equipped with multiloggers collecting in the real-time the information about: temperature, conductivity, pH and redox potential. The results from the monitoring-modelling tool, which can be used as a feedback for the remediation process, included two types of estimation:

1) Assessment of the background conditions for the oxidation process: Before the injection at the Spanish loggers could be used to determine, what levels of basic parameters (pH, Eh, temperature, conductivity) can occur in natural conditions.
2) After the injection at the Spanish site: remediation results were presented in form of graphs (of pH, Eh, temperature) with background threshold values assessed in the step 1 described above.

Alarm function
For the post injection phase an alarm function was tested using the loggers' data from MW-3 and MW-4. As boundary conditions for alarms the background parameters from the pre-injection phase (described above) were used. Exceeding of these values are reported in alarm messages and shown the following figure. All alarm graphs start with the warm-up period when loggers installed and calibrated and unstable conditions were observed in monitoring wells. The warm-up period lasted till the 12th of July. The green line on figures presents the injection time. For all parameters monitored in MW-3 a change was observed after the injection and two parameters: pH and Eh exceeded the boundaries that were reported in the alarm message sent to the test operator.

All the information here indicated is provided and extended on the following external deliverables available in the UPSOIL web page:

PUBLIC DELIVERABLES
D6.3 Closing evaluation report ensuing successful results and final conclusions

4.1.4. Potential impact (including socio economic impact and the wider societal implications)

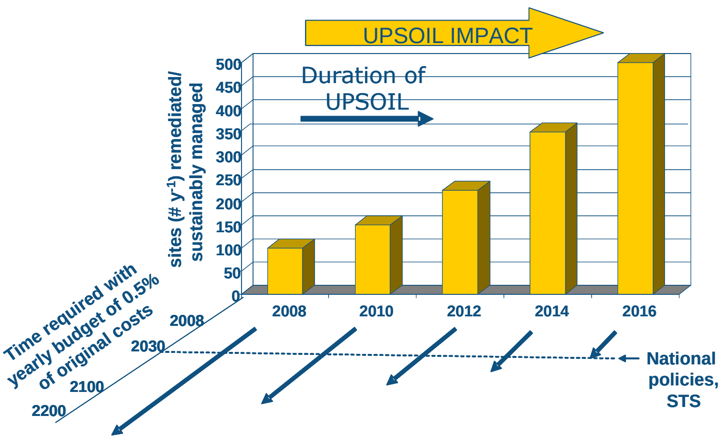
Development towards more sustainable remediation technologies

Sustainable remediation technologies (SRT) have been addressed extensively in the past two decades by EU RTD and network programmes, i.e. in FP4 (CLARINET, NICOLE, BAMBI), in FP5 (PURE, CORONA, INCORE, WELCOME, EUGRIS), FP6 (EURODEMO, PROMOTE), and LIFE0plus (ETV), and EU member state innovation programs (for example KORA, SAFIRA, D; NOBIS, SKB, NL).

Although in principle sustainable soil remediation techniques are thus available, their practical implementation is still limited, even in so called early adaptor EU member states, thereby hampering the timely execution of the soil remediation programme throughout Europe.

For sustainable soil remediation of contaminated sites to become in line with the STS and fully implemented by national soil quality management programs in EU member states within a time frame of 20-30 years, Figure 1.16 shows that cost-effectiveness needs to be increased by at least a factor of five. This, of course, is under the condition that sufficient budget is made available by member state governments (in Figure 1.16, 0,5 % of the total original cost for conventional remediation is assumed as a yearly budget). A time frame of 30 years would be compatible with the ambitions expressed in the STS.

Figure 1.16 - Impact scenario of UPSOIL, National remediation programmes adopting the Soil Thematic Strategy guidelines and Groundwater/Water framework directive (WFD) can be further improved by the newly developed sustainable cost-effective technologies that can result in a faster re-use of sites with an adequate soil function, as proposed by UPSOIL. Impact increases from the start and is followed by a sustained impact after the ending of UPSOIL due to further implementation of UPSOIL approaches and technologies, in line with the Soil Thematic Strategy in the various EU member states.



Cautiousness in accepting new and not yet well-known/widely-proven techniques plays a role in the slow market penetration of in-situ techniques. However, in addition to perceived disadvantages also real demerits of the current techniques preclude their embrace. As identified in the current call FP7 ENV 2008.3.1.2.1, these include cost-inefficiency and inability to recover soil sustainability. Uncertainty about the time-scale at which soil remediation can be achieved forms an additional impeding factor.

UPSOIL is focused to remove these important barriers, by the intelligent combination of existing technologies and the creation of new, contaminant targeted ones, for the remediation of organic contaminated sites.

The technologies and methodologies resulting from UPSOIL will provide a direct means for fast and cost-effective sustainable remediation relevant for stakeholders involved in either construction or environmental sectors. By means of this novel set of technologies stakeholders will be able to optimize all factors involved in urban redevelopment related activities, i.e. environmental, social and economic factors (sustainability). Previously established clean-up goals will therefore be achieved with a minimum cost and impact.

UPSOIL will achieve improvement in the cost-effectiveness of remediation technologies for contaminated sites through a faster source remediation followed by a polishing second phase, not hindering the re-use of the site and with adequate soil functions. Successful application of the UPSOIL project results in practice, as a standard procedure for soil remediation will:

- accelerate the remediation of contaminated sites in Europe,
- broaden the market of soil remediation for SMEs,
- help in preserving soil and its function on redeveloped sites (sufficient market edge for *in sit*u technologies over *ex situ*, dig and dump and pump and treat technologies),
- convince regulators in using the *in-situ* methods as the preferable approach for remediation of contaminated sites.

Lower remediation costs

By lowering the remediation costs and thus minimizing the economic barrier hampering the remediation efforts, the proposed improvement of the technologies can have also an impact on the remediation policies in the member countries. Just the economic benefits of UPSOIL project consist of the following:

- Soil as a resource can be more cost-effectively and sustainably maintained. In this way energy and resource consumption for remediation can be reduced significantly, thus contributing to a sustainable Europe. The in-situ application of the newly developed technological approaches will both eliminate the considerable burden of excavation – transportation work (with their significantly unsustainable characteristics) and the risk for people and environment in the contaminated area. So, a double social benefit results: human and ecological health risk attenuation and conditions for new opportunities development,

- Cost effectiveness of remediation; considering a factor of 5 cost reduction for the total soil remediation operation in Europe, the cost savings in a period of 50 years can amount to billions of Euro’s per member state, and hundreds of billions of Euro for Europe as whole,

- Faster revitalisation of derelict land: in many countries polluted not well maintained (post) industrial areas impede the economic situation in many regions. Better and cheaper remediation based on in-situ technologies restoring vital soil functions in a time frame of one to two years will strongly help to enhance the economic vitality of these regions,

- An impulse to remediation technology providing companies: UPSOIL will contribute to creating of enhanced and novel remediation technologies together with a core group of cooperating SME's. Thus the position of SME's in local and international market will be strongly enhanced. Effective technologies that are then available to address one of the biggest environmental concern, historically contaminated sites. Their application has a huge potential for replication, leading thus to restoration of the basic condition for one of the most valuable planet resource: the Earth soil.

4.1.5. Main dissemination activities and exploitation of results

During the UPSOIL project 3 years duration most dissemination activities have been executed following the dissemination plan initially prepared (D7.1), with appropriate adaptation of the schedules and concrete arrangements to achieve the most efficient and most fruitful dissemination results (Task 7.1 development of the UPSOIL project dissemination plan).

Task 7.2 Preparation of the common Project Website & brochure

In task 7.2 common project website was updated with distribution of the promotional materials. It is available at the address: www.upsoil.eu. UPSOIL brochure was prepared and printed in 1000 copies and distributed among partners during Wrocław, Vienna, Antwerp, Utrecht and Prague General Assembly meetings. Brochure was placed on the web page in .pdf format as downloadable. Brochure provides a brief presentation of the project with main objectives and concepts.

Task 7.3 Preparation of Stakeholder Panel (ShP) meetings

Key ShP members were contacted in the beginning of the project. These include: Large industry/Problem owners: BAYER MaterialScience – Global manufacturer of polymers and high quality plastics, REPSOL YPF – International Oil and Gas company, NICOLE – Network for Industrially contaminated land in Europe, PKP - Polskie Koleje Państwowe SA (Polish State Railways, SA), EUCETSA (European org. of environmental technology providers), SPRILUR (Basque society of industrial site redevelopment), European group on Brownfield development, Thomas Erthel from Revit, SBNS - Stichting Bodemsanering NS (Foundation for the remediation of NS sites), Rota Madencilic A.S. – Producer and seller of natural zeolites. Among the authorities and funding institutions the following institutions were contacted: Common Forum, Romanian Government, IHOBE - Basque Government owned company focused on environmental protection and management, World Bank, Polish National Environmental Fund.

Various stakeholders were also approached by partners during these three years of project duration including regional authorities. They were invited to take part of

Stakeholder Panel activities. Apart from the high level stakeholders a list of approached European SME and professional bodies and National Governments was prepared as a wide stakeholder forum. The stakeholders were informed about project activities by personal contacts of the partners. The UPSOIL project information materials were delivered to them through electronic means. They were invited to comment on the activities and to provide information on contaminated soil policies, and other relevant information. Due to organisational reasons presence of particular stakeholders during the stakeholder panel meetings depends in general on the meeting location and main focus of the meeting.

The initial plan of organising separate stakeholders meetings and workshops was changed as to facilitate the participation of stakeholders. The stakeholders were also informed about the project progress during other events: conferences and workshops. A total of Four ShP meetings in conjunction with project meetings were held:

- 1st Stakeholder Panel meeting took place in Wrocław (14.04.2010) with participation of 20 representatives of site owners, organisations, consultants. The discussion during the meeting provided information on the current practices in Poland and in Eastern Europe concerning contaminated site remediation and to evaluate practical potential for UPSOIL project approaches.
- 2nd Stakeholder Panel meeting in Antwerp (23.03.2011) was integrated with the workshop "*Combination of injection and detection*". The meeting was organised during KVIV (Flemish engineers association) event. The workshop agenda was furthermore adjusted according to the confidentiality issues. The arrangement proved very fruitful with keen engagement of the audience.
- 3rd Stakeholder Panel meeting was integrated with the workshop: *"Smart coupling of chemical and biological techniques and soil function sustainability"*, and took place in Utrecht on the 19th of October 2011 in conjunction of CityChlor (INTERREG) and Hombre projects (7th FTP) and with reference to CIRCUS project (Central Europe Program). In the meeting 100 representatives of site owners, organisations and consultants participated.
- 4th Stakeholder Panel meeting and workshop: *"Monitoring, Control and Evaluation of Remedial Efficiency"*, which took place in Prague on 21st of March 2012, was integrated with the Czech research activities lead by Dekonta company. In the workshop around 30 participants took active part.

From all the ShP meetings public brochures and reports were prepared and put up in the UPSOIL web page. Real interest in the project results expressed by the stakeholders is a good starting point for their future implementation in practice. The policy implications were discussed during the meetings and the results of the discussion will be put into policy briefs (after the mid-term meeting). The continuous exchange of information through e-mail, personal contacts is kept with feedback on the presented materials pursued.

Task 7.4 Design, organisation and conduction of a series of workshops

During the project lifetime a total of four workshops together with Stakeholder Panel meetings were organized:

* *1st workshop "Combination of injection and detection (Geoprobe-MIP) and use of chemical oxidants"*: On 25th of March 2011 first workshop was organised together with ShP meeting. The workshop was organised by VITO and ECOREM together with IETU, Ejlskov, WUR and Deltares. The workshop *Combination of injection and detection (Geoprobe-MIP) and use of chemical oxidants* was organised during KVIV (Flemish engineers association) event. It was also organised in conjunction with the 2nd ShP meeting. The agenda was related to the specific issues of smart injection technology development and application. The workshop aim was to identify the potential barriers for the implementation of the developed approaches as well as help finding effective and broadly acceptable solutions to overcome them. The remediation approaches were discussed in conjunction to relevant activities carried out in Flanders and other EU regions. The workshop agenda included presentation of Flanders site selected to demonstrate on-site technology applications. Summary report with findings and outcomes was developed.

* 2nd workshop *"Smart coupling of chemical and biological techniques and soil function sustainability":* It was organised in Utrecht (The Netherlands) together with the CityChlor (INTERREG) and Hombre projects (7th FTP) and with reference to CIRCUS project (Central Europe Program). The workshop was organised by WUR and Deltares together with IETU. In the meeting 100 representatives of site owners, organisations and consultants participated. Meeting brochures and external report from the meeting (D.7.6) were produced and put up in the web page. The agenda of the workshop was prepared for a wide group of land redevelopment in particular SMEs such as consultants, site developers, technology providers and authorities dealing with site remediation and remediation firms. UPSOIL presentations were merged within the general scope of the meeting. The agenda was related to new circular land redevelopment concept and the role of innovative thinking and technologies in achieving sustainability and cost-efficiency of site redevelopment. The remediation approaches were discussed in conjunction with relevant activities carried out in Netherlands and other EU regions. The workshop agenda included presentation of innovative thinking of redevelopment of Utrecht railway station. Tailored made brochure in pdf was developed and distributed to a wide audience through website and sent to identified stakeholders. Summary report with findings and outcomes was developed.

* 3rd workshop *"Monitoring, Control and Evaluation of Remedial Efficiency":* It was combined with event organised in Prague with the Stakeholder Panel meeting. It took place Prague (Czech Republic), on the 21st of March 2012 and was integrated with Czech research activities lead by the company Dekonta. In the workshop around 30 participants took part. External report from the meeting was prepared. The meeting was focused on monitoring and evaluation of remediation results and the possibilities of controlling remediation with regard to administrative requirements. UPSOIL project was presented with detailed presentation of the on-line monitoring scheme, the MIP IN technique and the modelling tool as a support in controlling the chemical remediation. Examples of chemical and biological remediation performed in Czech Republic were presented with evaluation of their final results. Summary report with findings and outcomes was developed.

* 4th workshop *"Rehabilitation of contaminated soil and sites":* The last of UPSOIL open stakeholder workshops took place in Bucharest (Romania) on the 2nd of July

2012. It was organized in conjunction with 7th EU FP TIMBRE – Tailored Improvement of Brownfield Regeneration in Europe project. The workshop was organised by ECOIND as the National Workshop "Rehabilitation of contaminated soil and sites" It was attended by 51 participants representing scientific community (higher education, research), industry, civil society, policy makers. The agenda of the one-day workshop consisted of 2 sessions dedicated to technical presentations with introduction followed by UPSOIL project session and TIMBRE project session. During the discussion the issue of the awareness of site owners on site contamination problems was underlined as the most important in Central and Eastern European countries. It was agreed that UPSOIL project results can provide an input to TIMBRE management tools for optimising the remediation.

Workshop brochures and external public reports from all meetings were prepared and are accesibel in the UPSOIL web page.

Task 7.5. Common final conference

The final UPSOIL conference was organised together with the AQUAREHAB project as a joint conference: *"Remediation Technologies and their Integration in Water Management Symposium"* in September the 25th -26th of 2012 in Barcelona (Spain). The conference was organised by VITO in cooperation with Tecnalia and IETU. Conference UPSOIL project brochure was prepared by the leaders of technical workpackages (VITO, Tecnalia, Deltares, SGI, WUR), supplemented and edited by IETU, printed and provided as pdf file. - D7.7. Other promotional materials including: folder, banner and 3d Newsletter were prepared and distributed during the conference.

UPSOIL session was merged with other activities of the Symposium with UPSOIL thematic presentation incorporated in the technical sessions and poster session. The one and a half hour was devoted to evaluation of the UPSOIL results in the context of their implementation in practice. The objective of the UPSOIL session was to present the project, its approaches undertaken, results and the key messages, to discuss the results and the ensuing benefits and to share experience and knowledge related to innovative in-situ remediation technologies with other projects and activities undertaken in Europe with respect to further research needs, business opportunities, practical aspects of remediation activities and future innovative policy. One of the key messages formulated during the conference was that a new thinking on remediation has to be promoted among all stakeholders, remediation which takes into account sustainability, integrated with revitalization schemes and related to future land use.

Task 7.6. Policy Briefs creation.

Two external policy briefs were prepared. The first policy brief, based on the results of Stakeholder Panel meetings and workshops in Wrocław, Antwerp and Utrecht was prepared in December 2011. In the policy brief barriers and bridges to implementation of innovative in situ remediation technologies were identified and the position of UPSOIL consortium on activities and to overcome them was outlined. The second policy brief was prepared in September 2012 with regard to the first policy brief results and UPSOIL workshop and Stakeholder Panel meeting organised in Prague and Bucharest and discussions held in final conference in Barcelona. In the document, the factors of implementing smart in-situ approaches were further discussed and a set of requirements and actions were pronounced in regard to successful implementation of UPSOIL results. In particular, the actions on real life demonstrations, training and promotion of good examples were identified as the most important in stimulating implementation of UPSOIL results. Both documents are available in the UPSOIL web page.

Task 7.7 Communication of results to the general audience

Communication of results to the general audience, IETU in cooperation with TECNALIA, comprised distribution of brochures and newsletter and press release. The objective of this task is to communicate the objectives and results of the project to the general audience.

External Project Newsletters were prepared each year and put on the UPSOIL webpage. Additionally, paper version were delivered in each workshop event (a total of 300 copies printed). Each year one edition of project newsletter was developed, printed and provided as downloadable document in pdf on the web page (2010, 2011 and 2012). The first newsletter summarizes and promotes project aims, recounts the initial work performed and announces the planned activities and events, the second edition summarizes and explains project activities in the second year of UPSOIL project duration and announced the planned activities and events and finally the third issue of UPSOIL project newsletter summarizes the activities in the third year, presents final results of UPSOIL project and promotes their use in practical applications.

They have been distributed during all stakeholder panel meeting events: Antwerp, Utrecht, Prague and Bucharest, conferences: CONSOIL 2010 in Salzburg, the Belgrade NATO workshop in 2011, the TASK Symposium in Leipzig in 2010, the UPSOIL final conference, as well as individually by project partners in several conferences.

Regular flow of information was promoted between the Consortium and previously chosen specialized information agencies. Some of the key information agencies selected included:

- DG Environment Webmaster
- Soil Technical Unit of DG Environment Webmaster
- Ispra: The Soil Portal. European Soil Data Center (ESDAC) (http://eusoils.jrc.ec.europa.eu)
- Newsletter: Science for Environment Policy
- Click green - portal and newspaper (http://www.clickgreen.org.uk/)
- SOILTECH cluster initiation by the European Commission
- UPSOIL dissemination in conferences and publications

The aim was to translate the results arising from the project into a useful and interesting outcome for the general public, as well as presenting the information in a clear and attractive manner. The first press release was launched in September 2010 and the second in September 2012 initiating information exchange with the media with the focus on electronic media.

A final external deliverable for the general public was prepared as article in International Innovation Journal (October 2012) in which UPSOIL coordinator Nerea

Otaegi was interviewed and a wide coverage of the project was prepared and prepared for publishing in the electronic media.


Remediation now:
how soil pollution can no longer be ignored

With over 10 years' experience in soil and water contamination, Nerea Otaegi of UPSOIL explains how new areas of research may finally find a breakthrough in soil and groundwater remediation techniques

A sustainable soil solution

Traditional soil and groundwater remediation techniques have proven, time and again, to be too time-consuming, expensive and unsustainable. The research team at UPSOIL, however, may have just found a solution

Figure 1.17 – International innovation report – UPSOIL article

Figure 1.18 – UPSOIL logo

www.upsoil.eu

Table 1.2 – Beneficiaries contact list

Nº	BENEFICIARY NAME	CONTACT
1	TECNALIA Parque Tecnológico de Bizkaia, Calle Geldo, Edificio 700, 48160 Derio, Spain	Mrs. Nerea Otaegi Tel: +34902760000; Fax: +34946073349 Email: nerea.otaegi@tecnalia.com
2	VITO-MPT Boeretang 200, 2400 Mol, Belgium	Dr. Leen Bastiaens Tel: +3214335634; Fax: +3214580523 Email: leen.bastiaens@vito.be
3	DELTARES-TNO Daltonlaan 400, 3584 BK, Utrecht, Netherlands	Dr. Pauline Van Gaans Tel: +31883357736; Fax: +31883357720 Email: pauline.vangaans@deltares.nl
4	WUR Bomenweg 2, 6703 HD Wageningen, Netherlands	Dr. Tim Grotenhuis Tel: +31317482561; Fax: +31317482108 Email: Tim.Grotenhuis@wur.nl
5	IETU Kossutha, 6, 40-844 Katowice, Poland	Mr. Janusz Kupranek Tel: +48322547413; Fax:+48322541717 Email: krupanek@ietu.katowice.pl
6	ECOIND 90-92 Panduri Road, Sector 5, 050663 Bucharest, Romania	Dr. Maura Teodorescu Tel: +40214106716; Fax:+40214100575 Email: pi@incdecoind.ro
7	SGI Avd Markmiljö, Hugo Grauers gata 5B, 412 96 Göteborg, Sweden	Mr. Lennart Larsson Tel: +4613201800; Fax:+46317785940 Email: lennart.larsson@swedgeo.se
8	ENACON Krcska 16, 140 00 Prague 4, Czech Republic	Mr. Petr Kozubek Tel: +42241404911; Fax:+42241405765 Email: kozubek@enacon.cz
9	ECOREM-BALTIC Kontichsesteenweg 38, 2630 Aartselaar, Belgium	Mr. Patrick Hambach Tel: +3238710900; Fax:+3238710901 Email: Patrick.Hambach@ecorem.be
10	DEKONTA Volutova, 2523, 15800 Prague 5, Czech Republic	Mr. Jan Kukacka Tel: +42602133383; Fax:+42235522254 Email: kukacka@dekonta.cz
11	POWIZ Fabryczna, 10/13, 53-609 Wrocław, Poland	Mr. Jan Marek Tel: +48713565268; Fax:+48713565068 Email: jan.marek@powiz.com.pl
12	EJLSKOV Voldbjergvej 14, 2.sal; 8240 Risskov, Denmark	Mr. Ole Stubdrup Tel: +4587310071; Fax:+4587316160 Email: ops@ejlskov.com
13	RDS Calle Torpedero Tucumán 26, bajo A, 28016 Madrid, Spain	Mr. Enrique Muñoz Tel: +34913431737; Fax:+34913431738 Email: enrique.munoz@rds.es
14	BIUTEC Seeböckgasse 32b, Wien, 1160 - Austria	Mr. Helmut Effenberger Tel: +434083580; Fax:+43408358034 Email: helmut.effenberger@biutec.at
15	GEOCISA Calle Los Llanos de Jerez 10-12, 28823 Coslada, Spain	Mr. Pedro Avellanosa Tel: +34916603257; Fax:+34916716460 Email: pavellanosas@geocisa.com