Cost-effective methods of soil and groundwater treatment, contaminated with petroleum and chlorinated hydrocarbons - UPSOIL project example

Janusz KRUPANEK, Mariusz KALISZ - Institute for Ecology of Industrial Areas (IETU), Katowice

Please cited as: CHEMIK 2010, **64,** 6, 434-439

Despite current experiences, abundant knowledge and well developed remediation technologies, there still exists huge potential to raise effectiveness of remediation; It concerns especially non-invasive ***in situ*** techniques for remediation of soil and groundwater contaminated with organic pollutants with perspective of sustainable soil quality improvement and its final full rehabilitation. In this area many EU funded projects are carried out. One of them is the EU Framework Program project UPSOIL which objective is to develop methods effectively coupling technologies of chemical and biological in situ remediation of soil and groundwater.

Huston, we have a problem...

The inventories of contaminated sites in Europe show that in EU-25 countries there are around 3.5 mln of contaminated sites. The main sources and groups of soil and groundwater contamination identified are

- mining waters, energy production facilities, and transport
- heavy metals
- spills of fuels (hydrocarbons) and chemical substances in industries
- degreasing agents and solvents – chlorinated hydrocarbons
- solvents and aromatic hydrocarbons: benzene, toluene xylene and ethylene
- gasification installations and partial burning – poliaromatic hydrocarbons (WWA)
- military activities

Taking into account the complexity of the problem and high environmental risks related to groundwater contamination the soil and ground water pollution has a special importance. The current experience shows that systemic remediation of contaminated soil and groundwater is a slow process, and the scale of the problem requires appropriate legal conditions and public support for the actions and funds availability. Furthermore, there is a need for available effective remediation solutions and methods and adequate implementation potential. According to health and environmental risk criteria especially important are organic contaminants – the most frequently occurring hydrocarbons, aromatic hydrocarbons, BTEX and chlorinated compounds. According to the European inventories the percentage of sites characterized with the contaminants is as follows (Fig. 1).

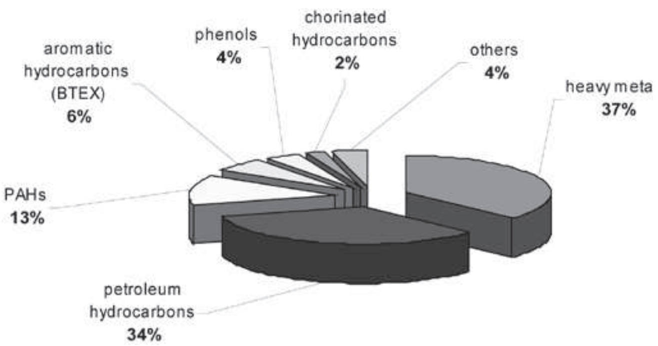

Fig. 1. Main pollutants species on contaminated sites

In cost-effective sustainable remediation of contaminated soil on a European scale, three optimisation dimensions need to be addressed:

- COST: the cost effectiveness of remediation should be significantly increased as compared to current practices
- TIME: the technologies employed should allow fast release of sites for urban/industrial or ecological redevelopment
- SUSTAINABILITY: the technologies employed should ensure that there are no pending (post-remediation) liability issues and that soil functions are maintained or restored.

Current experiences

Commonly used traditional remediation methods ***ex situ*** such as removal (exchange) of contaminated soil and its disposal as hazardous wastes does not guarantee full recovery of the soil quality and leads to disturbances of soil functions. Furthermore, they are costly from socio-economical perspective. Nevertheless, in many cases – especially where remediation time is crucial and the site is small (e.g. preparation of sites for investments), use of these techniques is preferable.

Moreover, in specific conditions these solutions are preferred because of their relative effectiveness and reliability. Negative aspect of these techniques is relatively high cost (especially in areas with high and extensive contamination) and disturbance of hydrological and natural soil conditions connected with soil removal and lack of sustainable soil improvement after remediation. Much more adequate in this respect are non-invasion ***in situ*** soil and groundwater remediation techniques. Positive aspect of these techniques, besides the environmental benefits arising from the non invasiveness is the possibility of active remediation on urban, industrial and transport areas with existing infrastructure, during normal cycle of site usage according to its function and its current use.

Despite current experiences, abundant knowledge and well developed remediation technologies, still exist a huge potential to raise effectiveness of remediation work. Innovativeness in this matter covers complex technological solutions, coupling known and accessible techniques, aiming at minimalisation of costs and achieving accepted risk level. One of the solutions is to couple chemical and biological non-invasive ***in situ*** techniques***, based on*** short term remediation process with further long term environmental rehabilitation process established (natural attenuation).

The innovative approach for soil and groundwater remediation – the UPSOIL project

The key innovative concept of project Sustainable Soil Upgrading by Developing Cost effective, Biogeochemical Remediation Approaches (acronym UPSOIL) is based on smart coupling of chemical and biological remediation methods (Fig. 2).

Project is carried out in the period 2009-2012 within Seventh European Union Framework Program. Consortium realizing the project is composed of 7 scientific institutions, including Institute for Ecology of Industrial Areas (IETU - Poland), VITO –TMP (Belgium), WUR and Deltares (Netherlands), Labein Tecnalia (Spain), ECOIND (Romania), SGI (Sweden), and 8 firms specializing in soil and groundwater remedia-

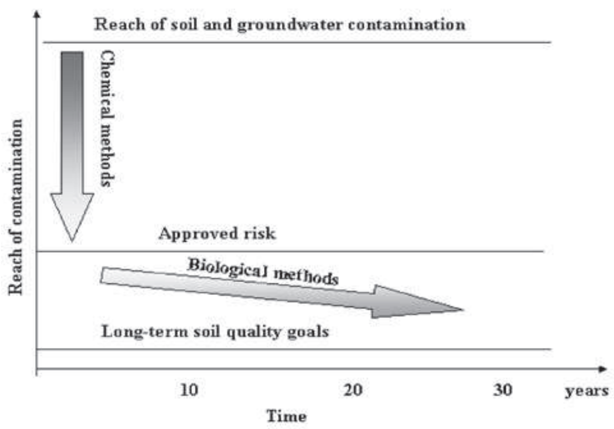

Fig. 2. Concept of environmetal remediation in UPSOIL project

tion: ENACON and DEKONTA (Czech Republic), ECOREM-BALTIC (Lithuania), POWIZ (Poland), EJLSKOV (Denmark), BIUTEC (Austria) and GEOCISA and RDS (Spain). The project's aim is to make the required breakthrough in in-situ (bio)chemical remediation for organic contaminants, by developing robust technologies for fast, cost-effective, integrated source zone and plume treatment that result in both allowable (risk) levels and maximal use of the natural soil rehabilitation potential at a longer term.

The UPSOIL project goals are set at three ambition levels for the different research lines, thereby giving a fair chance of success in each line:

- improvement of the existing ***in situ*** biological and chemical remediation technologies through smart coupling and optimisation of their use, including assessment of soil functions rehabilitation
- development of physical and IT remediation management schemes for further cost-optimization
- development of highly innovative techniques with a potential of strengthening the remediation capabilities of biological and chemical ***in situ*** technologies.

The basis of the project is smart coupling of technologies and the development of new frontier technologies, whereby:

- soil structure, properties and functions are integral factors in selecting the type of remedial treatment
- side-effects of treatment, for example at multi-contaminant sites, on overall risk are taken into account
- active remediation (chemical or biological) is designed in such a way that the natural attenuation potential is fully utilized and stimulated
- the injected remedial agent is better targeted at the location/distribution of the contaminant within the soil
- modelling and dynamic monitoring of the remediation progress are used in realtime to allow feed-back driven remediation
- reactant species are developed that are more selective towards the contaminant and less degrading towards the soil matrix
- indicators are developed that diagnose whether viable microbial soil populations are present and that microbial dynamics are such that the natural attenuation capacity of the soil has been restored.

The sites designed for pilot tests

There are 4 industrial sites contaminated with organic compounds, provided for pilot tests during the project:

1) Railway site - internal combustion engine locomotives fuelling point, area of locomotives cleaning-up (also steam locomotives). 40 years of land usage, from 1998 excluded from use (fueling), cleaning completed in 70's. Main polutants: petroleum hydrocarbons (diesel oil), naphta (detail analyses in progress).

2) Industrial site – with approx. 40 years of chemical plant operations, currently excluded from use. Main pollutants: chlorinated hydrocarbons, e.g. dichloromethane (CH_2Cl_2), trichloromethane (chloroform $CHCl_3$), 1,2 - dichloroethane (Ethylene Dichloride - ETE).

3) Industrial site – with main polutants: kerosene (naphta). According to actual lab-analysess, there are mainly hydrocarbons C6-C18 (detail analyses in progress).

4) Port terminal built in 1977-78, gasoil station for ships. Partly excluded from use. Main polutants: mineral oil, petroleum hydrocarbons (diesel oil) and BTEX.

The field experiments conducted on selected sites, is divided in two stages:

PHASE I – active remediation, chemical degradation of contaminants

The main concept of UPSOIL approach is the initiation of basic, simple chemical reactions (oxydation, redox) leading to contaminants decomposition under condition that natural soil biodegradation potential is preserved. As a result natural biodegradation of pollutants process is triggered after active remediation phase. Chemical reagents could be added as liquids or gas phase, as direct injection, or infiltrated to wells or piesometers (temporary or permanent well points). One of the applied solutions, is ISCO approach (**I**n-**S**itu **C**hemical **O**xidation). The idea of ISCO is a soil and groundwater remediation that involves the injection of a chemical oxidant into the subsurface to breakdown complex organic contaminants by reacting with the contaminants to produce innocuous substances such as carbon dioxide and water. The effectiveness of ISCO is mostly determined by contact time of the chemical oxidant with contaminants, local soil/water conditions (ground type, hydro geological conditions), the amenability of the contaminant(s) to breakdown by the applied oxidant, and also oxidant half-life. These parameters determine quantity of added oxidant, and injection spacing in full-scale approach. Several different chemical oxidants can be used for ISCO, e.g:

- Fenton's reagent OH^{-}• (catalyzed hydrogen peroxide H_2O_2)
- activated persulfates $SO4^{-}$•

Table 1

Generally well-established for a wide range of contaminants reactions

Contaminant type	Oxidants				
	MnO_4	S_2O_8	SO_4-•	Fenton's	O_3
Petroleum Hydrocarbons	G	G/E	E	E	E
BTEX	P	G	G/E	E	E
Phenols	G	P/G	G/E	E	E*
Polycyclic Aromatic Hydrocarbons (PAHs)	G	G	E	E	E
Chlorinated Ethenes (PCE, TCE, DCE, VC)	E	G	E	E	E
Chlorinated Ethanes (TCA, DCA)	P	P	G/E	G/E	G
Polychlorinated Biphenyl's (PCBs)	P	P	P	P	G*

P-poor, G-good, E-excellent oxidation efficiency, *- combinations of gas/liquid-injections (e.g. ozone and permanganate etc.)

- Ozone O_3
- persulfates (eg. sodiumpersulfate $Na_2S_2O_8$)
- hydrogen peroxide H_2O_2
- permanganate (eg. potassium or sodium $KMnO_4$, $NaMnO_4$).

These oxidants can rapidly destroy many organic chemical contaminants as e.g.: chlorinated hydrocarbons, PAHs, BTEX, phenols, TCE, PCE, DCE, VOC. The oxidant efficiency is mainly determined by its oxidation potential (V). Reactions are generally well-established for a wide range of contaminants, as shown in Table 1.

Furthermore new machines and monitoring system are developed in the project. Innovative, real time monitoring of remediation progress, and mathematical modeling are to be applied (hydrogeological as well as biochemical processess modelling) to allow for feedback driven remediation process.

PHASE II – natural biodegradation process

According to project settings, after active remediation stage, the biological potential of soil/water matrix, should be sufficient for natural bioremediation process initiation (/monitored/ natural attenuation). In this case, during the field-experiments soil microbiological activity and environment regeneration potential investigations will be made.

Laboratory and practical aspects

The complex set of analyses and testing covering laboratory work (chemical, biochemical, hydrogeological and hydrogeochemical) gives a chance for improvement and determination of coupling in situ biological and chemical methods through developed new technical knowledge on effective use of available materials and tools. The basic research on new innovative techniques, tools and materials opens new possibilities for raising the effectiveness of biological and chemical methods.

In this part new materials and new techniques are tested in laboratory and on pilot scale. The existing knowledge on soil and groundwater natural attenuation and the methods is used to fully recover the environmental quality. At the same time knowledge on long term soil rehabilitation is used to deliver complex solutions (biological and chemical) for sustainable recovery of soil properties with full regard to risks of negative side effects and integrated through advanced management and control tools.

Methods and approaches developed on the basis of laboratory analyses are in the next step tested on selected sites with active participation of small and medium enetrprises in real business conditions to show their applicability and effectiveness. The results are disseminated with the focus on the potential stakeholder interests in practical application of the project results in full scale (including financial institutions, industry representatives, consultants, decision makers).

Summary

UPSOIL approach addresses at the same time two aspects of sustainable remediation: short term action allowing for quick site redevelopment (investor and socio-economical perspective) and long term rehabilitation of soil properties (ecological perspective). It gives a chance to include in best business practices redevelopment of degraded land and fulfilling social expectations of sustainable development.

English translation by the author.

Bibliography

1. Siegrist R.L, Environmental Science and Engineering, 2006: Site Remediation Using Chemical Oxidation Techniques, report of NATO/CCMS Pilot Study "Prevention and Remediation in Selected Industrial Sectors: Small Sites in Urban Areas" Golden, Colorado USA.
2. Sperry K.L, Cookson J, Jr, 2002. "In Situ Chemical Oxidation- Design & Implementation" NJDEP Public Hearing Room.

Janusz KRUPANEK, Ph.D., 1989 - Silesian University, Faculty of Biology and Environmental Protection, - M.Sc. in environmental protection, 2005 – Institute for Organisation and Management in Industry. Ph.D. in business organization. From 1989 employed at the Institute for Ecology of Industrial Areas (IETU), Head of the Ecological Policy Unit. He has an experience in environmental policy and management. He has been involved in research concerning management of renewable resources, ecological and health risk assessment, eco-innovativeness. He participated in several international projects (UNEP, EU framework programs WELCOME, INCORE, NORISC). He is involved in realization of the European Environmental Technology Action Plan in Poland. In that scope, He is involved in studies of the environmental technology current situation in Poland. He is active in Polish Environmental Technologies Platform and scientific network ENVITECH-NET.

Mariusz KALISZ, M.Sc., 1999 - AGH University of Science and Technology Kraków, Faculty of Geology, Geophysics and Environment Protection, M.Sc. in environmental protection, 1999-Faculty of Electrical Engineering, Automatics, IT and Electronics, Post-graduate studies "Open IT systems"). From 2000 employed at the Institute for Ecology of Industrial Areas (IETU), at the Waste Management and Brownfields Revitalisation Department. Position: junior member of research staff (assistant). He has an experience in environmental policy, waste management and revitalisation issues. He is involved in research concerning waste management, brownfields redevelopment and eco-innovativeness in Poland. He participated in and several dozen projects concerning waste management and the others environment protection aspects.