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# **NATO/CCMS Pilot Study**

Evaluation of Demonstrated and Emerging Technologies for the Treatment of Contaminated Land and Groundwater (Phase III)

## 2001 SPECIAL SESSION

Performance Verification of In Situ Remediation Technologies

Number 251

NORTH ATLANTIC TREATY ORGANIZATION

### **NATO/CCMS Pilot Study**

### Evaluation of Demonstrated and Emerging Technologies for the Treatment of Contaminated Land and Groundwater (Phase III)

### 2001 SPECIAL SESSION

### Performance Verification of In Situ Remediation Technologies

Liege, Belgium September 10-14, 2001

March 2002

### NOTICE

This Special Session Report was prepared under the auspices of the North Atlantic Treaty Organization's Committee on the Challenges of Modern Society (NATO/CCMS) as a service to the technical community by the United States Environmental Protection Agency (U.S. EPA). The report was funded by U.S. EPA's Technology Innovation Office. The report was produced by Environmental Management Support, Inc., of Silver Spring, Maryland, under U.S. EPA contract 68-W-00-084. Mention of trade names or specific applications does not imply endorsement or acceptance by U.S. EPA.

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### **INTRODUCTION**

The Council of the North Atlantic Treaty Organization (NATO) established the Committee on the Challenges of Modern Society (CCMS) in 1969. CCMS was charged with developing meaningful programs to share information among countries on environmental and societal issues that complement other international endeavors and to provide leadership in solving specific problems of the human environment. A fundamental precept of CCMS involves the transfer of technological and scientific solutions among nations with similar environmental challenges.

The management of contaminated land and groundwater is a universal problem among industrialized countries, requiring the use of existing, emerging, innovative, and cost-effective technologies. This document reports on the fourth meeting of the Phase III Pilot Study on the Evaluation of Demonstrated and Emerging Technologies for the Treatment and Clean Up of Contaminated Land and Groundwater. The United States is the lead country for the Pilot Study, and Germany and The Netherlands are the Co-Pilot countries. The first phase was successfully concluded in 1991, and the results were published in three volumes. The second phase, which expanded to include newly emerging technologies, was concluded in 1997; final reports documenting 52 completed projects and the participation of 14 countries were published in June 1998. Through these pilot studies, critical technical information was made available to participating countries and the world community.

The Phase III study focuses on the technologies for treating contaminated land and groundwater. This Phase is addressing issues of sustainability, environmental merit, and cost-effectiveness, in addition to continued emphasis on emerging remediation technologies. The objectives of the study are to critically evaluate technologies, promote the appropriate use of technologies, use information technology systems to disseminate the products, and to foster innovative thinking in the area of contaminated land. The Phase III Mission Statement is provided at the end of this report.

The Phase III pilot study meetings were hosted by several countries and at each meeting, a special session was held for the discussion of a specific technical topic. The meeting dates and locations were:

- February 23-27, 1998: Vienna, Austria
- May 9-14, 1999: Angers, France
- June 26-30, 2000: Wiesbaden, Germany
- September 9-14, 2001: Liège, Belgium

The special session topics were:

- Treatment walls and permeable reactive barriers (Vienna)
- Monitored natural attenuation (Angers)
- Decision support tools (Wiesbaden)
- Validation of in situ remediation performance (Liège)

This and many of the Pilot Study reports are available online at <u>http://www.nato.int/ccms/</u> and <u>http://www.clu-in.org/intup.htm</u>. General information on the NATO/CCMS Pilot Study may be obtained from the country representatives listed at the end of the report. Further information on the presentations in this special session report should be obtained from the individual authors.

Stephen C. James Walter W. Kovalick, Jr., Ph.D. Co-Directors

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### **EXECUTIVE SUMMARY**

Robert L. Siegrist<sup>1</sup> and Bert Satijn<sup>2</sup>

Subsurface contamination by toxic chemicals, including natural and synthetic organic compounds and heavy metals, is a widespread problem at industrial and military sites around the world. At many contaminated sites, there is a sufficiently serious current or future risk to public health and environmental quality such that remediation is warranted. To eliminate a current or future risk, remediation approaches increasingly employ *in situ* technologies comprised of engineered as well as natural attenuation systems. In situ remediation in source areas of contaminated soil and groundwater can be accomplished using mass transfer and recovery methods such as soil vapor extraction, air sparging, and surfactant/cosolvent flushing. In destruction methods can also be employed such as bioremediation and chemical oxidation/reduction. These source area treatment methods can sometimes be enabled by techniques such as soil mixing, soil fracturing, and soil heating. Ground water plumes can be treated by some of these methods as well as through natural biogeochemical attenuation. Finally, for the control of the leading edge of ground water plumes, treatment walls and permeable reactive barriers can be applied.

As site cleanup goals are established (whether it be by a quantitative risk assessment or another method), one must delineate the current nature and extent of contamination in the subsurface and also the desired end-state after in situ treatment has been completed (e.g., risk-based concentrations throughout a volume of soil). Then, the needed technology performance with respect to the contaminant concentration, mass, mobility or toxicity must often be prescribed to achieve the risk reduction judged necessary. Verifying (or validating) potential performance capabilities can be based on process theory, research, and full-scale implementation and nationally standardized test programs (e.g., U.S. EPA Superfund Innovative Technology Evaluation (SITE) program). Verifying actual performance achieved at a specific contaminated site is necessarily based on measurements made at that site to quantify treatment effects that result in changes in contaminant concentration, mass, mobility, and/or toxicity as well as environmental conditions indicative that the desired treatment is occurring.

Verifying that the treatment performance goals set for an in situ remediation technology have been achieved at a specific site is very challenging due to several factors. In general, the effective verification of in situ performance at a particular site becomes more and more challenging with: increasing site size and heterogeneity, presence of dense nonaqueous phase liquids (DNAPLs), cleanup goals that involve high mass removals of contaminants or very low levels of residual contaminants, and remediation technologies that require long time frames and don't readily permit mass balances.

In this Special Session of the NATO/CCMS Pilot Study on the Evaluation of Demonstrated and Emerging Technologies for the Treatment and Cleanup of Contaminated Land and Groundwater (Phase III), was focused on "Validation of Performance of In Situ Remediation Technologies." During this 1.5-day session, there were 14 presentations made. The initial afternoon of the session was devoted to an introduction to the topic (Bert Satijn, The Netherlands) and an overview of process features and challenges (Bob Siegrist, USA). There were also presentations on the needs, views and concerns of the regulators (Victor Dries, Belgium), the site owners (Terry Walden, UK), and the insurance companies (Dominique Ranson, Belgium). The second day was focused on site-specific validation of several technologies including soil vapor extraction (Michael Altenbockum and Oliver Kraft, Germany), surfactant/cosolvent flushing (Leland Vane, USA), bioremediation (Frank Volkering, The Netherlands), chemical oxidation (Robert Siegrist, USA), and permeable reactive barriers (Volker Birke, Germany). These presentations were followed by a presentation on the site-specific validation of in situ remediation at sites with dense nonaqueous phase liquids (DNAPLs) (Arun Gavaskar, USA). The special session was

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to end with a presentation on future developments including expectations, instruments, and goals, The Netherlands) followed by an open discussion period. However, this period was not nearly as productive as it might have been, as the news of the tragic terrorist attacks in the USA became known and attention was refocused on the events of the day.

Based on the presentations made during the Special Session and the discussions that occurred during the meeting, several concepts emerged with regard to validating in situ remediation performance. The cochairs of the Special Session (Siegrist and Satijn) captured the following concepts that appeared to be recurring themes during the presentations and discussions:

- Verifying (or validating) potential performance capabilities is not the same as verifying actual performance achieved.
- The right combination of several in situ techniques in place and time will often provide the best solution. In this case the verification of the processes is even more challenging. It may also be appropriate to combine in situ methods with ex-situ techniques in a proper way to achieve the most cost efficient result.
- Engineers, regulators, site owners and others need to set realistic goals for in situ remediation and the methods for verifying performance achieved at a particular site. We need to set realistic expectations, which we can, deliver on and defend.
- Clean up of the 3-dimensional subsurface completely to a specific performance goal is challenging, and it is unreasonable to expect that every cubic meter of treated soil will be at or below a target goal.
- Validation requires careful application of monitoring and measurement methods, and methods must be applied to deal with uncertainty. Subsurface investigations that rely on soil sampling and analyses are generally poor and need improvement. Existing, as well as new and more sophisticated, techniques need to be integrated and used to provide multiple lines of evidence enabling conclusions to be made regarding performance goal achievement.
- In situ remediation technologies should be designed and implemented at a particular site to enable performance verification to be achieved.

This report includes the visuals used during the presentations made at the NATO/CCMS meeting in Liège, Belgium on September 10-11, 2001. In most cases, these presentation materials have been supplemented with an extended abstract or paper. Individuals who are interested in learning more on the subject of an individual presentation or on the Special Session should feel free to contact the participants at the address listed in the back of this report.

We would like to acknowledge the participants in this Special Session for their efforts in preparing insightful presentations and contributing papers and presentation materials to this report. We are also grateful to the input and support received from Steve James, Walter Kovalick, Volker Francius, and John Moerlins.

### PRESENTATIONS AT THE SPECIAL SESSION

### INTRODUCTION TO THE TOPIC AND THE SPECIAL SESSION

Bert Satijn<sup>1</sup>

### **1. INTRODUCTION**

Validation of in situ remediation techniques is the topic for this NATO/CCMS Special Session. Before going into the technical aspects, it is necessary to agree on the definition of the word "validation", which in this Special Session, may be used interchangeably with "verification". Validation (or verification) could be defined as a protocolized method to determine the performance of a remediation technology, applying quantitative criteria. So in simple words: *to prove that is it working*.

In many projects the validation of the performance of a remediation system starts at the end of the remediation technique, but in fact it should start with the soil investigation and the design of the remediation system. Important questions are:

- 1. Do I have a complete view on:
  - a. the site-specific conditions of soil, groundwater, contaminations, subsoil processes of migration and attenuation;
  - b. function (present and future);
  - c. risk profiles of the site;
  - d. the boundary conditions for a clean-up;
  - e. and especially the goal for remediation (preferably in semi-quantitative criteria).
- 2. What system of remediation could be successful and cost effective? Normally we are thinking of applying one technique, but it often becomes clearer that the right combination of techniques, depth and time-dependent, provides most probably the most cost-efficient solution. A combination of in-situ processes creates an extra challenge for the validation.
- 3. How will the exploitation of the remediation system be organized? Which steering parameters will be measured and how will they be used?

So the validation process is the last in a chain of activities and depending very much on the first steps. Before going into the discussion on validation, first some statements on the in-situ techniques will be made.

### 2. STATE OF THE ART OF IN SITU TECHNOLOGIES

In-situ techniques for remediation are relatively new. In the U.S., Germany, the Netherlands and some other countries, our experience is not more than ten years. It started with the pump and treat systems that became in many cases pump & spill. The reason for this was that we didn't understand the relation between diffusion and advection processes, and determining the effectiveness of cleanup by pumping alone.

The goals for in situ techniques are not always realistic, as they can be set by an opportunistic consultant. Subsoil processes in biogeochemistry are not well understood. The complexity of processes in biogeochemistry is high and not easy to monitor. The depth, the simple monitoring devices, and related costs are important factors that explain why there is always a lack of enough data, both in space and time. Heterogeneity is our challenge, on the mm-, cm- and m-scale. Results of the monitoring system are seldom smoothly declining graphs. Uncertainties about the effect of remediation activities are stuff for long discussions between the stakeholders. Soil is heterogeneous while legislation and criteria do not know how to deal with uncertainties and fluctuating results. There is a big gap between policy and

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legislation on the one hand and the practical possibilities on the other hand. Lack of long term monitoring results and thorough evaluations of in-situ techniques can hinder good performance testing and validation of these techniques.

### **3. VALIDATION OF IN SITU TECHNOLOGIES**

The question at hand is, "How to prove that the in-situ technique is working?" There are several methods and approaches that, in combination, can provide information on the performance of an in situ technology at a specific site and support its validation:

- Reduction of concentrations, macroparameters and microparameters;
- Change of process conditions, redox, temperature, Ec, etc.;
- Mass flux reduction;
- Restoration of ecosystem (e.g., nematodes);
- Isotope analyses and other specific analyses; and
- Risk reduction

In the technical sessions various approaches for validation and performance testing will be presented. But the following statements could be made as key issues for this special session:

- Subsoil processes in biogeochemistry have to be studied in more detail:
  - Macro-parameters versus micro-parameters;
  - Primary processes versus secondary processes;
  - Optimization of combination of physical, chemical and biochemical processes.
- Thorough evaluations and verification programs including proper validation do have to provide the performance indicators and bottlenecks;
- Development of monitoring devices has to lead to technologies and methods that provide more, better and cheaper data; and
- The needs and criteria of regulators and site owners have to be translated into validation and verification concepts that deal with field heterogeneity, but nevertheless fit into legislation and performance criteria.

### 4. PRESENTATION VISUALS ~ presented by Bert Satijn

NATO	O/CCMS Special Session	Introduc	tion of the session		
Validation of <i>In Situ</i> Remediation Performance		Validation	• Validation of in situ techniques:		
		$\rightarrow$ to prove that is it working			
		<ul> <li>State of the</li> </ul>	e Art of in situ techniques		
Introduction to the session Bert Satijn		- Relatively	<ul> <li>Relatively new technology</li> </ul>		
		- Complex	- Complex processes in biogeochemistry		
	SKB	– Heteroge	neity is our challenge		
10-09-01	NATOCCMS godal assister 1	10-09-01	NATO/COMS-special resolution 2		
Introdu					
• How to	ction of the session (2) prove that the in situ	Program	Monday Afternoon		
<ul> <li>How to technique</li> <li>Reduce</li> </ul>	ction of the session (2) prove that the in situ te is working ction of Concentrations	Program • 13:30 - 13:45	Monday Afternoon Introduction to the session Bert Satiin.		
How to technique • Redue • Mass • Risk	ction of the session (2) prove that the in situ te is working ction of Concentrations flux reduction reduction	Program • 13:30 - 13:45 • 13:45 - 14:30	Introduction to the session Bert Satijn, Challenges for validation Rohert Siegrist		
<ul> <li>How to technique</li> <li>Reduce</li> <li>Mass</li> <li>Risk reduce</li> <li>Within</li> <li>Within</li> </ul>	ction of the session (2) prove that the in situ te is working ction of Concentrations flux reduction reduction n the timeframe n the budget	Program • 13:30 - 13:45 • 13:45 - 14:30 • 14:30 - 15:00	Monday Afternoon Introduction to the session Bert Satijn, Challenges for validation Robert Siegrist The needs, views and concerns from the regulators		

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### Program Monday Afternoon

<ul> <li>15:30 - 16:00</li> </ul>	The needs, views and concerns from the site owners	
• 16:00 - 16:30	Terry Walden The needs and criteria for the	
	insurance companies Dominique Ranson	
<ul> <li>16:30 - 17:00</li> </ul>	Plenary discussion of the scientific challenges	
*	-	
10-09-01	NATO/COM5 special session 5	

### VERIFICATION OF IN SITU REMEDIATION PERFORMANCE: PROCESS FEATURES AND CHALLENGES

Robert L. Siegrist<sup>1</sup>

### 1. CONTAMINATED SITES AND RISK MANAGEMENT

Subsurface contamination by toxic chemicals is a widespread problem in soil and ground water at industrial and military sites in the U.S. and around the world (NRC 1994, NRC 1997, USEPA 1997, Visser 1993, CARACAS 1998, NATO 1999a). Organic chemicals are often the primary contaminants of concern (COCs) and they commonly include volatile organic chemicals (VOCs) such as tetrachloroethene, trichloroethene, and benzene, and semivolatile organic chemicals (SVOCs) such as polyaromatic hydrocarbons and pesticides (Riley *et al.* 1992, Siegrist and Van Ee 1994, ATSDR 1999, USEPA 1997). In addition, there may be metals (e.g., Pb, Cr) and radionuclides (U, Tc) as co-contaminants of concern (Evanko and Dzombak 1997).

In the beginning, when contaminated sites were first discovered and their potential impacts on human health and environmental quality were first revealed, appreciable levels of hazardous chemicals in uncontrolled environmental settings (e.g., soil or groundwater) were presumed to present a condition in need of action and implicitly, an unacceptable risk. Risk reduction was typically achieved by excavation of soil and waste with subsequent treatment and disposal offsite, combined with pump and treatment of contaminated groundwater (Mackay and Cherry 1989, USEPA 1997, USEPA 1999). Now more explicit risk assessment and management underpins cleanup programs for Superfund and most other contaminated sites (USEPA 1989, Labieniec *et al.* 1996, Sheldon *et al.* 1997, CARACAS 1998). Baseline risk assessments are first completed to define the need for and extent of site cleanup and to develop site specific remediation alternatives to mitigate unacceptable risks to an agreed upon goal. Generic, rather than site-specific, risk assessments can also be done to develop screening level criteria for assessing sites and establishing cleanup goals (e.g., Visser 1993, USEPA 1996).

Varied exposure scenarios can present serious current or future risks at many contaminated sites. At many sites, risk is often governed by human exposures to chemicals in drinking water. Such contamination has commonly resulted from wastes released at or near the land surface and the subsequent migration of chemicals through soil into the underlying ground water (Figure 1).

To mitigate current or future risks, remediation approaches increasingly employ in situ technologies comprised of engineered as well as natural attenuation systems (Figure 2) (NRC 1994, NRC 1997, USEPA 1997, NATO 1998, NATO 1999a,b, Siegrist *et al.* 2001). In situ remediation in source areas of contaminated soil and groundwater is being accomplished using mass transfer and recovery methods (e.g., soil vapor extraction, air sparging, surfactant/cosolvent flushing) and in place destruction methods (e.g., bioremediation, oxidation/reduction), sometimes aided by enabling techniques (e.g., soil mixing or fracturing, soil heating). For treatment of the distal regions of groundwater plumes, natural biogeochemical attenuation and permeable reactive barriers are being employed.

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**Figure 1:** Illustration of a common contaminated site scenario where land disposal of industrial wastes has led to organic chemicals leaching into the subsurface being transported to receptors exposed by ingestion of contaminated drinking water or inhalation of vapors.







### 2. VERIFICATION OF PERFORMANCE POTENTIAL VS. SITE-SPECIFIC ACHIEVEMENT

Risk reduction can be achieved using in situ remediation technologies by treating the COCs and decreasing their concentrations, mass, mobility and/or toxicity. Verification that risk has in fact been reduced to a target level established using a site-specific risk assessment or application of screening-level cleanup criteria is based on a quantitative assessment of technology performance. In its broadest sense, technology performance encompasses more than just treatment efficiency and risk reduction. In general, it may be defined as: "Performance is a measure of a technology application with respect to a specified function". Example functions include:

- Treatment efficiency (and risk reduction),
- Ease of implementation,
- Degree of site disruption and aesthetic impact,
- Compatibility with long-term land use plans, and
- Cost effectiveness.

Technology performance with respect to treatment efficiency is of concern in this paper and NATO special session. Treatment efficiency and risk reduction must necessarily be incorporated into remediation practice, either implicitly or explicitly. As site cleanup goals are established (whether it be by a quantitative risk assessment or another method), one must delineate the current nature and extent of contamination in environmental media throughout some location in space and time and also the desired end-state after treatment (e.g., risk-based concentrations throughout a volume of soil). Then, the needed technology performance with respect to the contaminant concentration, mass, mobility or toxicity must be prescribed to achieve the risk reduction judged necessary (e.g., treatment to reduce COC levels below drinking water limits). Technology performance goals related to treatment are thus set such that achieving them would enable overall site cleanup to be realized.

Verifying (or validating) *potential performance capabilities* is not the same as *verifying actual performance achieved*. Potential performance capabilities can be established based on knowledge gained from different methods and scales of realization (Figure 3). Performance potential is often initially projected based on an initial treatment concept, along with process theory based on contaminant properties and site characteristics. An example is the projection of potential performance of soil vapor extraction to remove volatile organic compounds from unsaturated, permeable soils located above the ground water table. Understanding and confidence in potential performance can be increased through confirmatory testing and evaluation completed during laboratory testing and field pilot-scale demonstrations as well as through full-scale implementation and nationally standardized test programs (e.g., U.S. EPA Superfund Innovative Technology Evaluation (SITE) program). As technology implementation occurs at a large number of sites, a standard of practice can emerge and continue to evolve.

Verifying actual performance achieved at a specific contaminated site is necessarily based on measurements made at that site to quantify treatment effects that result in reduced risk. Assessment of technology performance related to risk reduction are often based on quantifying changes in contaminant concentration, mass, mobility, and/or toxicity as well as environmental conditions indicative that the desired treatment is occurring. Verifying that the treatment performance goals set for an in situ remediation technology have been achieved at a specific site is very challenging due to several factors. Contaminants often have complex and uncertain distributions among multiple phases (e.g., vapor, aqueous, solid, and non-aqueous liquid) and over time and space in the subsurface. This results in great difficulties to interpolate and accurately estimate values at unobserved locations. Verification of performance achievement to reach stringent cleanup goals (e.g., the 5 ug/L U.S. drinking water standard for trichloroethylene (TCE)) can be challenging due to the small range for error and uncertainty (i.e., 0 to 5 ug/L) in estimating that treatment has achieved the goal. Finally, some treatment technologies can

constrain the viability of performance verification methods due to their process function and treatmentinduced heterogeneities (e.g., inability to close a mass balance on COCs, development of preferential pathways).

In general, the effective verification of in situ performance at a particular site becomes more and more challenging with: (1) increasing site size and heterogeneity, (2) presence of dense nonaqueous phase liquids (DNAPLs), (3) cleanup goals that involve high mass removals of contaminants or very low levels of residual contaminants, and (4) remediation technologies that require long time frames and don't readily permit mass balances.

**Figure 3:** Methods and scales of information gain during development of an understanding of the *potential performance capabilities* of in situ remediation technologies.



### 3. APPROACHES TO SITE-SPECIFIC PERFORMANCE VERIFICATION

Verifying actual performance achieved at a specific contaminated site must often be accomplished by quantifying, to some degree of certainty, changes in contaminant concentration, mass, mobility, and/or toxicity as well as environmental conditions consistent with treatment process function. These approaches are highlighted below.

### 3.1 Quantifying Contaminant Concentrations

A common cleanup goal for contaminated ground water can be drinking water standards (e.g., 5 ug/L TCE). At a specific site where this cleanup goal might be set for a nearby drinking water well, the technology performance goal could be to decrease the concentrations of TCE to some target level in soil and/or ground water within the contaminated site boundaries so that natural attenuation would yield a concentration at or below drinking water standards at the nearby drinking water well. Performance verification for this goal normally would involve sampling at multiple locations and times with analyses for the COC of interest. The resulting dataset would then be subjected to statistical analysis to enable comparison of post-treatment conditions to the goal of 5 ug/L TCE. Potential problems and challenges with this type of goal and verification approach include (1) the need for large numbers of samples to address site heterogeneities and temporal and spatial variability, (2) the potential for large measurement errors with some COCs in some media (e.g., volatile organic compounds in soil), (3) the potential errors in interpolation methods used to estimate levels at locations without measurements, and (4) the fact that concentration changes may not be due to in situ treatment (e.g., changes could be due to rate-limited processes and dilution effects during in situ flushing or extraction technologies). These problems and challenges can be overcome, at least in part, by careful and integrated use of modern sampling and analyses methods, field analytical methods, in situ sensor technologies, and geostatistical modeling methods (Crumbling et al. 2001, NATO 2001).

### 3.2 Quantifying Contaminant Mass

Another type of cleanup goal is to decrease the mass of COCs to a target level within a specified region of the subsurface such that the release rate for contaminants to soil gas or ground water is reduced to an acceptable rate (often a rate that results in no further growth or even contraction of plumes with concentrations in them being below a set value). To enable application of this type of goal, the COC mass present before and after treatment must be determined and this is normally done by characterizing contaminant concentrations and multiplying them by the volume of media and its density. The COC mass reduction is then estimated by comparing the post-treatment mass to the pre-treatment mass. Verifying that a specified mass reduction (e.g., 90%) has been achieved requires the same elements as required for quantifying contaminant concentration changes (see Section 3.1). In addition, it requires knowledge of the media volume and density. Potential problems and challenges with quantifying contaminant mass include the same ones confronting quantification of contaminant concentrations, namely: (1) COCs can be distributed in a complex manner among phases and in vertical and horizontal dimensions, (2) the potential for large measurement errors with some COCs in some media (e.g., volatile organic compounds in soil), (3) the potential errors in interpolation methods used to estimate levels at locations without measurements, (4) the fact that concentration changes may not be due to in situ treatment, but also (5) the added fact that in situ remediation can alter subsurface conditions and make comparison of post-treatment masses invalid (e.g., treatment-induced mobilization of DNAPLs). As noted previously, these problems and challenges can be overcome by careful and integrated use of modern sampling and analyses methods, field analytical methods, in situ sensor technologies, and geostatistical modeling methods. In addition, at sites contaminated by DNAPLs, diagnostic tools such as partitioning tracers represent a group of methods that can interrogate the subsurface and potentially provide a more accurate estimate of contaminant mass within a volume of the subsurface as compared to that provided by discrete samples and geostatistical analyses. Other emerging methods that enable integrated assessment of subsurface regions include largescale pump tests and mass flux meter techniques.

### **3.3 Quantifying Contaminant Mobility**

Quantifying contaminant mobility traditionally has been applied to characterize leachability of COCs from solid media such as soil, sediments, debris, or waste products. This is normally done using various laboratory leaching procedures such as the U.S. EPA toxicity characteristics leaching procedure (TCLP). However, quantifying COC mobility can also be used to assess the risk reduction achieved by changes in

### Performance Verification of In Situ Remediation

concentrations in plumes emanating from source areas. For example, at sites contaminated by DNAPLs, depending on the DNAPL properties and subsurface distribution along with the site heterogeneities and ground water flow regime, reducing the initial DNAPL mass present by some amount (but not necessarily 100%) can reduce the mass flux from the DNAPL and thereby reduce the concentration in the ground water plume to a specified goal. Many of the same problems and challenges that confront efforts to quantify contaminant concentrations and mass also confront assessment of COC mobility. Likewise, the same approaches to overcome limitations are also available.

**Figure 4:** Classic approach to quantifying COC concentrations by discrete sampling and analyses to enable geostatistical modeling of COC concentration and mass distributions, and the basis for error and uncertainty due to complex subsurface conditions and site heterogeneities.



### 3.4 Quantifying Contaminant Toxicity

Performance goals can be targeted at changing COC toxicity through treatment to some target level in soil and/or ground water within some region of the subsurface. One example of such a goal is in situ treatment to transform 100% of the chromium in soil from  $Cr^{+6}$  to the less toxic,  $Cr^{+3}$ . In addition to the problems and challenges associated with quantifying concentrations or mass in the subsurface, there can be questions about verifying long-term stability of the observed toxicity reduction effect. This requires long-term testing or sufficient fundamental understanding to predict long-term effects with certainty.

### **3.5 Supporting Measures**

Measurements and observations of conditions that are indicative that in situ treatment is being accomplished can also be used to aid verification of in situ remediation technology performance. Examples of these types of supporting measures include: (1) remote sensing and geophysical mapping of treatment agent (or effect) delivery into a subsurface zone to be remediated, (2) measurement of biogeochemical conditions indicative of treatment process function (e.g., pH, Eh, dissolved oxygen, microbial activity, matrix chemistry), and (3) measurement of reaction products (e.g., CO<sub>2</sub> produced by biodegradation of petroleum hydrocarbons or chloride ions produced by oxidative degradation of TCE).

### 4. SUMMARY

In situ treatment technologies are increasingly being considered for remediation of contaminated sites, yet questions remain regarding how one can effectively and reliably verify performance. Verification of performance of in situ technologies and the achievement of cleanup goals at a specific site can be extremely challenging for many reasons, most notably perhaps, due to the complex distributions of contaminants in multiple phases over space and time in the subsurface and the difficulties to interpolate and accurately estimate values at unobserved locations. Multiple types of data that demonstrate one or more measures of treatment effectiveness (i.e., reduction in concentration, mass, mobility, and/or toxicity) are normally needed to effectively verify treatment performance at a particular site. In acquiring these data, careful application of multiple monitoring and measurement approaches and methodologies is critical to ensure that the proper data are collected and sufficiently comprehensive and accurate for the intended purpose. As one contemplates in situ remediation and the verification of performance at a particular site, questions emerge such as:

"What are realistic expectations for verification of in situ performance? For example, is 95% mass removal with 90% confidence a reasonable expectation?"

"What is the best verification approach for a given type of in situ remediation technology and sitespecific performance goal?"

"What is an appropriate level of investment in verification at a particular site? For example, is 5% of total project cost appropriate? What about 15% or 30%?"

"Should the choice of an in situ technology for a specific site depend on the ability to effectively verify performance at that site?"

As the practice of in situ remediation continues to evolve and field experiences are complemented by the results of research and development efforts, answers to these and related questions will hopefully emerge.

### **5. REFERENCES**

- 1. ATSDR (1999). Agency for Toxic Substances and Disease Registry (ATSDR). ToxFAQs. http://www.atsdr.cdc.gov. April 1999
- 2. CARACAS (1998). Risk Assessment for Contaminated Sites in Europe. LQM Press, Land Quality Management Ltd., Nottingham NG26FB, United Kingdom.
- Crumbling, D.M., C. Groenjes, B. Lesnik, K. Lynch, J. Shockley, J. Van Ee, R. Howe, L. Keith, and J. McKenna (2001). Managing uncertainty in environmental decisions. *Env. Sci. & Technol.*, October 2001, p. 405A-409A.
- 4. Evanko, C.R. and D.A. Dzombak (1997). Remediation of metals-contaminated soils and groundwater. Technology Evaluation Report, TE-97-01. Groundwater Remediation Technologies Analysis Center, Pittsburgh, PA.
- 5. Labieniec, P.A., D.A. Dzombak, and R.L. Siegrist (1996). SoilRisk: A risk assessment model for organic contaminants in soil. *J. Environmental Engineering*. 122(5): 388-398.
- 6. MacKay, D.M. and J.A. Cherry (1989). Groundwater contamination: limits of pump-and-treat remediation. *Environ. Sci. & Technol.* 23: 630-636.
- 7. National Research Council (NRC) (1994). Alternatives for groundwater cleanup. National Academy Press, Washington, D.C.

- 8. National Research Council (NRC) (1997). Innovations in ground water and soil cleanup. National Academy Press, Washington, D.C.
- 9. NATO (1998). Treatment walls and permeable reactive barriers. NATO/CCMS Pilot Study Special Session, February 1998, Vienna. EPA/542/R-98/003. May 1998. www.nato.int.ccms.
- 10. NATO (1999a). Evaluation of demonstrated and emerging technologies for the treatment and clean up of contaminated land and groundwater. Pilot study reports, 1985-1999. U.S. EPA 542-C-99-002.
- 11. NATO (1999b). Monitored natural attenuation. NATO/CCMS Pilot Study Special Session, May 1999, Angers, France. EPA/542/R-99/008. www.nato.int.ccms
- 12. NATO (2001). Decision Support Tools. Special Session report from the NATO/CCMS Country Representatives Meeting on Evaluation of Demonstrated and Emerging Technologies for Contaminated Land and Groundwater, June 26-30, 2000, Wiesbaden, Germany. EPA 542-R-01-002. 135 pgs.
- 13. Riley, R. G. and J. M. Zachara (1992). Nature of chemical contaminants on DOE lands. DOE/ER-0547T. Office of Energy Research, U.S. Department of Energy, Washington, D.C.
- 14. Sheldon, A.B., H.E. Dawson, and R.L. Siegrist (1997). Performance and reliability of intermedia transfer models used in human exposure assessment. In: Environmental Toxicology: Modeling and Risk Assessment. ASTM STP 1317, Philadelphia, PA.
- 15. Siegrist, R.L. and J.J. van Ee (1994). Measuring and interpreting VOCs in soils: state of the art and research needs. EPA/540/R-94/506. U.S. EPA ORD, Washington, D.C. 20460.
- 16. Siegrist, R.L., M.A. Urynowicz, O.R. West, M.L. Crimi, and K.S. Lowe (2001). Principles and Practices of In Situ Chemical Oxidation using Permanganate. Battelle Press, Ohio. 336 pg.
- 17. USEPA (1989). Risk assessment guidance for Superfund, Volume I: Human health evaluation manual (Part A). EPA/540/1-89/002. U.S. EPA, Washington, D.C.
- 18. USEPA (1996). Soil screening guidance: technical background document. EPA/540/R95/128. U.S. EPA Office of Solid Waste and Emergency Response. Washington, D.C. May 1996.
- 19. USEPA (1997). Cleaning up the Nation's waste sites. Markets and technology trends. EPA 542-R-96-005. Office of Solid Waste and Emergency Response. Washington, D.C.
- 20. USEPA (1999). Groundwater cleanup: overview of operating experience at 28 sites. EPA 542-R-99-006. Office of Solid Waste and Emergency Response. Washington, D.C.
- 21. Visser, W.J.F. (1993). Contaminated land policies in some industrialized countries. Technical Soil Protection Committee, the Hague, The Netherlands.

### 6. PRESENTATION VISUALS ~ presented by Robert L. Siegrist



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indicative of treatment

more challenging with:

Iong time frames

Cleanup goals that involve...

high mass removals of contaminants

don't readily permit mass balances

very low levels of residual contaminants

Remediation technologies that require...

Validating <u>actual</u> performance achieved at a single, specific contaminated site .....

## Site-Specific Validation

### Validating that technology performance goals have

- been achieved at a specific site is <u>very challenging</u>
- Complex distributions of contaminants among phases and over space in the subsurface
- Difficulties to interpolate and estimate values at unobserved locations
- Validation of performance against stringent cleanup goals (e.g., drinking water standards)
- Treatment technologies can affect the ability to validate in situ performance (e.g., mass recovery vs. destruction)

### Site-Specific Validation

#### Quantifying contaminant concentrations

- Technology goal is to decrease concentrations to some target level in soil and/or ground water within some region (e.g., yield 5 ppb TCE at the property boundary)
- Validate performance by media sampling & COC analysis with statistical analysis for comparative purposes
- Potential problems and challenges ...
  - Need for large numbers of samples to address site heterogeneities and temporal and spatial variability
  - Potential for large measurement errors (e.g., VOCs in soil)
  - Errors in interpolation to estimate levels at locations without measurements
  - Concentration changes may not be due to treatment (e.g., ratelimited processes, dilution)



Site-Specific Validation

performance at a particular site becomes more and

In general, the effective validation of in situ

Increasing site size and heterogeneity

Presence of nonaqueous phase liquids

achievement of a goal at a specific site can be

Careful application of multiple monitoring and

critical to effective validation at a specific site

measurement approaches and methodologies is

and/or toxicity) are normally needed

Multiple types of data that demonstrate one or more

measures of treatment (concentration, mass, mobility

extremely challenging



site depend on the ability to effectively validate performance at that site?

e.g., 95% mass removal with 90% confidence

e.g., 5% of total project cost? ...15%? ...30%?

Should the choice of an in situ technology for a specific

What is an appropriate level of investment in validation

at a particular site?

### NEEDS, VIEWS, AND CONCERNS OF THE REGULATORS

Victor Dries<sup>1</sup>

### **1. INTRODUCTION**

Soil remediations absorb quite a lot of time of money. Most people don't really adore spending either of these on a factor that doesn't seem to have a positive impact on the future results of the company. Every party concerned is looking eagerly for means to make remediations cheaper and more efficient. In-situ remediation technologies offer quite some advantages: they are often quite a bit cheaper than excavation concepts, you don't spend all of your money at once, but spread payments over quite some years and the use of your land can be more or less continued. In-situ treatment is not evident, though; the soil matrix is very complex and prediction and optimisation of the process is very hard. Problems may arise at several steps in the decision procedure.

### 2. SOIL INVESTIGATION

Every remediation concept starts with a soil investigation to know whether or not you have to remediate, and to offer the data necessary for the evaluation of different remediation concepts and for the modelling of the chosen concept. Yet, even soil investigations may pose quite a few problems.

### **2.1 Investigation Problems**

Classical soil investigations have a number of limitations. A number of samples are taken on specific places on a site. The information you get out of this is of course only relevant for the place where you take the sample and even then, for the depth where you take the sample. Enough samples give you a quite good idea of a site, but it will never be better than "quite good". You never know you haven't missed a spot, you never know that the concentration of chlorinated solvents is the highest on the depth where you have taken your groundwater sample. Apart of that, the question arises how you organise your site investigation. Mostly, the first investigation (we call it exploratory) gives you a general idea of whether your site is contaminated or not. The next investigation (we call it descriptive) tries to find the boundaries of the pollution. Two procedures may be used to achieve this. Firstly, you tell the investigator to do take as many samples as he likes, as long as you get the result as fast as possible. This may imply quite a large lot of samples, and can be quite expensive. To avoid this, most people prefer a tiered soil investigation, where a round of samples is taken and analysed; based on the results, a next round of samples is taken in the most relevant direction. This procedure is more cost-effective, but takes a lot of time.

### **2.2** Alternatives

To avoid those problems, alternative detection and analysis technologies can be used, such as so-called intelligent probes, mobile XRF, mobile GC, and geo-radar. Those technologies are still quite young, though, and most still need thorough validation. Even when such a technology is validated, most of the times a few classical samples need to be taken and analysed to verify the obtained data.

### 2.3 Laboratories

A very critical factor in soil investigations is the quality of the laboratories used. Samples are analysed and the results are used to check whether or not certain standards have been passed of whether the concentrations found pose any risk. A question most people dare not ask is what the relevance is of the data obtained from the lab. In annex to this text, I put the results on organic compounds of a round robin organised about 2 years ago among labs already accredited to analyse different sorts of samples (waste,

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### Performance Verification of In Situ Remediation

waste water, ...). If the results of the round robin were positive, a lab also got the accreditation to carry out analyses on soil and groundwater. The Flemish regulation implies that laboratories have to be accredited in a double procedure: not only the instruments, personnel and procedures in the lab are evaluated, but also a lab must prove its qualities in a round robin. This round robin was already the second try; the results of the first run were so bad, we couldn't even use the data to do a proper statistical analysis. Even though the labs knew the test was extremely important for them (access or not to a fast growing market of soil analyses) the results were quite poor. Recoveries for e.g. benzene in soil ranged from 4% up to 131%, for styrene from 10% to 182%, for dichloromethane from 1,5% up to 199%, for naphthalene from 0,2% to 128%! In water recoveries ranged e.g. for octane from 3,5% up to 75%, for tetrachloromethane from 62% to 194%, for 1,4 dichlorobenzene from 45% up to 174%, for naphthalene from 17% up to 126%. I want to stress that the samples were all well homogenised and stored in optimal conditions until taken in by the labs. How often is this true during soil investigations?

We were lucky, we found those problems, and we did not accept the labs with bad recoveries for soil or groundwater analyses. Some of the labs we did not accept where quite big foreign labs, which were accredited in their mother country according to "classical" accreditation systems (do you have quality control procedures and do you follow them thoroughly). How many countries, though, have an accreditation system where also the quality of the analyses is evaluated? Those problems forced us to set up a system of blind controls of the laboratories, as we wonder what the quality of an analysis is when a lab is not working for such an important goals as a market entry, but rather under the stress of delivering results as soon as possible. For relatively volatile compounds, the problems are even larger, because it's very hard to prevent loss during sample taking.

A lot of work still has to be done to improve analyses, and we have to view very closely if certain parameters cannot be measured better in the field. What's the use of spending a lot of energy in a thorough risk assessment if even your input is not sure? What guarantee do you get if a risk assessment states that a risk is present, but that it's not really serious?

### **3. REMEDIATION**

The Flemish soil remediation decree states that historical soil pollution needs to be remediated if the soil contamination poses a serious risk for man, groundwater or environment. The moment of the remediation depends on the priority given to the pollution (except when the ground is transferred; then the transfer triggers the remediation). To remediate all historical soil pollution that poses a serious risk, a period until 2036 has been dedicated.

### 3.1 In-situ Concepts

*In situ* techniques are applied quite a bit at sites in Flanders, although I am skeptical about the ability of current techniques to offer complete solutions. Pump and treat solutions are generally accepted, but with the proviso that the chances of P & T offering a complete solution are not high. Poor site investigation work often limits P&T effectiveness. Hydrogeological containment is used for managing active waste sites, but is not popular as a remediation approach.

Soil venting and bioventing are popular technologies, and air sparging is growing in importance as a remedial technique, all are well accepted by regulators. A recent study on emissions from these processes indicates that the emissions control is of limited effectiveness, with significant transfer of volatile organic compounds from soil to atmosphere. Currently used in situ techniques are not apt to deal with very severe contaminations, as treatment times may span several decades. Most concepts offer not a complete remediation of a site; on the long run, we have to take into account that when the use of the ground changes, the contamination may pose serious risks again and that the future use may be hindered.

I think the new boosting concepts that have been developed in the United States may offer solutions for heavy contaminations, that cannot be solved in an easy way by classical concepts in a relatively short time span. Good care has to be taken of the control of the system, as mobilisation of the contaminant opens also the risk that contamination is spread beyond the present boundaries of the contamination or even of the property.

### 3.2 Natural Attenuation

A second alternative that looks very attractive is natural attenuation. Just count on the biodegradability of the pollutant, and make sure the pollutant doesn't leave your ground. To check this, a sound monitoring system is installed. Sounds pretty good, but we have to focus on a few problems. Firstly, this monitoring may last many years, thus implying important organisational aspects, as well as a cost that may prove to be quite high on the long term. Secondly, we only accept a concept of attenuation if you can prove that attenuation is taking place and is guaranteed on the long term. As attenuation depends on many factors, a very good knowledge of the soil and of the soil processes is needed. Our experience is that very few consultants have the experience and the know-how to do a good modelling and that the amount of data needed to do this modelling requires a thorough (and expensive) soil investigation. If your problem is quite big, this is no problem of course, but we still have the problem of the monitoring. Above, I already stated that laboratory analyses are not always exact, even for parameters that are more or less common. This problem is even much larger when one has to analyse parameters that are not common at all. A great example is the degradation of chlorinated solvents. I have already heard very nice speeches of consultants indicating that they measure a lot of parameters to prove attenuation is taking place, even vinyl chloride and ethene. I know very few labs capable of analysing these parameters in a proper way. Even when you find one, taking a sample, conserving it properly until it reaches the lab and sample preparation is not evident at all of this case, so it may quite well be that the plume of dissolved product and by-products is much larger than you measure. We are not very likely to accept this if the plume is moving towards a neighbour who is not too far away.

### 3.3 "Stimulated Attenuation"

I like the term *stimulated attenuation;* however it's just a nice name for existing concepts. Either it's an in situ remediation concept, or an attenuation concept where the source is removed, or a combination of both, where the source is removed and afterwards an in situ treatment of the plume is started. I like them quite a bit better than natural attenuation, because at least you have a decent idea that part of the contamination is removed.

Especially the combination looks quite good, because most often in situ treatment without taking away the source takes ages, and on the other hand a well designed in situ treatment can reduce the term of monitoring with many years. Again, we have to stay critical to try design a treatment and to monitor the plume as well as possibly.

### 3.4 Isolation Concepts

You can opt for alternative soil remediation technologies that don't take away the pollution in a short term. A first one is isolation of the pollution. By isolation, you break the pathway and reduce the risk. Isolation is quite often much cheaper than removal of the pollution for very large contaminations, but has some disadvantages. Firstly, an isolation always implies a duty of care: whatever you do on a ground, you have to take care that you don't break the isolation. This may pose problems, for instance when you want to construct a new building on the ground.

### Performance Verification of In Situ Remediation

You have to take into account that the isolation has to be maintained; this can make foundations quite a bit more complex (and thus more expensive). This also impacts the value of a ground when you want to sell it. Secondly, each isolation needs to be monitored to make sure the isolation is still functioning well. This monitoring is strictly spoken eternal; this implies important organisational aspects to make sure the monitoring is assured and may imply important costs. Another disadvantage is that every isolation is temporal: after a while the isolation will break down. I know of no system that has eternal life. A good choice of the isolation concept is extremely important; as a basic principle, one can state that every more or less "natural" system is safer than artificial concepts. To reduce infiltration of rain in a polluted area, I trust more in a well-designed natural vegetation system than in an HDPE-liner. Producers of liners currently use a 40 year-guarantee for their products, when their products are properly placed. A good control of the installation of a liner is extremely important, but also extremely difficult. We have already encountered landfills which had been covered 7 years ago and needed remediation, because the liner was not properly installed. Even if the liner is properly installed, you have to be aware that after 40 years, your isolation is quite likely to break down.

An isolation concept I really adore, are active walls. Firstly, the contamination is isolated; thus making sure it poses no unacceptable risks for the surroundings. Where classical isolation concepts tend to be almost eternal and require a good control of the permeability of the wall, the groundwater in this concept can stream quite freely, as long as we are sure it passes through a treatment zone. Thus permeability demands of the wall are a bit less stringent, the wall is quite often quite a bit cheaper, and in a middle-long run most of the mobile fractions of the contamination moves through the active zone, where it is remediated. Again we have to be aware that modelling of an active wall is not very easy, as you have to know what processes you need in your wall. Such a wall also demands maintenance and sound monitoring. The monitoring though may depend of the level of "self-control" the system can deliver. A good concept of the wall can make sure that all contaminated water has to pass through the active zone, and then monitoring of the groundwater downstream of the wall can be reduced strongly.

### 4. CONCLUSIONS

I like in-situ remediation technologies quite a bit. They have quite some advantages: they are often quite a bit cheaper than excavation concepts, you don't spend all of your money at once, but spread payments over quite some years and the use of your land can be more or less continued. We have to spend enough attention to good soil investigation and risk evaluation, as those are the basis to decide whether or not soil remediation is necessary and how the risks can be controlled and reduced in the most effective way. We have to be very careful, as risk evaluation by models seems to be quite exact, but many doubts remain. One of the larger problems is the lack of guarantee offered by laboratory analysis.

Soil remediation is expensive, so we try to look for most cost-effective remediation concepts. Isolation seems quite interesting for large contaminations in the short run, but it may pose organisational and maintenance problems on the long run, as well as problems to transfer the ground. Natural and stimulated attenuation seem very attractive, but we have to be very careful. A consultant has to prove that he knows well enough all relevant soil parameters and that he can model decently what will happen in the future. Monitoring of attenuation is not always evident and may prove to be rather expensive in the long run. Most in-situ concepts offer not a complete remediation of a site; on the long run, we have to take into account that when the use of the ground changes, the contamination may pose serious risks again and that the future use may be hindered.

### 5. PRESENTATION VISUALS ~ presented by Victor Dries





### NEEDS, VIEWS, AND CONCERNS OF THE SITE OWNERS

Terry Walden<sup>1</sup>

### **1. ABSTRACT**

In-situ remedial systems generally fall into two category types. The first is a *Stationary* system that involves the use of installed wells (or trenches) for moving air or other remedial fluid through the formation. In these systems the soil is left relatively undisturbed. The second system is a *Disruptive* system where the soil is physically disturbed to achieve treatment. Examples here include landfarming or in-situ soil mixing with large augers.

Remedial performance validation is dependent on the type of system employed. Sentinel wells at the downgradient boundary and within the footprint of the treatment area are normally used for a Stationary system, where the goal is for all (or at least 95%) of the sentinel wells to meet a risk-based clean-up concentration. In a Disruptive system, it is typical to place a regular grid pattern over the area following treatment and take samples at each node to verify that the target has been achieved. The grid is sized so that any untreated - or less than satisfactorily treated - area has a radius less than a specified maximum.

While conceptually it would be appealing to perform grid-based verification on all remedial systems, site owners would be very reluctant to agree to this approach on Stationary system designs. Experience has shown that such systems typically take longer than specified – and may require additional infill wells – to achieve the promised goals, or may never achieve the objective within a satisfactory time frame. Even more fundamentally, the heterogeneous nature of an undisturbed soil media almost guarantees that some zones will by bypassed, typically those having a lower permeability where contamination may be concentrated. So having typically spent additional money and time to achieve a clean-up target on the sentinel wells, site owners would be leery of sampling additional locations where one exceedence could delay a real estate transfer (even though it may little impact on overall risk). If a gridded validation were specified by the regulator at the time the system decision is taken, it could well result in selection of a more predictable ex-situ remedial design.

### **2. INTRODUCTION**

This paper expresses the perspective of the site owner with regard to the validation of in-situ remediation performance. The site owner view in this case is the oil company, BP, and the experience shared is BP's European practice on the topic. The experiences discussed are not to suggest that these are BP's policies, but simply the approach that is commonly taken at BP's retail stations, terminals, lube plants and refineries in Europe.

### **3. BP'S PRESENCE IN EUROPE**

BP has operating sites or plants in 10 countries in Western Europe, including the UK, France, Benelux, Germany, Austria, Switzerland, Spain, Portugal, Greece and Turkey. In addition there are a few countries, like the Scandinavian countries and Italy, with a lubricant presence due to the recent acquisition of Castrol. In-situ remediation systems have been installed in most of these countries over the past several years. Primarily these consist of soil vapor extraction systems for treating soils in the vadose zone, and air sparging systems for in-situ treatment of groundwater. In addition, in-situ systems for free product removal include dual or multi-phase extraction using a high vacuum blower.

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### 4. REMEDIAL GOALS

Other than in jurisdictions where it is prohibited, remedial goals in BP are generally determined on a risk basis. There are actually few (or no) countries in Europe where a risk approach is explicitly stated as unacceptable, although there are always local regulators to whom the process may need to be demonstrated and validated before getting their approval.

Remedial goals generally start with a requirement to remove a certain amount of - perhaps all - the free product in wells. The treatment endpoint in this case is a thickness of product not to be exceeded in one or more wells across different seasons. Note that free product usually manifests itself to the greatest extent in the dry season when water tables are low.

Human health or ecological risk goals generally require achievement of a soil and/or groundwater concentration that meets acceptable risk criteria. So the overall remedial goals at a site are generally to leave no more than a minimum thickness of free product in certain or all recovery wells, and to achieve a soil/groundwater concentration protective of human health and the environment.

### **5. SYSTEM CLASSIFICATION**

For purposes of validating performance, in-situ systems can basically be broken down into two types:

- a. Stationary Systems: By this is meant that the soil is left relatively undisturbed by the remedial system, with only wells (or perhaps trenches) installed for in-situ treatment. Examples are soil vapor extraction, air sparging or multiphase extraction wells.
- b. Disruptive Systems: In this case the soil is disturbed in order to treat it. In-situ examples include landfarming (where the surface soil is tilled to facilitate bioremediation) and soil mixing (use of large augers to mix biological or chemical reagents with the soil or to stabilize it by introducing a cementing mixture).

### 6. REMEDIAL VALIDATION PRACTICE

From a site owner perspective, the method of validating remedial performance is a function of the type of system installed:

- a. Stationary Systems: It is preferred to have a series of sentinel wells identified for achievement of the remedial target concentration. These wells are typically not the vapor extraction or sparge wells, as these wells would receive preferential treatment by virtue of being part of the remedial design. The sentinel wells are normally located at both the downgradient boundary of the site and within the footprint of the treatment area. The layout of the wells within the footprint should be such that achievement of the target at their locations assures overall treatment of the whole of the remedial area.
- b. Disruptive Systems: When the soil has been disturbed for treatment, the preferred validation approach is to *grid the site* for validation monitoring. The grid is normally a square or rectangular pattern with a spacing appropriate for ensuring that any inadvertently untreated, or less than satisfactorily treated, source zone has a radius less than a specified maximum. Again the targets to achieve are generally risk-based concentrations.

### 7. CONCLUSIONS AND DISCUSSION

The use of sentinel wells for stationary systems and a validation grid for disruptive systems seems fairly straightforward. A good question to ask however is why a validation grid is not used for all in-situ systems, regardless of type.

Site owners would not be happy to have a validation grid for stationary systems. One hidden message here concerns the lack of confidence in stationary in-situ systems. This is especially true in countries which have traditionally conservative standards, such as Germany or the Netherlands, where meeting a target is difficult. In some cases the systems have not been able to achieve the promised remediation target within the scheduled time frame and often, additional treatment wells must be installed to reach areas or locations in the soil column where the air does not appear to travel. In certain circumstances, the systems have been abandoned in favor of a *dig and dump* scheme at significant cost while also delaying a potential real estate transfer date.

There may be plausible reasons for the shortcomings of the in-situ system. Perhaps it was ill suited for the geology or contaminant type. Perhaps the design was flawed with too large a spacing between wells. But more importantly, it is probably unrealistic and asking too much of a system to achieve very detailed clean-up over a wide area in a media (soil) where there are natural heterogeneities, such as low permeability strata. These anomalies can trap contamination and are un-amenable to treatment by airbased systems where the flow may bypass them.

Having normally spent additional time and money to achieve a risk-based concentration target at all the sentinel wells, operators would be very reluctant to open the site up to gridded monitoring from new well locations. The likelihood is too high that lower permeability untreated zones may be encountered, thus further delaying the closure or sale date, even though concentration exceedences at a few wells would likely have a negligible impact on the overall human health or ecological risk. If a gridded requirement were specified by the regulatory authorities in advance of the decision on the remedial system, it could likely change the outcome in favor of an ex-situ disruptive system, such as composting or thermal desorption.

### 8. PRESENTATION VISUALS ~ presented by Terry Walden





### NEEDS, VIEWS, AND CONCERNS OF THE INSURANCE COMPANIES

Dominique Ranson<sup>1</sup>

### **1. SUMMARY**

Investigating and redeveloping contaminated property used to have more risks than benefits. The potential for environmental liability or unknown cleanup costs often turned an attractive real estate deal into a financial nightmare.

Environmental insurance has made investment in contaminated property less risky over the past decade. The insurance industry has found solutions for environmental uncertainties by offering pollution insurance for known, as well as unknown environmental liabilities.

A site cleanup project for known environmental liabilities represents, in general, one of the most important environmental liability exposures. Insurers have developed their own specific way to assess the insurability of a clean-up program via a review of the remedial action plan, contemplation of containment of the cleanup costs within the insurance program, and inclusion of unknown as well as known pollution conditions in an environmental insurance program. Environmental insurance now permits optimization of internal risk management capabilities and prevents the break down of property transfer negotiations due to uncertainty associated with known or unknown environmental liabilities. Conclusions will be illustrated during the lecture with claims scenarios and cases in which insurance solutions facilitate property transactions.

### 2. KNOWN VERSUS UNKNOWN POLLUTION CONDITIONS

A property owner can protect himself against unforeseen and unexpected cleanup costs that are above the anticipated cost for a cleanup project by purchasing Cleanup Cost Cap insurance. These <u>known pollution</u> <u>conditions</u> are always within the self-insured retention and the Cleanup Cost Cap insurance is excess of this self-insured retention.

Pollution conditions may also be <u>unknown</u> because there is no relevant data on the historic use of the property, the pollution or its consequences (cleanup, bodily injury, property damage) have never manifested, or current legal obligations or orders by the authorities may significantly change. These types of environmental liabilities may be insurable as <u>unknown pollution conditions</u>.

### **3. POLLUTION AND ENVIRONMENTAL LIABILITIES**

Polluted sites often result in third party liabilities. These preexisting conditions resulting from historic site operations or gradual releases typically are not insured within the classical general liability insurance program in Europe, with a limited exception for Germany, where certain types of facilities have the obligation to buy coverage for third party liability related to pollution conditions (UHV). However, on-site cleanup costs are almost in every case not insured and even excluded. Policy wordings must be carefully reviewed, particularly when more than one policy is in place: Not only "known" versus "unknown" but also origin, causality, sudden & accidental versus gradual coverage, primary versus excess (UHK- lower retention/ deductibles under one policy verses another) as well as historical pollution issues may become serious sources of discussion in a claim situation when more than one policy is involved.

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Clean up of soil and groundwater is generally expensive, can be unpredictable and can turn into a financial nightmare. In some European regions, soil and groundwater contamination already jeopardize property transfers and lease and rental agreements.

In order to be able to provide insurance, the insurance industry has techniques to assess the likelihood of occurrence of unknown environmental liabilities and the uncertainty related to environmental cleanup. The likelihood of occurrence of unknown environmental liabilities is essentially assessed by examination of the underwriting information. This underwriting information consists essentially of detailed data regarding site history, dangerous goods and waste storage management, dangerous goods processing and transport, environmental compliance and management, security, hydrogeological characteristics, air and surface water emissions and sensitivity of the neighborhood.

# 4. MOST IMPORTANT UNCERTAINITY FACTORS RELATED TO ENVIRONMENTAL LIABILITIES

# 4.1 Site Related Factors

One of the most important site related factors in the <u>site history</u>. During the environmental underwriting process the site history is assessed in detail because it contains relevant information with regard to the potential presence or absence of different types of pollutants resulting from improper waste handling (buried waste), gradual releases over the facilities operating history, effluent discharges, etc... The site history may also explain the presence of third party liabilities or other outside influences. In some cases due diligence audits or phase I environmental audits contain sufficient site history information. Sometimes more investigation may be required by the underwriter to fill gaps prior to underwriting the exposure. Some site related factors are site or facility specific. Those features are essentially related to the local environment (such as use of land, surrounding land use, presence of drinking water wells, natural resources (lakes, rivers, streams...), the general exposure to third parties related to the pollution and the extent of the contaminants.

Especially with regard to cleanup cost potential, knowledge of <u>surface soil and groundwater</u> <u>characteristics</u> is essential. In most of the European region the environmental authorities require riskbased assessments in relation to the necessity and efficiency of cleanup. Factors such as permeability, transitivity, depth of groundwater table and ground water vulnerability, clay/organic matter content, presence of ground water wells and their application, hydrogeologic characterization...are typical data required for the environmental underwriting process.

Sites under exploitation on which environmental cleanup occurs or will occur need specific attention with regard to the <u>management of the site</u>. In general, environmental management, dangerous goods storage and distribution, waste handling and storage, are important risk factors and may cause additional pollution conditions or complications during cleanup. Also of vital importance is the accessibility to third parties and the way construction and remediation are implemented by the contractor.

### 4.2 External and Other Factors

Environmental underwriting requires a good understanding of the <u>expertise and experience of the</u> <u>environmental consultant</u> working for the insured as remedial expert. One of the basic requirements is the presence of a multi disciplinary team working within the environmental consulting organization, as site assessments and remedial design require such a multi disciplinary approach. The ongoing exponential development of new remedial technologies requires sufficient up-to-date know-how of the environmental designer. Especially in those regions where the local authorities are part of the cleanup project, the environmental Consultant Company must be able to provide local specialized employees able to negotiate with local authorities or other official bodies. In order to be able to assess the comprehensiveness of the remedial budget (or self-insured retention), <u>the level of investigation performed</u> is elemental.

The most important factors are:

- Degree of reliability of the laboratory results
- Geostatistical criteria related to the sampling of soil and ground water
- The sampling procedures and representativeness of the analyzed samples
- Degree of reliability of site history analysis, data on subsurface soil and ground water characteristics, site features and analysis of the extent of the contamination.

In many cases, environmental law, future use of the property, surrounding environment, exposure to public and the environment, will influence the way in which cleanup has to be performed.

Depending on the attitude of the public towards the facility of the insured (and its eventual contamination) the requirements of the degree of cleanup could become completely different form that expected in a "normal" or similar situation elsewhere. It is therefore crucial to be aware of any known or reported claims, pending claims, consent orders, prosecutions, against the insured. Public perception generally does not influence the obligation to cleanup (which is based upon environmental law). Public perception will however push the insured to be more compliant and environmentally conscious.

Unexpected clean up costs are in many cases related to the (sometimes) unpredictable <u>conduct of the</u> <u>pollutants</u>, <u>unknown historic uses of the property</u>, <u>surrounding operations</u>, <u>or poor delineation</u>. Knowledge, therefore, regarding hydrogeological conditions and hydrodynamic behavior of the pollutants, historic uses of the property and proper investigations are essential. Because in many regions the environmental authorities apply a risk based approach, it is also essential to understand the biological attenuation and the toxicology (including the availability) of the pollutant.

Environmental authorities are a significant party within the remedial cleanup process. Their <u>attitude</u> influences the way cleanup will be performed and their likelihood of changing their orders. The political factors, sensitivity of the authorities towards pollution and the legal frame are criteria of consideration during the environmental underwriting process.

# 5. INSURABILITY OF ENVIRONMENTAL (SITE) CLEANUP

# 5.1 How are Environmental Risks Dealt with in Terms of Underwriting?

Environmental insurers rely primarily on their own evaluation and assessment of the factors stated above rather than on insurance industry loss statistics.

Many property and general liability losses with environmental causalities are generally not reported as environmental losses. One of the most important distinctions to be made is the difference between known and unknown pollution conditions, as there is generally no possibility to insure known losses, above environmental law, on a risk transfer basis. **Figure 1:** Loss -, frequency and knowledge indices determine the field in which environmental insurers are willing to participate in the risk (RT or risk transfer section). Outside this delineated field, whereof shape and extent is on a case-by-case level, the risk/loss is within the SIR.



For known pollution conditions however, there are possibilities to insure in excess of the self-insured retention (SIR). This self-insured retention level also depends on the know-how on existing pollution conditions and environmental care (Figure 1).

Statistical know-how based upon experience with similar cleanup projects, loss history analysis of the site, and knowledge of privileged partners (external and own consultants – in the case of AIG, AIG Consultants, Ltd.) gives the insurer the ability to offer environmental insurance solutions. Other extremely important consideration criteria in the underwriting process are the results of the detailed analysis of the remedial action plan and the financial strength of the insured. In-house environmental underwriting experts do environmental underwriting at AIG.

### 5.2 Environmental Insurance Solutions

In the case of presence of known conditions on which a cleanup is legally required, the insurance industry is able to provide coverage for the costs in excess of the SIR. This insurance solution is called: Cleanup Cost Cap insurance.

Unknown pollution conditions and third party liabilities are generally covered by site-specific environmental insurance policies, such as the Pollution Legal Liability policy, perfectly fitting between property and liability insurance policies. Especially in those cases in which property transactions occur, brownfields are developed, multiple year coverage is necessary or balance sheets protections are required, blended insurance programs (such as the environmental protection program) provide tailor made solutions.

### 6. CLEANUP COST CAP PROGRAM

The Cleanup Cost Cap policy indemnifies the insured for cleanup costs, as defined in the remedial study, that are above the anticipated budget for cleanup of the site or facility. The policy offers coverage for cleanup costs at, adjacent to, or from a defined site location. The coverage consists of an attachment over the SIR, which is generally equal to the expected costs of cleanup plus a buffer layer (Figure 2). For the known pollutants, there's coverage provided in the event:

- The actual contamination is greater than estimated
- Off site cleanup is required adjacent to the covered site
- Off site cleanup due to emanation of the pollution from covered site
- Governmental authorities change orders in course of the cleanup project

The policy covers the remedial action plan, becoming a part of the policy and describing exactly the area in which environmental cleanup occurs. The Cleanup Cost Cap also offers an option covering newfound contamination while conducting the cleanup. This option also includes coverage for cleanup in case offsite contamination from those newfound pollutants occurs from the covered location.

**Figure 2:** Basic insurance structure of the cleanup cost cap program: The SIR is equal to the expected costs of cleanup plus a buffer layer. Above this SIR there is a cost overrun coverage (a "cap" or excess of loss). Premium discounts are available in case the insured participates in the excess of loss section. Numerical example: SIR= 2,240,000 Euro; cost overrun coverage= 3,760,000 Euro



The information required to underwriting a Cleanup Cost Cap policy includes the environmental site assessments (phase I, II, risk assessments (REBECCA, C-SOIL, Volasoil etc.), hydrogeological assessments, etc.), the remedial action plan (including different cleanup alternatives and budget estimates) and the eventual agreement with the contractor who will execute the remedial work.

The Cleanup Cost Cap (CCC) properties at AIG are:

- 100,000,000 US\$ available per site
- Multi-site programs can be offered
- In suitable for blended insurance solutions
- Terms up to 10 years available.

# 7. POLLUTION LEGAL LIABILITY

AIG's Pollution Legal Liability policy (PLL Select) generally provides coverage for operations facilities. The coverage includes on-site and off-site cleanup from pre-existing and new pollution conditions, on-site and off-site third party bodily injury as well as on-site and off-site third property damage due to pollution conditions. The insurance program can be tailor made (different basic coverage options) depending on the risk-management needs of the (insured). In addition to the insurance program, PLL Select offers coverage for business interruption and transportation to and/or from a covered location. There's generally no distinction made between sudden or gradual pollution, because in many claims scenarios it is almost

impossible to differentiate between the two. The policy trigger of PLL Select is the legal obligation to carry out environmental cleanup. Coverage is provided for owned, leased or rented sites.

The PLL policy doesn't provide coverage for existing contamination (this is done by the Cleanup Cost Cap policy), but provides coverage during the policy term in case pollution conditions arise, which is not covered under new found conditions in the Cleanup Cost Cap policy, a cleanup is required. PLL can be combined with a CCC program or can be purchased after execution of the remedial work.

### 8. BLENDED INSURANCE: ENVIRONMENTAL PROTECTION PROGRAM

By means of example of blended insurance solutions, the Environmental Protection Program (EPP) gives the ability to combine numerous advantages related to environmental insurance:

- The policy creates a well defined scope of action
- There is an excess coverage provided
- Expected costs are discounted
- Rewards are provided in case of favorable loss experience
- Provides high guarantees in case of property transaction
- Protects budgets and balance sheets

The Environmental Protection Program is, technically speaking, a combination of a finite risk insurance construction (RF) and an excess of loss coverage (Figure 3). For example, a known condition might require environmental cleanup and is associated with a budget of 10,000,000 US\$. The legal obligation to execute cleanup may be expected within the first 10 forthcoming years. The known potential loss is ventilated over this period, resulting in a net present value (NPV) over the amount of years. The average NPV is a criterion to determine the RF premium. In addition to the RF section, the insurer provides an excess of loss coverage.

### Figure 3: Environmental Protection Program construction



#### 9. CLAIMS SCENARIOS

By investigating the different claims, which have occurred within the industry, as presented during the lecture, the most frequent causalities of losses are due to the discovery of additional or new soil contamination. In a lot of cases additional costs arise due to accessibility problems for excavation, difficulties in site geology and greater ground water contamination extensions. Other cases of loss are related to inadequate soil and ground water sampling, under-estimation of laboratory and consulting costs and insufficient defined actions to be taken within the Remedial Action Plan (RAP).

Many claims are also associated with discovery presence of unknown pollutants during the execution of the environmental cleanup (such as asbestos, pesticides, PCB's, etc). Claims vary between 20-300% of the SIR.

# **10. CONCLUSION**

Environmental underwriting can not be compared with the daily way of underwriting risks in the insurance industry. It requires a detailed assessment of all kinds of factors that might influence the extent and scale of known and unknown pollutants. Environmental liability exposures, whether known or unknown, can jeopardize property transactions, as they are normally insufficiently insured or not insured at all within the general liability or property insurance programs (the classical insurance). Environmental insurance is the adequate answer to situations in which financial guarantees are required to cover environmental liabilities. Environmental insurance and blended insurance programs are oftentimes purchased in cases of mergers and acquisitions and brownfield development situations. Contractors are also interested to offer coverage for cost overrun due to environmental cleanup. Insuring the environmental liability might create financial advantages such as off-balance sheet and budgetary protection.

#### **11. PRESENTATION VISUALS** ~ presented by Dominique Ranson







#### NATO/CCMS Pilot Project Phase III



#### NATO/CCMS Pilot Project Phase III









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clean-up

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Manager Environmental Insurance AIG Europe

# Why purchasing environmental insurance?

- Meets to specific requirements to obtain financial guarantees
- Essential in mergers and acquisitions
- Brownfield developers and contractors have high interests
- ▼ Off balance sheet protection

AIG

#### SITE-SPECIFIC VERIFICATION OF SOIL VAPOR EXTRACTION

Michael Altenbockum<sup>1</sup> and Oliver Kraft<sup>2</sup>

#### **1. ABSTRACT**

In 1998 data from a number of soil-vapor remediation projects have been reviewed in a research project. The results revealed that most of the reviewed projects showed deficits in important features as field testing procedures, technical standards and criteria for starting, implementing and stopping soil-vapor remedial action. The results also made clear that there is a big demand for standardized procedures and technical guidance in dealing with volatile contaminants in the unsaturated zone.

The German Association of Remediation Engineers (ITVA) will publish directions in the near future that will provide standards for field-testing and data collection. Together with a recently published direction by the environmental state authorities of Nordrhein-Westfalen / Germany, these two publications will provide technical standards as well as criteria to evaluate the effectiveness of soil vapor remediation projects. They also deal with quality control and quality assurance (ITVA) and strategies for terminating soil-vapor remedial action (LUA).

If remedial goals cannot be met, a key number for the evaluation of remedial effectiveness is defined as the specific energy consumption. If specific energy consumption is calculated as being not within tolerable limits, it is suggested that the remedial concept has to be reviewed critically or remedial action should be terminated.

#### 2. INTRODUCTION

In 1998 environmental authorities in Nordrhein-Westfalen launched a research- and development-project to investigate different approaches to soil vapor extraction (SVE) in practical remedial projects. The aim of the research project was as follows:

- 1. Explore the state-of-the-art of this technology which is meant to be a proven technology,
- 2. compile the fundamental knowledge about SVE,
- 3. develop guidelines for SVE remedial practice which should end up in a guidance document and
- 4. define the frame conditions for an optimized application of this technology.

In the research project, data from one hundred remedial projects and 146 treatment plants from all over Germany were collected and evaluated. To avoid any bias it was made sure that not more than four projects per source were used. The sources were consulting companies, cities, counties, state agencies and others, public and private. Furthermore, laboratory testing has been carried out to gain a broader knowledge about the extraction properties of contaminants under ideal, laboratory conditions.

When evaluating the collected field data, the main focus was put on the following points:

- Field tests of extractions before starting remedial measures,
- documentation of remedial goals and rationale for their specification,
- documentation of procedures to evaluate the effectiveness of remedial action (e.g. effective radius of extraction, extractability of contaminants, mass balance, etc.).

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The following points are given to summarize the results of the data evaluation:

Field-testing before remedial measures:

- In only sixty-five percent of the evaluated case studies extraction tests were carried out in the field before remedial measures were started.
- The duration of the tests ranged from a couple of hours to 99 months [which, in the second case, led to the conclusion that no further remedial action is necessary in this case!].
- In 26 percent of the field tests there were no provisions to treat the off gas.
- None of the field test data sets were considered and implemented in the subsequent design of the treatment plan. Frequently, it was concluded that the process applied during the test would also be the best process for the remedial measures.

#### Remedial goals:

In Germany, remedial goals are usually specified as numeric goals - as numbers. The specification of these numbers can be named more or less arbitrary because it is frequently done without consideration of the site conditions. Mostly, remedial goals were set up by supervising authorities. Having a look at the numbers that were used as remedial goals, it looks like a "Who has the strictest regulations"-contest has evolved between authorities in charge (Figure 1). The result was that in more than 70 % of the cases, the remedial goals could not be met.



Figure 1: Comparison of remedial goals in field applications (LUA 2001).

Another number that is usually specified by supervising authorities is the off-gas concentration. A technical standard by the German Association of Engineers (VDI) from 1999 provided guidance by giving numbers as maximum levels for contaminant off-gas concentration. These numbers have become mandatory for many, if not the most remedial measures. However, these maximum emission concentrations have to be criticized especially in housing areas, where the maximum concentration levels are obviously too high.

But using adequate technical features and the appropriate technical design of the plant could reduce this problem. In most cases, the off-gas is treated by adsorption of contaminants on activated carbon. It is well known that moisture content plays an important role in the performance of the activated carbon. Adsorption on activated carbon is much less effective with moist gas. There is no activated carbon producer in Europe who gives any warrant for the performance of his activated carbon with moist gases.

With feed gases having the moisture content of natural soil vapor and contaminant concentrations around or below 50 mg/m<sup>3</sup>, the performance of the activated carbon is not really good and the contaminated soil vapor could not be treated properly. Nonetheless, clean-up criteria and remedial goals are specified in this range every day.

#### Performance and effectiveness of remedial action:

Not all substrates are suitable for using soil vapor extraction as the remedial measure of choice. So, the minimum result of a soil vapor extraction test is to evaluate if soil vapor extraction is an adequate remediation technique or it is not suitable for the given site conditions. The one criterion that is directly connected to substrate properties is the determination of the soil volume influenced by the extraction. The proof for the influenced volume is the determination by measurements of the under-pressure in neighbored monitoring wells. This determination of the range is used to prove that a negative pressure could be established in the full extension of the contaminated zone.

Data for this determination are gathered during the extraction test and the actual remediation in a representative monitoring grid. Frequently, qualitative tests like smoke candles are used, but data revealed from these kinds of tests are not representative and therefore the conclusions about effectiveness based on those kinds of data are not objective. On the other hand, it is an open question if data gathered from quantitative measurements are only numbers describing negative pressure conditions or if those numbers can be used to evaluate the effectiveness of a remedial measure. To come closer to an answer for this question, we should have a close look at the theory and at some results from laboratory and field tests.

In 1997, the German Association of Engineers published mathematical approaches for the determination of the treatment ranges of SVE. These approaches used ideal conditions (homogeneous sediment with no organic content and zero moisture). Based on these theoretical approaches and depending on some boundary conditions (e.g. screen length, screened zone oft the subsurface, diameter of the well, grade of ground surface sealing), it provides an equation and also an analytical solution which allows to calculate the under pressure of a point at a given distance from the well and therefore to calculate the width of the treatment range of SVE. It is well known that in most of the 'real world' cases the conditions in the subsoil are everything but ideal, and they usually cannot be explored in very deep detail. It is therefore more than questionable if mathematical models are really helpful.

Information could again be gained from the research project described several times before, although during the information collection only a limited number of representative data sets could be found. For comparable soil types, in this case fine to medium sand, something like a general trend could be found. This trend was checked in a remediation test at a dry-cleaners site by extracting vapor from different extraction wells in different constellations and monitoring seven wells by under-pressure measurements. Here, negative pressure has been controlled several times during the one-week test. Figure 2 shows a diagram of the results, which were surprising, since obviously there is a negative linear dependency between the under-pressure in the monitoring wells and the distance between monitoring wells and the extraction well. This statement is true for all monitoring wells except KP3, which shows significantly less under-pressure. An explanation for this phenomenon could be found in the files: a massive concrete foundation could be detected between the extraction well and this particular monitoring well, lowering the radius of influence in this direction. All in all, it has to be considered that it is not really clear if other specific site conditions had an influence of the data from this particular field test, since we were not able to further investigate the specific conditions with regards to other inhomogeneities.





But the effectiveness is not only dependent from site / subsurface conditions, but also from specific properties of the contaminant. To evaluate the extractability of different chlorinated hydrocarbons standardized laboratory tests were also part of the research project. Those tests have been carried out by using a column filled with 1.8 kg of fine sand and 20 g of chlorinated hydrocarbons. Moisture content has been set to 90 % and the temperature during the test was adjusted to 20° C.

Different test series have been done with negative pressures of 1, 5, 10 and 25 mbar, these pressures can be reached in field tests and remedial action under good field conditions. Figure 3 shows a typical example of a concentration curve that was revealed with negative pressures of 10 mbar. Other tests with different negative pressures showed similar results. The concentrations curves of 1,1,1-trichloroethane (111-TCA), trichloroethylene (TCE) and tetrachloroethylene (PCE) are different due to the natural gas law and the Henry constant.

In the beginning, the concentration is high. The reason is the balanced condition in the closed laboratory system. After a while, concentrations decreased rapidly and after a test duration of 48 hours, the efficiency of the extraction was detected to be low and not sufficient. No single test showed a contaminant removal higher than ten percent within the test period. If concentrations had remained stable, treatment times of several years would have been necessary to achieve a sufficient contaminant removal.

These results from evaluation show that in remedial practice, there are a lot of unknowns that have to be taken into account in the planning of soil vapor remedial action. Some of those questions about the status of soil vapor extraction in practice can be summarized as follows:

- What are optimal conditions for SVE in the subsoil?
- What is the influence of moisture, temperature and organic carbon content?
- How can optimal conditions be established?
- What happens with the contaminants in the subsoil under these optimal conditions?



Figure 3: Contaminant concentrations in the Extraction Tests at 10 mbar Negative Pressure (LUA 2001).

### **3. DEVELOPMENT OF SUFFICIENT REMEDIAL CONCEPTS**

In 1997 the Federal German Soil Protection Act was released. This besides a lot of other things it states, that if sufficient suspicion of a hazard is given, further investigation may be required. But when the act was released, some people may have been disappointed, because no evaluation criteria, no numbers for the evaluation of soil vapor concentrations to specify the need for a soil gas remediation were given. Soil vapor is not mentioned at all in this act.

Yet, there are no guidance's available to classify contaminant concentration levels in the soil gas. However, the soil protection act requires the use of numeric quality standards and orientation values (for soil) during decision making as a basic principle. But still, some people need these numbers also for soil vapor extraction.

All decisions according to the Federal German Soil Protection Act should be based on the evaluation of risks from the contamination on different receptors. According to the law, these receptors are water, soil and human health. One exemplary question is, why should the same concentrations of a contaminant pose an identical level of hazard to different receptors?

In Germany only the state of Hessen has identified orientation values for the evaluation of soil gas contamination (Table 1). But these numbers were not designed as limits to decide whether to start remedial action or not. They have been set up to function just as indicators if further investigations should be carried out, the decision about remedial action has to be based on these further investigations, which should focus on the evaluation of the different pathways mentioned above. These investigations include analysis of contamination in solids, groundwater and indoor ambient air as well as the conduction of column tests (leachate prognosis).

**Table 1:** Orientation values for soil gas concentrations (LUA 2001).

Orientation Values for Soil Gas					
	Groundwater	Indoor ambient air	Soil		
Σ LCHC	5 mg/m³	5 mg/m³	5 mg/m³		
canc. LCHC	1 mg/m³	1 mg/m³	1 mg/m³		
Σ ΒΤΕΧ	5 mg/m³	5 mg/m³	5 mg/m³		
Benzene	< 1 mg/m³	< 1 mg/m³	1 mg/m³		

With defining orientation values under the described conditions, the state of Hessen showed that they have realized the problem of strict regulations just based on numbers without taking into account the circumstances of any unique case. We should keep in mind that especially for soil vapor contaminant concentrations unique criteria are obviously the wrong approach. The pathways have to be investigated. These are the ambient air and the leachate.

If the evaluation of the pathways results in the decision, that there is no hazard, no action will be necessary. If some indicators for hazards are found, the need for remedial measures must be stated. One of those indicators may be adequate concentrations of volatile contaminants in the soil vapor.

The evaluation of results from soil vapor investigations can be very difficult, because frequently soil gas data lack reproducibility. Practical experiences have shown that these data sets are very often not reproducible by repeated sampling and measurements in the field. Some of the potential reasons are:

- Further influx of contaminants,
- missing documentation of the sampling procedures,
- matrix effects in the non-saturated zone of the subsoil, and
- unknown additional soil vapor properties (e.g. moisture-content).

It is obvious that authorities responsible for the Federal Soil Protection Act and the underlying ordinance knew, that it is not possible to derive soil vapor contaminant concentrations plausibly from solids-concentrations and vice versa. Therefore, soil gas concentration values are missing in these regulations. As true as this statement is, it doesn't help in the daily remedial practice.

The definition of a hazard is one step towards a remedial action. The other one is a remedial investigation, which must document the need for remedial measures. With respect to this, the main point of a remedial investigation should not be the continuing examination of site conditions but more the development of remedial strategies to avoid or reduce hazards in the particular case.

The remedial investigation has to prepare and support the official decision making process on the type and extent of the remedial measures. It should include interim remedial goals and also an evaluation of the applicability and sustainability of potential technological options. The general goal is always to reduce contaminant potential.

## 4. DIRECTIONS AND REGULATIONS

To support the steps mentioned above, a number of general rules and regulations have been developed by the German states and in engineering associations. These directions and regulations have been designed to formulate the requirements of the different investigation steps according to the Federal Soil Protection Act as well as to standardize methods and techniques used during the investigational work.

As an approach to standardize appropriate procedures and techniques used with SVE remediation projects, the German association of remediation engineers "ITVA" will issue direction for SVE field tests in fall 2001. The research and development project mentioned above was taken as one basis for those general rules. The direction includes clear recommendations for the duration, the technologies, the sampling, documentation and data-evaluation. Some important points will be described briefly in the following part of this paper.

It should be obvious that a SVE field test should be the basis of any SVE remedial action, but the results of the R & D project in Nordrhein-Westfalen showed clearly that the accomplishment of a reproducible field test is not a standard at all. Table 2 summarizes the technical features of a standardized SVE field test. With this standard it will hopefully be possible that field tests reveal datasets that allow the evaluation of the extractability with respect to the subsoil conditions and that can be used as a basis for an appropriate SVE plant design. It will also make it possible to compare results from different sites.

Table 2: Standards for SVE field-testing (ITVA 2001).

```
• Duration of Field Test: 5 - 10 days;
· Technical setup:
    Design of extraction- and monitoring wells:
    Inner diameter: 50mm, 1 m tubing, 2 m screen-tubing
    Gravel-package: 0.5 m clay, 2.5 m gravel
    Distance between extraction- and monitoring well: 5m and 10m
    Water- (= particle-) separator;
    Compressor: 250±50m³/h,240±30mbar;2.4±0.4kW
    Adsorption-unit: 1x200 liters, 70 - 80 kg activated carbon

    Sampling:

    Feed gas after 0.1h, 3.0h, 24h, 48h, 96h (=the end of the test)
    Off gas after 24h, 48h, 96h (=the end of the test);

    Documentation of the sampling;

· Sampling with field measurement of volumetric flow rate,
 temperature, moisture in feed and off gas streams;

    Evaluation of results regarding the need for remediation,

 estimation of consumption of activated carbon and energy,
  development of a sampling and analytical program for the
  remedial action, short report.
```

The technology to perform the extraction testing is suggested according to internationally accepted standards. Remarkable is the waiving of an additional safety filter unit behind the adsorber. The safety filter can be ceased in routine five-day tests. However, it may be necessary if contaminant mass fluxes are expected to be very high and there is a risk of contaminant breakthrough. This evaluation has to be conducted prior to the test.

For the evaluation of SVE field-test results, a number of datasets are needed. These data can be divided into two groups:

1. Quality assurance data:	- feed gas temperature,
	- moisture content of the feed gas,
	- oxygen content of the feed gas.
2. Performance data:	- moisture and dew point of the feed gas,
	- volumetric flow rate,
	- under-pressure in the extraction well,
	- under-pressure in the monitoring wells,
	- contaminant concentration-curve,
	- contaminant mass-flux,
	- energy consumption,

- specific energy consumption.

To ensure the comparability of contaminant concentration data, only two sampling methods can be accepted as adequate: adsorption of target compounds on activated carbon and gas-samples in crimp-cap VOA-vials in a septum-cap under overpressure. The latter need to be injected directly into the GC in the following analysis procedure. The direction includes helpful information about the selection of the appropriate sampling method.

# 5. QUALITY CONTROL AND QUALITY ASSURANCE DURING REMEDIAL ACTION

The mentioned guidance's and regulations intend to contribute to an improved quality assurance in SVE application. These include the evaluation of applicability of SVE, the planning and design of remedial action and the control and supervision of remedial measures. Most documents are considered being well on-track, because the technical parts are based upon practical field experiences as well as on theoretical fundamentals. Both elements, practical and theoretical, have to be considered

To enlarge the pool of useful and reproducible information as a basis for future SVE projects, there is an obvious need for Quality Assurance (QA) and Quality Control (QC) during all periods of SVE remediation projects. The following issues appear to be of special importance to this subject:

- Sampling as a foundation for quality management (data gathering),
- calculation of mass streams and mass balances, and
- evaluation of data.

Quality assurance and quality control with respect to data gathering can be assured by using appropriate equipment and well-trained staff. All sampling should be done with consciousness about potential sources of error. One comparably simple way to avoid a large number of problems related to the subject of data gathering is to use a mobile sampling tube (Figure 4) with probes for temperature, moisture, flow rate, oxygen-content and negative pressure, which allow a parallel registration of relevant QA/QC-data. Data can be recorded in an electronic data logger; simple connection plugs allow a mobile use at different sampling locations in a plant.

Figure 4: Mobile sampling tube (ITVA 2001).



All relevant data have to be identified in the planning phase and an appropriate monitoring program has to be installed. These data are necessary to calculate mass streams at relevant points within a plant (input - process steps - output) and to set up a mass balance for the complete plant. This is a suitable way to plausibly document mass fluxes and fate of contaminants and water in the plant as well as energy and activated carbon consumption rates.

Figure 5: Characteristic concentration curves and conclusions (LUA 2001).

Parameter	Tendency		Comments
	Tendency increasing	Prognosis 0,1 3 24 48 96 h	Defendable prognosis of the further concentration curve is not possible Extraction well is not located in the center of contaminated area.
Contaminant Concentration mg/m <sup>5</sup>	Tendency unclear	Prognosis 0,1 3 24 48 96 h	Prognosis of the further concentration is uncertain It needs to be checked if an extension of activity is necessary.
	Tendency decreasing	Prognosis 0 3 24 48 96 h	Extraction well is located in the center of contaminated area Continous decrease allows for a reliable prognisis.

In combination with the calculation of mass fluxes, the development of contaminant concentrations with time are of great importance with respect to the evaluation of performance during SVE field tests as well as during the subsequent remedial action. Figure 5 shows 3 characteristic concentration curves and gives also general interpretations of the curves.

The examples show that reliable data are the basis for plausible conclusions. Plausible conclusions are essential for the acceptance during negotiations with permitting authorities. Quality assurance / quality control promotes acceptance and allows efficient remediation.

## 6. STRATEGIES FOR TERMINATION OF REMEDIAL ACTION

The "ideal" SVE remediation project, like any other remediation project, is terminated when contaminant concentrations are below the remediation goal. Then, remedial action is stopped and a monitoring starts to assure the success of the remediation. But what happens if the remedial goals cannot be met in a reasonable time? Then, a new strategy has to be applied. The keyword is feasibility of remedial goals.

There have been some approaches to describe the "effectiveness" of remedial action and to define criteria when to terminate it. The LUA-direction (2001) defines specific energy consumption as the critical criteria. Based on those criteria, it suggests a flowchart for the decision whether or not terminating SVE remedial action (Figure 6).

It is defined as the amount of energy that is needed in the particular case to remove one kilogram of chlorinated hydrocarbons (LCHC) from the unsaturated subsoil using SVE. The critical value is 1000 kWh (Kilowatt hours) per Kilogram (kg) LCHC. If less then 1000 kWh/kg LCHC are needed, the SVE is regarded being efficient.

With specific energy consumptions between 1000 and 2000 kWh per kg LCHC, SVE projects should be critically reviewed and a discussion about modifications should be made. Possible solutions to increase the effectiveness of SVE remedial measures may be modifications in plant configuration and/or to continue the remediation in an alternating mode. This means switching the extraction system on and off in specific time intervals.

If more than 2000 kWh of energy are needed to remove one kilogram of LCHC, the soil vapor extraction is insufficient or not a suitable method. Then, SVE remedial action should be terminated and different remedial concepts have to be developed.

The critical values of 1000 or 2000 kWh/kg LCHC have been diverted from the R+D project mentioned a couple of times before. There, more than 400 single extraction phases have been evaluated. The values for specific energy consumption in these project phases have been calculated between more than 8 kg of removed LCHC per kWh and 125.000 kWh for one kg of removed LCHC. Of course, these values depend on the contaminant potential in the subsoil. If there is a significant contaminant potential, there is a good chance of removing the contaminants effectively. On the other hand, the results show clearly that some contaminants cannot be removed no matter what amount of energy is used in the remedial measure.

Data collected in the research project mentioned before showed that a large number of soil-vapor remedial projects have to be evaluated as being ineffective with respect to those criteria (Figure 7).

Figure 6: Decision Support for Termination of SVE remedial measures (LUA 2001).



When reviewing the effectiveness of SVE as a remedial measure, the first step should be to check the conceptual approach for plausibility for this particular case. Therefore, the following data are needed:

- Review of all site-specific data (e.g. geology, soil characteristics, contamination in plane and depth, investigations, contaminants/components, development of contaminant levels with time, etc.),
- Components and configuration of the treatment plant,
- Performance data.

If it is found out that the SVE remediation does not work effectively, optimization of the configuration and/or components of the present measure have to be reviewed critically. Possible options for optimization may be more extraction wells or exchange of plant components / modification of technology. Another approach may be in a critical review of remediation goals with respect to site conditions and potential risks from the contamination.

If no concept to optimize the performance of SVE remedial action and remedial goals are found to be suitable, we have to conclude that SVE is not the right technology for the remediation of the subsoil in this particular case and different technologies and approaches have to be discussed.

**Figure 7:** Specific energy consumption in SVE remediation projects (modified after Altenbockum & Odensaß (1998).



# 7. CONCLUSIONS

If we want to apply soil vapor extraction and if we want to assure quality, we have to meet the right boundary conditions. In a risk-based approach for evaluation of the necessity of remedial measures, the decision has to be based upon the realistic chance to remove the contaminant-potential for the different receptors. Therefore, the reduction-potential is the crucial factor for the identification of a remedial necessity and for the choice of an appropriate remedial method and technology. Therefore, this decision should not be based on contaminant concentration levels alone.

SVE is without doubt a suitable remediation technology to reduce or remove contaminant-potential in the unsaturated zone if the site conditions and the contaminant potential are appropriate. The suitability of SVE as the remedial method of choice must be proven by a standardized extraction field test. The results of the field test have to be considered in the evaluation of remediation necessity and design of the remedial measure. Field test data must also comprise the deduction of the expected efficiency of the SVE application. The criterion of specific energy consumption is considered to be suitable for the choice of technology as well as for a critical review of an operating remedial measure.

### 8. REFERENCES

- ALTENBOCKUM, M., ODENSAβ, M (1998): Die Bodenluft in der täglichen Sanierungspraxis. TerraTech. - 6/1998
- 2. *ALTENBOCKUM, M., LIESER, U., LOHAN, N, KRAFT, O.* (1999): Neue Ansätze bei der Durchführung von Bodenluftabsaugversuchen. Flächenrecycling. 3/1999
- 3. ITVA (Hrsg.) (2001/in press): Richtlinie Bodenluftabsaugversuch
- 4. LUA LANDESUMWELTAMT NRW (2001): Arbeitshilfe Bodenluftsanierung. Materialien zur Altlastensanierung und zum Bodenschutz
- 5. *VDI (Hrsg.)* (1999): Emissionsminderung, Anlagen zur Bodenluftabsaugung und zum Grundwasserstrippen. VDI-Richtlinie 3897

#### SITE-SPECIFIC VERIFICATION OF SUFACTANT-COSOLVENT FLUSHING

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#### **1. SUMMARY**

The use of surfactant and co-solvent solutions to remove non-aqueous phase liquids (NAPLs) from soils has seen significant research and development activity over the last decade. These soil flushing technologies are now entering the full-scale implementation stage of their development. Since performance assessment is critical to the acceptance of a new technology, methods for assessing the NAPL removal efficiency of soil flushing technologies have been concomitantly evaluated and developed. In this paper, several performance assessment approaches will be described and the use of these approaches during a surfactant-based soil flushing field demonstration project will be detailed.

#### 2. INTRODUCTION – FLUSHING TECHNOLOGY BACKGROUND

Soon after recognizing the importance of removing NAPL sources to reducing long term risks and costs, a number of "flushing" technologies were investigated. In this approach, one or more chemicals (alone or as an aqueous solution) are introduced into the NAPL-contaminated subsurface zone and caused to flow to a collection system under a hydraulic gradient. These chemicals act to enhance either the solubilization or the mobilization of the NAPL, or both. When the additives are co-solvents, the desired result is the solubilization in a homogeneous single-phase solution. Often, such a result is achieved at relatively high co-solvent concentrations, generally greater than 50 wt%. Alcohols ranging from ethanol to pentanol and higher have been evaluated for this application (Jawitz et al. 2000, Sillan et al. 1998). In some cases, the co-solvents will partition into the NAPL to an extent which alters the interfacial tension properties, thus causing NAPL migration.

The addition of surfactants to the flushing solution can result in both solubilization and mobilization (Butler & Hayes 1998, Chevalier et al. 1997, Shiau 1996). Surfactants (surface active agents) are molecules composed of two differing parts: a hydrophobic tail and a hydrophilic head. Because of this, surfactants accumulate at interfaces such as air-water interfaces or water-NAPL interfaces. By tailoring the properties of the surfactant, significant reductions in interfacial tension can be achieved, thus allowing the movement of NAPL trapped by capillary forces. In general, as the concentration of surfactant is increased, the interfacial tension is reduced. However, at a concentration referred to as the "critical micelle concentration" or CMC, surfactants form self-aggregates referred to as "micelles" (Rosen 1989). The CMC is determined by the properties of the surfactant and the aqueous solution. Below the CMC, surfactants are present in solution as individual molecules called "monomers". Any surfactant added above the CMC will aggregate into micelles, although monomers will still be present at a concentration equal to the CMC. It is the monomer concentration that most effects interfacial tension. Thus, interfacial tension reaches a minimum when the surfactant concentration is 1 CMC and stays fairly constant for surfactant concentrations above 1 CMC

Micelle structures are such that the hydrophobic tails of the surfactant molecules intermingle to form a hydrophobic core while the hydrophilic head groups form a (usually) spherical outer "shell". As depicted in Figure 1, molecules of the NAPL compounds will partition into the hydrophobic core, thus raising the apparent solubility of the NAPL compounds in the aqueous solution. The number of surfactant monomer units in a micelle (the aggregation number) is fairly constant for a particular surfactant/solution system. As surfactant is added above the CMC, more micelles, all of approximately the same size, are formed. As a result, the solubilization capacity of the micellar solution increases as the surfactant concentration increases. The increase in apparent solubility can be several orders of magnitude. For example,

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tetrachloroethylene (PCE) solubility increases from 240 mg/L to ~100,000 mg/L upon the addition of 4.0 wt% Alfoterra 145-4-PO sulfate<sup>TM</sup> surfactant and 16.0 wt% isopropyl alcohol (IPA). Addition of 0.18 wt% CaCl<sub>2</sub> to the system raises PCE solubility to 700,000 mg/L (Duke Engineering 2000).

Flushing solutions are delivered and extracted via screened wells. Thus, proper design, installation, and operation of the well field and flow rates are critical to the success of *in situ* flushing technologies. Subsurface flooding simulators, such as UTCHEM (Brown *et al.* 1994, Delshad *et al.* 1996), combined with hydrogeological and biogeochemical data for the subsurface formation, NAPL, and flushing solution allow for design optimization and the estimation of process efficacy.

# **3. PERFORMANCE ASSESSMENT FUNDAMENTALS**

The performance of soil remediation technologies has traditionally been assessed using groundwater monitoring and/or soil sampling. The former assumes that a unique relationship exists between the aqueous concentrations observed at a monitoring well and the mass or volume of NAPL in adjacent portions of the aquifer. Unfortunately, this assumption is patently invalid because of the diffusion and solubility limitations of the NAPL components; therefore groundwater monitoring is inaccurate for assessing the performance of a NAPL remedial action. Under ideal conditions, the analysis of soil samples will yield a satisfactory performance assessment. However, this requires that the samples be representative of the unsampled regions and that all sediments and interstitial fluids are recovered from soil samples. Thus, spatial variations in NAPL distribution and soil heterogeneities must be minor for soil sampling to be an accurate performance assessment method, and proper sampling tools and sampling procedures must be followed to maximize recovery of all solids and liquids from a soil sample. Otherwise, the number and size of samples necessary to obtain an accurate estimate of the NAPL mass within a subsurface volume must be impractically large. One of the main issues related to soil sampling is the representative elementary volume (REV) which is the volume of soil required to yield a single sample representative of the region being sampled (Mariner et al. 1997). In many cases, the REV is larger than the volume of typical soil samples. Thus, accurate information concerning the local NAPL saturation and distribution is difficult to obtain using soil samples.

To address issues related to REV, a relatively new method of NAPL characterization and remediation performance assessment, called partitioning interwell tracer tests (PITTs), has been introduced (Jin et al. 1995). In this technique, an aqueous solution containing multiple tracers is injected via wells into the NAPL-contaminated formation. The tracers are selected to provide a range of water-NAPL partition coefficients ranging from conservative (non-partitioning) tracers to highly partitioning compounds. Most of the tracers are straight- and branched-chain alcohols. The tracers are then recovered at another well or set of wells. The appearance of each tracer at the recovery well is a function of the retardation of transport caused by partitioning of the tracers into the NAPL phase. In fact, the tracer concentration vs. time relationship observed at the recovery wells is guite similar to that observed during the chromatographic analysis of compounds – tracers which do not partition into the NAPL appear first and at relatively high concentrations. Those that have high partition coefficients appear later and tend to have significant peak tailing. Examples of tracer recovery during PITTs in the presence and absence (or near absence) of NAPL are shown in Figure 2a and 2b, respectively. The mathematical manipulation of the tracer concentration curves yields an estimate of the NAPL residual saturation  $(S_n)$  in the subsurface region swept by the tracers (Wilson et al. 2000, Mariner et al. 1997, Jin et al. 1995, Dwarakanath et al. 1999, Rao et al. 2000, James et al. 2000). Similarly, interfacial tracers can be used to estimate the NAPL-water interfacial area  $(a_{nw})$  (Rao et al. 2000). Multi-level sampling (MLS) devices positioned between the injection and extraction wells can yield information about the vertical variation in NAPL saturation (James et al. 2000, Sillan et al. 1998).

PITTs have a number of limitations and cannot be applied to assess all remediation technologies. Current methods of analyzing PITT data assume that the following conditions exist:

- 1 Tracer partition coefficients (K) are accurately known
- 2 Reversible sorption of tracers to sedimentary organic matter has been quantified
- 3 Tracers penetrate all parts of the NAPL zone including:
  - a. Free-phase NAPL zones
  - b. Low intrinsic permeability or low relative permeability zones
- 4 Multiple tracers with a wide range of Ks used
- 5 Sufficient time provided to assess tracer signals from all parts of NAPL zone.

Due to these assumptions, the ability of PITTs to accurately account for pooled free-phase DNAPL is limited. In addition, high levels of soil heterogeneity can result in tracers having reduced or no access to low permeability zones, for example into clay lenses. Thus, PITTs most effectively estimate NAPL saturation when the NAPL is fairly uniformly distributed as residual ganglia (Wilson *et al.* 2000).

A measure of remediation performance can be obtained by comparing the results of PITTs performed before and after the remediation. The use of PITTs for this purpose is relatively independent of the remediation technology employed. When applied to the performance assessment of in-situ thermal remediation (ISTR) technologies, the timing of the post-treatment PITT as well as the thermal stability of the tracers used will be an issue. Because of their inherent similarities, PITTs and enhanced flooding technologies are particularly well-matched. When conducted prior to the soil flushing process, the PITT design can be incorporated into the remedial flood design, due to the similar flow dynamics. The assumptions listed in the paragraph above must be true for both the pre- and post-remediation PITTs. If the flushing process alters any of these properties, then they must be separately determined for each PITT. For example, if the flushing process alters the makeup of remaining NAPL, then the water-NAPL tracer partition coefficients must be measured again. Such may occur when a surfactant is used to remove a complex NAPL consisting of organics with variable viscosities from the subsurface. A complex NAPL treated using a thermal technology may experience similar difficulties in the use of PITTs due to the preferential removal of NAPL components of low volatility. Flushing processes may also affect the sorption of tracers to the soil, for example if the fraction of organic content of the soil is altered. Therefore, tracer soil sorption must be characterized before and after the remediation.

Finally, monitoring of the extracted flushing solution as well as samples obtained from MLSs and other sampling wells during the flushing process will yield a direct and real-time measurement of remediation performance. The mass of NAPL compounds solubilized by the flushing solution is calculated by integrating the contaminant mass flow rate (concentration times flow rate) vs. time data for the extracted fluid. The sum of this solubilized mass and the mass, if any, of free product NAPL recovered yields the amount of NAPL removed due to the remediation. This amount can then be compared to initial NAPL mass estimates or to NAPL removal estimates obtained from soil sampling or PITT data. A mass balance on injected chemicals should also be conducted by integrating concentration data obtained from extraction wells to evaluate the efficiency of hydraulic containment. This is important as high residual concentrations of injected chemicals following surfactant/co-solvent treatment may cause unintended migration of solubilized chemicals beyond the treatment zone. Monitoring for injected chemicals and contaminant beyond the treatment zone, particularly in locations down gradient to and beneath the treatment zone, can also provide data about whether hydraulic control of fluids has been maintained during the soil flushing process. Finally, maintaining a log of the water levels at all wells to create potentiometric surface maps can provide further supporting evidence that proper control over injected fluids was maintained during flooding operations.

# 4. EXAMPLE –SURFACTANT FLUSHING FIELD DEMONSTRATION AT U.S. MARINE CORPS BASE CAMP LEJEUNE

# 4.1 Camp Lejeune Background and Site Details

In 1999, a surfactant enhanced aquifer remediation (SEAR) demonstration, funded by the Environmental Security Technology Certification Program (ESTCP), was conducted to remove a chlorinated hydrocarbon DNAPL present in the subsurface beneath the central dry-cleaning facility (Building 25, Site 88) at U.S. Marine Corps Base Camp Lejeune, North Carolina. The main contaminant was tetrachloroethylene or PCE, a common dry-cleaning solvent. At this site, groundwater contamination of the shallow and intermediate aquifers has resulted from the storage and disposal of PCE and Varsol<sup>™</sup> dry-cleaning solvents. The latter is a mineral spirit-type solvent. The footprint of the demonstration well field was 20 ft x 30 ft (6.1 m x 9.1 m), and the DNAPL contaminated zone targeted for remediation was the bottom 5 ft (1.5 m) of the shallow aquifer. The total aquifer pore volume treated was approximately 6600 gallons (25.0 m<sup>3</sup>). By design, the ESTCP SEAR Camp Lejeune demonstration treated only a portion of the entire DNAPL source area. In addition to the subsurface treatment by SEAR, the ESTCP SEAR demonstration was the first to incorporate above-ground treatment of the SEAR extraction well effluent (i.e., groundwater, surfactant, and DNAPL) by pervaporation and micellar-enhanced ultrafiltration (MEUF) for the objective of surfactant recycle. The objectives of this demonstration were to: 1) validate in situ surfactant flooding for DNAPL removal; 2) promote the effective use of surfactants for widespread DNAPL removal; 3) demonstrate that surfactants can be recovered and reused; and 4) show that surfactant recycle can significantly reduce the overall cost of applying surfactants for subsurface remediation.

The locations of the three surfactant injection, two hydraulic control, and six extraction wells relative to Building 25 are shown in Figure 3. Six MLS wells each with three vertical sampling locations in the 16.5 to 20 ft bgs range were positioned within the well field (not shown). Injection and extraction wells were screened across the bottom portion of the shallow aquifer from approximately 15 to 20 ft (4.6 to 6.1 m) below ground surface (bgs), which coincided with the depth interval of the DNAPL contaminated zone. Varsol<sup>™</sup>, present as an LNAPL in the upper portion of the shallow aquifer (8 to 10 ft bgs) was not targeted for remediation. However, some Varsol<sup>™</sup> was present as a component of the PCE DNAPL, varying between approximately 2-14 wt% across the test zone, and was removed incidentally with the PCE DNAPL.

The DNAPL zone at Building 25 was primarily in the shallow surficial aquifer at a depth of approximately 16-20 ft (5-6 m), and includes an area that extends about 20 ft (6 m) north of the building. The DNAPL occurs immediately above and within a relatively low-permeability layer of silty sediments (hereafter referred to as the basal silt layer). The basal silt layer occurs from approximately 18 to 20 ft (5.5-6 m) below ground surface (bgs) and grades finer with depth from a sandy silt to a clayey silt until reaching a thick clay layer at about 20 ft (6 m) bgs. Characterization activities associated with the SEAR demonstration revealed that this fining downward sequence can be roughly divided into three permeability zones: the upper zone (~16-17.5 ft bgs; 4.9-5.3 m bgs), the middle zone (~17.5-19 ft bgs; 5.3-5.8 m bgs), and the lower zone (~19-20 ft bgs; 5.8-6.1 m bgs). The site conceptual model, or geosystem, is shown in cross section in Figure 4.

The upper zone is generally characteristic of the overall shallow aquifer, which is primarily composed of fine to very-fine sand and is the most permeable of the three zones. The hydraulic conductivity (K) of the upper zone is estimated to be about  $5x10^{-4}$  cm/sec (1.4 ft/day). The hydraulic conductivity of the middle zone, which is composed predominantly of silt, is estimated to be approximately  $1x10^{-4}$  cm/sec (0.28 ft/day), or about five times less permeable than the upper zone. The lower zone is composed predominantly of clayey silt, with a hydraulic conductivity that is believed to be approximately  $5x10^{-5}$  cm/sec (0.14 ft/day) or perhaps even lower, although the permeability of the lower zone is not well characterized at this time.

#### 4.2 Camp Lejeune Performance Assessment

Soil core samples were obtained prior to SEAR activities to locate DNAPL, to delineate the boundaries of the DNAPL contamination and to characterize the subsurface hydrogeology. The soil core samples were preserved in the field with methanol to minimize contaminant losses by volatilization from the soil samples. Subsequent to the soil coring, a free-phase DNAPL recovery process was implemented. A pre-SEAR PITT was then conducted during May/June 1998 to measure the volume and relative distribution of DNAPL present in the test zone before surfactant flooding. The results of this pre-SEAR PITT indicated that approximately 74-88 gal (280-333 L) of DNAPL were present in the test zone (Duke Engineering 1999), which was later determined to be an underestimate. Average DNAPL saturations were found to be highest in the portion of the test zone adjacent to Building 25, at about 4.5% saturation (expressed as an average DNAPL saturation over the swept pore volume between an interwell pair of injection and extraction wells).

The SEAR demonstration at Building 25 included multiple phases of field activities that spanned 143 days. The surfactant flood was initiated with an 8-day water flood, followed by a 58-day surfactant injection period between April 6 and June 3, 1999, a 34 day post-SEAR water flood, 40 day post-SEAR PITT, and 3 days of post-SEAR soil sampling. Post-SEAR sampling was conducted under continued water flooding conditions to avoid re-entry of DNAPL from untreated contaminated zones adjacent to the treated zone. The injected SEAR solution contained 4.0 wt% Alfoterra 145-4-PO sulfate™ surfactant, 16.0 wt% IPA, and ~0.17 wt% CaCl<sub>2</sub> and was injected at 0.4 gpm (1.5 L/min). Calcium was used as the sole electrolyte to avoid ion-exchange induced mobilization of soils fines in the subsurface. The total extraction rate was 1.0 gpm (3.8 L/min). Groundwater samples were collected from all extraction wells (EX1-EX6) and from three of the six MLSs throughout the demonstration to monitor the recovery of both PCE and injected chemicals from the treatment zone. Not all of the selected MLS sampling points produced sufficient sample volumes for analysis due to the fine-grained nature of the soil. A gradient in DNAPL contamination with distance from the building was inferred by examining the PCE concentration curves for the six extraction wells. At EX-03 and EX-6, the extraction wells farthest from the building, PCE concentrations remained low, not exceeding 20 mg/L throughout the entire SEAR demonstration, most likely indicating that there was little DNAPL in the vicinity of these locations.

A significant increase in the extraction well effluent PCE concentration was observed in several extraction wells due to surfactant flooding. At extraction well EX1, the effluent PCE concentration increased from an average of approximately 200 mg/L to about 2,800 mg/L at the peak breakthrough. At EX4R, the PCE concentration increased from 80 mg/L to approximately 1,000 mg/L at the peak. In addition to the extraction wells, PCE concentrations were also measured in MLS points located next to EX1 and EX4R. At MLS-4T (16.5 ft bgs), the PCE concentration at the start of the surfactant flood was 5 mg/L. The effluent PCE concentration was seen to increase rapidly to 10,860 mg/L before declining to non-detectable concentrations at the end of the post-SEAR PITT. This is an excellent indication that the surfactant was highly effective in solubilizing and remediating DNAPL in the upper zone in the vicinity of MLS-4T. Relatively high aqueous PCE concentrations were observed at MLS-1B (18.5 ft bgs) at the end of the demonstration suggesting that some DNAPL still remained in the zone adjacent to MLS-1B. The MLS surfactant and IPA concentration data indicate that little surfactant injectate penetrated (i.e., swept) the lower-permeability basal silt layer compared to the upper zone. Thus, little or no DNAPL was removed at these lower depths. This result can be attributed primarily to the preferential flow of surfactant injectate through the more permeable upper zones and consequential bypassing of the lower zones, and secondarily to some surfactant sorption and/or biodegradation.

In addition to enhancing the solubility of the DNAPL, the surfactant flood also enhanced the recovery of free-phase DNAPL as a result of lowering the interfacial tension of the DNAPL. Because of the presence of a thick aquitard at the site and because of its greater mass removal efficiency, mobilization of DNAPL during the surfactant flood was desirable and intended by design. A total of 76 gal (288 L) of PCE was recovered during the surfactant flood and subsequent water flood, of which approximately 32 gal (121 L) of PCE were recovered as solubilized DNAPL and 44 gal (167 L) as mobilized free-phase DNAPL.

A table showing the volume of solubilized and free-phase DNAPL recovered per well is provided as Table 1.

Extraction Well	Solubilized PCE Recovered (gal)	Mobilized PCE Recovered (gal)
EX1	19.4	15.3
EX2	1.9	8.7
EX3	0.1	0.0
EX4	NS	3.6
EX4R	9.4	5.2
EX5	0.9	2.6
EX6	0.1	0.0
RW1	NS	2.0
RW2	NS	2.0
Other sources	0.0	4.6
Total	31.8 gal	44.0 gal
	(120 liters)	(166 liters)

Table 1: Recovery of Solubilized and Mobilized PCE from Camp Lejeune Wells.

NS: not sampled, PCE concentration data was only collected at the extraction wells

The post-SEAR PITT was conducted, along with soil core sampling, to measure the volume of DNAPL remaining in the test zone after the surfactant flood. During the post-SEAR PITT, the unexpected sorption of an impurity in the surfactant formulation caused interference with the partitioning tracers, making the post-SEAR PITT data unusable. The sorption of the surfactant impurity caused false detection of DNAPL as a result of tracer partitioning into the sorbed surfactant impurity. The surfactant manufacturer, Condea Vista, has tentatively identified the sorbing substance as a byproduct of the manufacturing process and has developed an alternative synthesis route that avoids the production of this impurity. However, soil column studies at The University of Texas at Austin indicated that extended water flooding following injection of the "purified" surfactant is still required to avoid tracer retention when calcium is used as the sole electrolyte. This indicates the possible formation of a calcium surfactant complex that retards the partitioning tracers. The change in the background tracer sorption behavior caused by the SEAR process violated assumption #2 listed in Section 2 for analysis of PITT data.

Due to the difficulties encountered with the accurate interpretation of the post-PITT data, SEAR performance was ultimately evaluated by examining combinations of the mass recovery of DNAPL at the extraction wells, and the pre- and post-SEAR soil sampling data. The pre-SEAR soil samples were not used to generate an initial DNAPL volume estimate because the sampling frequency used was intended to locate DNAPL, delineate the extent of DNAPL contamination and to identify an appropriate location for the SEAR well field. Additionally, during the intervening period prior to the surfactant flood a free-phase DNAPL recovery effort was conducted and there was difficulty in quantifying the amount of free-phase DNAPL removed. Therefore, any DNAPL volume estimate generated from the pre-SEAR soil samples would not accurately represent pre-SEAR conditions.

The post-SEAR soil sampling data consisted of 60 soil samples collected at 12 locations over the contaminated portion of the aquifer, and was used to generate a three-dimensional distribution of the DNAPL volume remaining in the test zone following the surfactant flood. Continuous cores were collected from the bottom 3 feet of the aquifer (representing the DNAPL contaminated zone) and then subdivided into six inch core samples. The lateral distribution of DNAPL indicates that the majority of the DNAPL that remains in the test zone is located near the building, between wells EX1 and EX4. DNAPL volume decreases away from the building, in the area between wells EX2 and EX5, and very little DNAPL is present in the portion of the test zone that is farthest from the building, between wells EX3 and EX6. The vertical distribution of remaining DNAPL indicates that DNAPL was effectively removed from the more permeable sediments, generally above about 17.5 ft (5.3 m) bgs, and that DNAPL

still remains in the lower permeability basal silt layer. These results are not unexpected, given that the highest pre-SEAR DNAPL saturations were near the building, as well as the expectation that it would be most difficult to remove DNAPL from the lowest permeability sediments at the site.

A geostatistical analysis of the post-SEAR soil sampling results was used to interpolate the post-SEAR soil sampling data to generate a DNAPL volume estimate, as well as to assign error bars to the resulting estimates. Analysis of the post-SEAR soil core data indicated that approximately 5.2±1.6 gal of DNAPL remain in the zone that was effectively swept by the tracers and surfactant (i.e. the zone above approximately 17.8 ft bgs). In addition, data analysis from the post-SEAR soil cores indicated that approximately 23.5±5.5 gal remain in the mid-to-bottom zone that was not effectively penetrated by the tracers or surfactant (i.e. from 17.8 ft bgs down to the clay aquitard). The initial PITT estimated that the volume of DNAPL in the test zone before the surfactant flood was approximately  $81\pm7$  gals ( $306\pm26$  L). It was concluded that the total volume of DNAPL present in the test zone before the surfactant flood is best represented by both the volume of DNAPL measured by the pre-SEAR PITT plus the volume of DNAPL estimated (from soil core data analysis) for the zone below 17.8 ft bgs, for a total pre-SEAR DNAPL volume of approximately 105 gal (397 L). Adding the 76 gallon estimate of DNAPL recovered at the extraction wells to the 29 gallon estimate of DNAPL remaining in the test zone by soil cores also vields a similar pre-SEAR DNAPL volume of 105 gallons. Thus the surfactant flood recovered approximately 72% of the DNAPL from the entire demonstration zone, including all zones above the aquitard (Duke Engineering 2000).

With respect to the efficiency of hydraulic control during the surfactant flood, IPA recoveries were sufficiently high, approximately 88%, but surfactant recovery was lower, on the order of 78%. The surfactant data declined much faster compared to the IPA concentrations in the middle and bottom zones during the late-time period of the test, which suggests surfactant sorption and/or biodegradation. Potentiometric surface maps of the shallow aquifer generated for several phases of the demonstration show that hydraulic control of injected fluids was effectively maintained, with the exception of a minor loss of hydraulic control at HC1 during Phase II of the surfactant flood. This loss was caused by a slightly exaggerated gradient between injection well IN1 and HC1 with the higher viscosity surfactant fluids. This temporary loss of hydraulic control was confirmed by increasing IPA concentrations with time at a monitoring well (RW03-not shown), peaking on July 27 (Day 112 of the test) at 2,798 mg/L (compare to IPA injectate concentration = 160,000 mg/L). However, recovery of 88% of the injected IPA by the end of the demonstration suggests that any loss of hydraulic control was very minor. During the post-SEAR water flood and post-SEAR PITT, the potentiometric surface maps show that hydraulic containment was fully established and maintained for the remainder of the demonstration. In support of this, IPA concentrations at well RW03 dropped to 428 mg/L with the last monitoring sample collected on August 27. Hydraulic control monitoring conducted beneath the test zone (i.e., below the aquitard) showed that no downward migration of injected chemicals and contaminant occurred during the SEAR demonstration.

### 4.3 Camp Lejeune – Performance Assessment Lessons Learned

With respect to performance assessment, while considerable data was collected for evaluating pre- and post-SEAR DNAPL saturations, only a subset of this data was usable. The pre-SEAR PITT provided valuable baseline DNAPL conditions in the test zone, although later data suggests that, because of the permeability contrast in the basal silt layer, the initial PITT did not detect a portion of the DNAPL that was present in the bottom 1-2 ft (0.3-0.6 m) of the shallow aquifer. The pre-SEAR PITT did, however, accurately detect and measure the volume of DNAPL in the accessible (i.e., higher permeability) zone above approximately 18 ft (5.5 m) bgs. Regarding the future use of PITTs, the influence of permeability heterogeneities as well as potential interference by surfactants when calcium is used as the sole electrolyte should be carefully considered in design. Finally, performance assessment is inherently limited when the remedial measure treats only a portion of a NAPL contaminated zone due to the potential for reinfiltration of contamination from untreated zones. Thus, when high quality performance assessment data is essential, as in this ESTCP technology validation effort, it is necessary to design the remedial technology to treat the entire source zone.

## 5. CONCLUSIONS

Surfactant and co-solvent flushing technologies offer attractive options for NAPL source area treatment. Soil core analysis and PITTs are the two most likely performance assessment tools. Soil sampling may provide significant cost savings for small homogeneous sites. Also, when a high degree of vertical heterogeneity exists, soil sampling may provide confirmation of DNAPL conditions in the lowest permeability zones. However, PITTs will be more cost effective and provide more defensible performance assessment for large-scale sites with a moderate degree of heterogeneity. Great care must be taken in the planning, execution, and analysis of PITTs in order to yield meaningful information. Although PITTs can be extremely powerful tools, they have limitations, some of which were evidenced during the Camp Lejeune field demonstration. In practice, the dual use of PITTs and soil core sampling can yield sufficient performance validation information.

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#### 7. REFERENCES

- 1. Battelle and Duke Engineering & Services, "Surfactant-Enhanced Aquifer Remediation (SEAR) Design Manual," Prepared for Naval Facilities Engineering Service Center (2001).
- 2. Brown, C.; G.A. Pope, L.M. Abriola, K. Sepehrnoori, "Simulation of surfactant-enhanced aquifer remediation," *Water Resources Research*, **30**, 2959-2977 (1994).
- 3. Butler, E.C., K.F. Hayes, "Micellar solubilization of nonaqueous phase liquid contaminants by nonionic surfactant mixtures: effects of sorption, partitioning, and mixing," *Water Research*, **32**, 1345-1354 (1998).
- 4. Chevalier, L.R., S.J. Masten, R.B. Wallace, D.C. Wiggert, "Experimental investigation of surfactantenhanced dissolution of residual NAPL in saturated soil," *Ground Water Monitoring and Remediation*, 89-98 (1997).
- 5. Delshad, M.; G.A. Pope, K Sepehrnoori, "A compositional simulator for modeling surfactantenhanced aquifer remediation: 1. Formulation," *J. Contaminant Hydrology*, **23**, 303-327 (1996).
- 6. Duke Engineering and Services, "DNAPL site characterization using a partitioning interwell tracer test at Site 88, Marine Corps Base, Camp Lejeune, North Carolina." Report prepared for U.S. Dept. of the Navy (1999).
- 7. Duke Engineering and Services, "Surfactant enhanced aquifer remediation demonstration at Site 88, Marine Corps Base Camp Lejeune, North Carolina," Final report prepared for U.S. Dept. of the Navy (2000).
- 8. James, A.I., W.D. Graham, K. Hatfield, P.S.C. Rao, M.D. Annable, "Estimation of spatially variable residual nonaqueous phase liquid saturations in nonuniform flow fields using partitioning tracer data," *Water Resources Research*, **36**, 999-1012 (2000).

- 9. Jawitz, J.W., R.K. Sillan, M.D. Annable, P.S.C. Rao, K. Warner, "In-situ alcohol flushing of a DNAPL source zone at a dry cleaner site," *Environ. Sci. Technol.*, **34**, 3722-3729 (2000).
- Jin, M., M. Delshad, V. Dwarakanath, D.C. McKinney, G.A. Pope, K. Sepehrnoori, C.E. Tilburg, "Partitioning tracer test for detection, estimation, and remediation performance assessment of subsurface nonaqueous phase liquids," *Water Resources Research*, **31**, 1201-1211 (1995).
- 11. Mariner, P.E., M. Jin, R.E. Jackson, "An algorithm for the estimation of NAPL saturation and composition from typical soil chemical analyses," *Ground Water Monitoring and Remediation*, 122-129 (spring 1997).
- 12. Rao, P.S.C., M.D. Annable, H. Kim, "NAPL source zone characterization and remediation technology performance assessment: recent developments and applications of tracer techniques," *J. Contaminant Hydrology*, **45**, 63-78 (2000).
- 13. Rosen, M.J., Surfactants and Interfacial Phenomena; John Wiley & Sons: New York, 1989.
- 14. Shiau, B.J., D.A. Sabatini, J.H. Harwell, D.Q. Vu, "Microemulsion of mixed chlorinated solvents using food grade (edible) surfactants," *Environ. Sci. Technol.*, **30**, 97-103 (1996).
- 15. Sillan, R.K., M.D. Annable, P.S.C. Rao, D. Dai, K. Hatfield, W.D. Graham, A.L. Wood, C.G. Enfield, "Evaluation of in situ cosolvent flushing dynamics using a network of spatially distributed multilevel samplers," *Water Resources Research*, **34**, 2191-2202 (1998).
- 16. Wilson, D.J., R.A. Burt, D.S. Hodge, "Mathematical modeling of column and field dense nonaqueous phase liquid tracer tests," *Environmental Monitoring and Assessment*, **60**, 181-216 (2000).
- Wise, W.R., D. Dai, E.A. Fitzpatrick, L.W. Evans, P.S.C. Rao, M.D. Annable, "Non-aqueous phase liquid characterization via partitioning tracer tests: a modified Langmuir relation to describe partitioning nonlinearities," *J. Contaminant Hydrology*, 36, 153-165 (1999).


Figure 1: Surfactant solution containing surfactant monomer and micelles.

\*NAPL = non-aqueous phase liquid

Figure 2: Example PITT tracer response curves (Battelle and Duke Engineering 2001).