Research pays off at Hanford site

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The responses will help us plan our next editorial calendar as well as help us provide the types of information you are looking for.

It is not too late to give your opinion. If you have suggestions or ideas, please feel free to e-mail them to me at the address above.

Jody Becker
Managing Editor
October 1998

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Write in 070

Soil & Groundwater Cleanup October 1998
Subsurface barrier technology results in cost savings showing that

Research investment pays off

By M.J. Scott, F.B. Metting, J.S. Fruchter, and R.E. Wildung

The U.S. Department of Energy (DOE) is landlord for the nation’s nuclear defense complex, which includes numerous waste sites, many of which harbor complex mixtures of metals and radionuclides, often with halogenated and other organic contaminants. DOE is responsible for more than 130 installations totalling about 7280 km² in 30 states and territories with collectively more than 2500 billion liters of contaminated groundwater and 200 million m³ of contaminated soils and sediments. It has been estimated that managing DOE’s legacy wastes and restoring contaminated subsurface environments across the nuclear weapons complex will entail a decades-long effort costing many tens of billions of dollars.

Realizing the scope of the problem led DOE to create the Subsurface Science Program (SSP) in its Office of Energy Research. Nearly 10 years of cross-disciplinary, multi-institutional research has significantly advanced our understanding of complex and interactive geochemical, microbiological, and physical processes and resulted in novel concepts for soil and groundwater cleanup.
Tests conducted at Hanford ISRM test site, 100 Area, showed that sediments in the aquifer were successfully reduced by treatment with a chemical reducing agent, reduced sediments substantially lowered the concentration of dissolved hexavalent chromium in the groundwater, and that reducing conditions can be maintained in the aquifer for extended time periods.

One example of a spin-off technology that can be directly traced to advances in basic science is a process for in situ reduction-oxidation manipulation (ISRM). ISRM treats reduction-oxidation (redox)-sensitive contaminants in unconfined aquifers by injecting chemical reagents into the subsurface to chemically or biologically create a permeable reducing zone or barrier that intercepts contaminants moving in a groundwater plume. Inorganic contaminants that are mobile under oxidizing conditions are immobilized by changing the

Continues on page 8 ➔

Figure 1: Permeable geochemical barrier approach
Subsurface, from page 7

redox status of the subsurface. This can be effective for metals and radio-nuclides such as chromium (Cr), uranium (U), and technetium (Tc).

Recently, a successful field demonstration of ISRM at DOE’s Hanford Site in southeastern Washington showed how, in select cases, basic research can be linked directly to technology innovation with the potential for significant cost savings.

**In Situ Redox Manipulation**

Companies and government agencies responsible for contaminated sites are limited in their choice of effective, inexpensive cleanup methods. The baseline technology for groundwater restoration is removal and aboveground treatment, known as pump-and-treat. This approach is now generally recognized as costly and largely ineffective, in part because of the decades-long treatment times that are often required. A number of promising concepts for in situ treatment to replace or augment pump-and-treat are being evaluated. These include different subsurface treatment zones, which typically consist of downgradient trenches backfilled with one or more reactive materials selected to promote a particular treatment process.

Trench-and-fill methods, however, become impractical deeper than about 12 meters below ground surface. Therefore, investigations have been directed toward creating permeable barriers at depth. Many deep aquifers are oxidizing environments in which contaminants such as Cr, U, and Tc are mobile in the oxidized state. Also, many aquifers thought to be reducing are nevertheless sufficiently oxidized due to recharge with oxygenated water to maintain contaminant mobility. If the redox potential of the aquifer can be made reducing, then a variety of inorganic contaminants can be treated. Reducing conditions can also favor dehalogenation of organic contaminants, such as trichloroethylene (TCE) and carbon tetrachloride (CCL4).

The aim of ISRM is the creation of a long-lived permeable treatment zone in the subsurface. See Figure 1, page 7. The treatment zone is created by reducing structural ferric iron to ferrous iron within the minerals of aquifer sediments, which in turn serve as a long-term, soli-phase reducing agent. See Figure 2, page 9. This is accomplished by introducing chemical reducing agents such as sodium dithionite.

After the aquifer sediments are reduced, excess reagent and soluble reaction products are removed from the subsurface. Redox-sensitive contaminants that pass through the zone are reduced and immobilized as solids. Chromate, for example, is immobilized by reduction to highly
insoluble chromium hydroxide or iron chromium hydroxide. This is particularly favorable because Cr is not easily resolubilized as groundwater flow gradually reoxidizes the environment with time. Uranium and Tc can also be reduced to less soluble forms, but their long-term stability to reoxidation has not been fully tested in the field.

**Field demonstration**

Injecting a solution of dithionite into a series of wells located downgradient of a contaminant plume at Hanford was originally proposed to test ISRM in the field. Within the aquifer, the injected dithionite reacts with structural iron in layered silicates and on the surface of oxyhydroxide minerals, reducing Fe(III) to Fe(II) according to the overall reaction:

\[ \text{S}_2\text{O}_4^{2-} + 2\text{Fe(III)} + 2\text{H}_2\text{O} \rightarrow 2\text{SO}_3^{2-} + 2\text{Fe(II)} + 4\text{H}^+ \]

Within the zone of dithionite-treated sediments, aqueous chromate reacts with Fe(II) produced by the dithionite reaction (as listed previously) and is precipitated as a solid hydroxide, such as Cr(OH)_3 according to the following equation.

\[ \text{HCrO}_4^- + 3\text{Fe(II)} + 4\text{H}^+ \rightarrow \text{Cr(OH)}_3 + 3\text{Fe(III)} + 2\text{H}_2\text{O} \]

Dithionite is unstable in aqueous solution at neutral and acidic pH and can undergo disproportionation reaction that can lower dithionite concentrations and the ultimate quantity of Fe(II) produced. Because its stability is greatly enhanced at high pH, dithionite in a potassium carbonate/potassium bicarbonate buffer at pH 11 was used successfully to demonstrate the reduction of iron-bearing minerals in Hanford Formation sediments and the subsequent removal of Cr(VI) from groundwater. The potassium salts in the buffer are used to prevent dispersion of the clays and loss of the barrier once the groundwater returns to its original ionic strength. A CO_3/HCO_3 buffer is used rather than a HCO_3/CO_2 buffer to minimize CO_2 gas production that would affect aquifer permeability.

The pilot-scale dithionite injection experiment was initiated in September 1995 at Hanford’s 100-H Area, southwest of a retired plutonium production reactor and about 730 m from the Columbia River. This site was chosen because hexavalent Cr is present at 70 ppb, below the 100 ppb regulatory limit for groundwater but still sufficient to demonstrate the technology.

Sixteen wells were drilled and completed, including an injection/withdrawal well, upper- and lower-zone monitoring wells, and up and downgradient monitoring wells. Before the full-scale injection, a series of site-characterization activities were completed, including hydraulic tests and a bromide tracer test. The experiment was designed to produce a 15-meter diameter reduced zone.

Around 77,600 liters of buffered sodium dithionite solution was injected into the aquifer over 17 hours. After an additional reaction time of 18.5 hours, the spent reagent was withdrawn from the aquifer over the next 83 hours, representing 4.8 injection volumes. The withdrawal task was designed to remove unreacted reagent and buffer, reaction products such as sulfate and sulfite, mobilized metals and residual bromide tracer.

Analysis indicated that 90 percent of the injected dithionite was withdrawn as sulfate or sulfite.

Data on cores taken after the injection showed that 60 percent to 100 percent of the available reactive iron in the sediments was reduced by the dithionite, depending on location within the treatment zone. This translated to levels of reducing capacity between 51 and 85 pore volumes, or seven to 12 years for groundwater with 1 ppm hexavalent chromium and 9 ppm dissolved oxygen.

Two years after the injection, groundwater in the injection zone remains anoxic. Hexavalent chromium levels remain below detection limits, while total chromium remains in the 1 ppb to 4 ppb range. Other trace metals such as arsenic and lead mobilized into the groundwater during the

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**M.J. Scott is staff scientist, F.B. Metting is senior program director, J.S. Frchter is staff scientist and R.E. Wildung is director, Environmental Science Research Center, at Pacific Northwest National Laboratory, Richland, Wash. This work was supported by the Subsurface Science Program, Office of Biological and Environmental Research, U.S. Department of Energy at Pacific Northwest National Laboratory, which is operated for DOE by Battelle Memorial Institute. The continued support of Dr. Frank J. Wobber is greatly appreciated. Work on the field testing of the ISRM process was supported by the DOE Office of Technology Development (EM-50), Subsurface Contaminants Focus Area.**

*Continues on page 10 →*
Subsurface, from page 9
reduction phase remain below maximum allowable drinking water concentrations. Concentrations of constituents in the water withdrawn for the test well met all applicable Hanford purgewater criteria. The water was disposed to the ground. This proof-of-principle test conducted at the 100-H Area demonstrated that:
• sediments in the aquifer were successfully reduced by treatment with a chemical reducing agent;
• reduced sediments substantially lowered the concentration of dissolved hexavalent chromium in the groundwater; and;
• reducing conditions can be maintained in the aquifer for extended periods of time.
Recently, the technology received a U.S. patent.

Cost savings from ISRM
To calculate the savings associated with the basic research investment in ISRM, costs associated with a hypothetical commercial application were estimated, with the research costs associated with the development of the concept subsequently subtracted. Estimates compare the full-scale 460 m ISRM barrier, formed with overlapping injection/withdrawal systems, with the baseline pump-and-treat system previously planned for treating a Cr plume at Hanford.
For purposes of this comparison, the baseline pump-and-treat system and the ISRM barrier system are both assumed to operate until 2030. The baseline program is assumed to involve five years of pump-and-treat, followed by a monitoring program through 2030. Because the baseline system, although well understood in principle, has not been applied to the Cr problem at Hanford, its costs are assumed to be subject to ±20 percent uncertainty. Because of its novelty, the cost of the ISRM barrier was assumed to be even more uncertain: ±50 percent is used.
Depending on the discount rate, the expected present value of the costs of conventional pump-and-treat technology were estimated to be between $21 million and $29 million. See Figure 3, page 12. A significant issue is whether five years of treatment will be sufficient. For example, if cleanup is incomplete and the baseline system must be active an additional five years beyond 2003, cost would increase to between $29 million and $35 million.
Costs are estimated to be between $9 million and $13 million for a full-scale ISRM barrier in place of the pump-and-treat system. See Figure 4, page 12. To develop this estimate, the individual components of the test operation at Hanford were scaled up for barrier size and adjusted for the operational differences between commercial and demonstration-scale units. The barrier was assumed to operate until 2030, with a renewal, or new injection of dithionite reagent, in 2015.
Unlike the pump-and-treat system,
which requires substantial operations costs to be effective, ISRM barriers can be left in place and are renewable. Unaccounted for is any additional value associated with the fact that because the barriers are unobtrusive and in the ground, human exposure to contaminants and use of operating machinery is minimal.

The expected savings associated with the application of ISRM technology at Hanford are shown in the first line of Figure 5, page 13. To obtain the economic benefit associated with the basic science and subsequent research and development of the technology, the costs were subtracted in the second line of the table. The difference, in line 3, is a very conservative estimate of the benefits of the basic scientific research because it assigns all research and development costs to this single application of the technology, even though the technology has a wide variety of potential applications at many sites across the country. Even with this conservative estimate, the internal rate of return on the subsurface science investment is about 31 percent a year. Independent calculations comparing ISRM and pump-and-treat for chromate remediation at Hanford showed a 62 percent savings over 10 years.

To fully understand the contribution made by basic science to this technology, it is desirable also to estimate the value of additional applications of the knowledge. For example, it is anticipated that ISRM will have many applications beyond the Hanford Site. Line 4 of Figure 5 provides some rough estimates of the potential cost savings associated with use at 146 sites on the EPA National Priorities List with susceptible inorganic contaminants. These sites represent an average 150,000 m³ of water per site. Pump-and-treat costs range from $10 to $100 per cubic meter treated. Based on the Hanford case, average cost savings of up to 30 percent are possible with ISRM.

An estimate of expected savings of $2.40 per cubic meter at a 5 percent discount rate was used in line 4 of Figure 5. The expected value was derived by calculating the average percentage savings from 100 random pairings of the present values of total costs under the pump-and-treat ISRM regimes for the Hanford case. These savings were then applied to the range of costs per unit of $10 to $100 per m³. Total potential net benefits range between $50 million and $73 million.

Basic research and technology commercialization

Figure 6, page 13, outlines the key steps in the proposed selection and development of new, cost-efficient cleanup technologies by the DOE Office of Environmental Restoration.

Continues on page 12 →

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<table>
<thead>
<tr>
<th>Absorbency Power</th>
<th>Size/Weight</th>
<th>Oil Absorbed</th>
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<td>RAMSORB-1</td>
<td>30lb/bag</td>
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<tr>
<td>RAMSORB-2</td>
<td>20lb/bag</td>
<td>20 to 30 gal.</td>
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<tr>
<td>Floor Sweep</td>
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<td>Sock</td>
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<tr>
<td>Pad</td>
<td>18&quot; x 18&quot;</td>
<td>30 to 40 gal./package</td>
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¹ All costs shown in the analysis are in constant 1997 dollars. Likewise, the discount rates used in the analysis are real discount rates: that is, they account for the time value of money after any inflation has already been removed.

**Figure 3:** Estimated costs of baseline pump-and-treat system for chromium plume, Hanford site in selected years.

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**Figure 4:** Estimated costs of ISRM Barrier for chromium plume, Hanford site in selected years.

**Subsurface, from page 11**

and Waste Management (DOE-EM). Technology development goes through a series of gates in this process, where each gate presents requirements to be satisfied by the technology. Depending on how the technology performs at each gate, it may be forwarded for further development, returned for further assessment, or stopped in its development.

The ISRM concept originated from basic research in the DOE Office of Biological and Environmental Research (OBER) and progressed to the demonstration stage, or Stage 6. Gate 5 leading to Stage 6 requires that a DOE-EM deployment schedule be established based on documented test results and that the

October 1998 Soil & Groundwater Cleanup
project meet gate programmatic driver criteria that include technology end-user needs, technology merit, costs, safety, health, environmental protection, risk, and stakeholder, regulator, tribal and commercial viability. Thus, the ISRM is a classic example of idea generation that leads to a viable product meeting a compelling environmental need.

Clearly, however, there is a complex, non-linear relationship between basic research and the final deployment of technology in the commercial world. The path from basic research to ultimate application is long and seldom straightforward; it can have beneficial impacts in areas of knowledge that can be completely unrelated to the original problem.

The main path in the process begins with directed research focused on some problems — in this case, understanding the nature of subsurface environmental contamination, which at its most basic level involves understanding coupled with biological, geochemical and hydrologic processes across temporal and spatial scales. In this case, directed research led to better basic understanding of the redox chemistry of chromium in iron-rich subsurface environments. The discovery of new basic knowledge can, in turn, lead to more applied research, such as research into how the redox processes might be manipulated in situ to influence chromium behavior in groundwater. There may be information feedback to the basic science, as well. Technology innovation and development spans the scale from concept through the lab bench up to prototype demonstration. Technology development often spins out its own research agenda, such as the need for a new pumping technology, as well as suggesting applications in unrelated fields. These spillover effects often mean that the total value of a successful innovation is often many times the cost savings associated with how and where the innovation is initially applied, but these additional benefits are often difficult to identify.

Once a technology or innovation has been successfully demonstrated, it can then be deployed and commercialized. The cost savings or sales associated with final application of newly developed products usually provide the basis for economic evaluation of the original research investment. The economic results realized from research development include increases in productivity in the federal or private sector, changes in economic growth rates and increases in value or decreases in costs — including environmental — of goods and services provided by private and public entities.

The most successful measurements of the value of research are those for which the line from original research to final application is more or less direct and the contribution is both clear and limited in scope. The ISRM approach provides clear economic savings in the treatment of certain groundwater contamination problems, which are also clearly related to the DOE's Subsurface Science and Technology Development Program. || Write in 757
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Exploratory data analysis can be tailored to provide site specific information

By Virginia A. Colten Bradley

As part of the licensing of uranium milling operations under Title II of the Uranium Mill Tailing Radiation Control Act of 1978, the U.S. Nuclear Regulatory Commission (NRC) establishes site-specific background levels for hazardous constituents deemed to be associated with the waste form, and listed in Criterion 13 of Appendix A, 10 CRF Part 40. The objective is to establish a site-specific groundwater quality baseline before the operations begin.

After a constituent has been detected above background at a monitoring well, compliance standards are established for individual constituents as:

- representative background concentration as approved by the Commission;
- EPA’s Maximum Contamination Level, also known as the Maximum Concentration Limit (MCL), or:
- an alternate concentration limit (ACL) established by the Commission (Criterion 5(B), Appendix A, 10 CFR 40; see also 40 CFR Part 192).

Criterion 7 of Appendix A, 10 CRF Part 40 states that one full year of pre-operational monitoring must be conducted to complete “baseline data for a milling site and its environs.” The technical basis for monitoring is to ensure spatial and temporal variability in the constituents of interest. An objective is to set the background concentration high enough to

Virginia Colten-Bradley is an environmental scientist with the Environmental Protection Agency, Washington D.C. Comments by Latif Hamden, K. Mcconnell, and M. Bradley were very helpful to the development of the ideas expressed in this article. The views expressed in this article are the sole opinion of the author, and do not represent the official position of the U.S. Nuclear Regulatory Commission.
Figure 1: Histogram and estimated density function for the 1977 nitrate data. Estimate of the density function was made such that the area under the curve approximates the area of the histogram.

reduce the frequency of false positives — concentrations that are part of the baseline distribution but greater than the representative value — while at the same time providing for adequate groundwater protection.

Often, a single value to represent the background level or standard is determined for individual contaminants, based on the mean or median of the collected samples. However, to ensure that the uncertainty in the representative value is properly represented, a confidence interval for the representative value is determined.

For example, if the data exhibit a normal distribution, the upper limit of the 95 percent or 99 percent confidence interval for the mean is often used as the representative background concentration. By choosing the upper limit of the 95 percent confidence interval for the mean as the representative value, the chance of a false positive is reduced to 2.5 percent.

Although this approach to estimating the background levels of constituents in soils and groundwater is a good rule of thumb, there are two fundamental constraints:

- Data do not always correspond to a known distribution and are thus not well-represented by values determined on the basis of parametric assumptions.
- Interactions among various constituents in soils and groundwater affect the observed concentrations.

Lack of consideration of these two points can result in estimating site-specific background concentrations that are not representative, which can ultimately result in setting compliance standards that are not achievable. The ability to accurately estimate representative background concentrations of contaminants is often affected by two situations: missing or censored data and small or limited data sets.

Censored data exists for two principal reasons. One reason is that many contaminants are not naturally occurring and are thus not detectable in natural materials.

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Figure 2: Histogram and estimated density function for the 1977 total dissolved solids (TDS) data. Note the nonparametric nature of the distribution. Two estimates of the density function are given to illustrate the effect of the smoothing interval on the fit: a smoothing interval equal to 0.75 times the interquartile range and a smoothing interval equal to 0.5 times the interquartile range.

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Another reason is that random errors associated with sample collection and analysis cause data to be excluded from that used for determination of background levels.

Small or limited data sets often reflect the conditions associated with characterization of a site. For example, it is difficult to collect water samples from wells that do not produce during certain seasons, thus limiting the temporal variability in the data.

Rising costs of characterization and remediation drive the effort to identify innovative methodologies for making accurate estimation of background concentrations with limited data sets. With the development of exploratory and interactive data analysis programs and interactive graphics programs, it is now relatively easy for the analyst to use a variety of techniques to statistically or visually analyze data. By combining graphical and statistical techniques with an understanding of groundwater and soil chemistry, the analyst can ensure that the estimates of background concentrations are representative.

The problem defined

The NRC-licensed uranium mill of interest in this evaluation operated between 1977 and 1983. Before disposal of mill tailings,
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Figure 3: Comparison of background levels and compliance standards for nitrate, sulfate, and total dissolved solids based on pre-contamination data. All concentrations in mg/L.

Groundwater samples were collected from seven wells upstream and downstream from the tailings disposal area over 10 months. The data from these wells collectively represent temporal and spatial variability at the site.

Monitoring for various naturally-occurring and contaminant species has been almost continuous since 1977. Remediation activities began in 1989. Under a Memorandum of Understanding with the EPA, background levels for the site were established in 1988 and compliance standards set accordingly. The background levels set in 1988 were purportedly based on the mean of data collected in 1977, before disposal of uranium mill tailings.

As part of the periodic evaluation and assessment of the progress in site remediation, the EPA and NRC recently elected to reevaluate various field levels to determine whether current background levels are equal to or greater than the background levels at the site. If a compliance standard is less than the background concentrations for a particular constituent, then further evaluation would be necessary to determine an appropriate compliance standard.

The focus in this analysis was to ensure that the variability in the data was accounted for in the representative background concentrations, thus minimizing the number of false positive that might be detected during periodic monitoring. In this context, the statistical analysis focused on the upper tails, or extremes of the distributions.

Because data for the three constituents nitrate, sulfate and TDS were difficult to describe in a parametric fashion, several non-parametric techniques were used. The empirical density function was used to estimate the upper tail of the distribution. Time-series analysis was used to determine the initial conditions, based on changes with time. Three-dimensional graphical analysis was used to evaluate the interaction of the three constituents. Although these techniques are not new, they are presented here to illustrate their

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applicability to the analysis of environmental data.

**Empirical density function**

Empirical estimation of the density function was performed to estimate the 97.5 quantile for the distributions of the 1977 data. The 97.5 quantile was selected because it is analogous to the upper limit of the 95 percent confidence interval of the mean for a normal distribution, a value often picked as representative of a distribution for regulatory purposes.

The estimated density function is effectively a smoothing of the histogram, which enables the analyst to better define the nature of the tails of the distribution. Empirical estimation of the density functions for the 1977 data was accomplished with the density function routine available in the interactive statistical analysis package, S-Plus. The estimated density function was estimated in such a way that the area under the curves approximated that of the histograms for the same distribution.

Figure 1, page 15, illustrates the histogram and the estimated density function based on the 1977 nitrate data. Sensitivity of the fit of the estimated density function to the interval over the smoothing was also evaluated. See figure 2, page 16. In general, as the width of the smoothing interval increases, the match of the area under the curve to the area under the histogram worsens. The 97.5 quantile of the distribution was estimated graphically by integrating under the density function to the 97.5 quantile.

The background levels of nitrate, sulfate, and TDS, as estimated using the estimated density function, the mean and the upper limit of the 95 percent confidence interval assuming a normal distribution are given in Figure 3, page 17. The compliance standards set in 1988 are also presented. Of note are the significant differences among the results of the three techniques for the nitrate and TDS data.

Specifically, the compliance standards for nitrate and TDS are significantly less than the background concentrations estimated in this analysis. Because it is generally not feasible to remediate a site to conditions cleaner than the background, these differences illustrate how the analytical approach to estimating background concentrations can affect how appropriate compliance standards are determined. By using a statistical technique that is not appropriate to the data at hand, it is unlikely that background and compliance standards will be determined correctly, thus affecting the nature and extent of the requisite remediation activities.

**Time-Series Analysis**

Occasionally, data collected over a long period of time are available for establishing background concentrations. This may be the case for old sites at which monitoring began after contamination took place. When such is the case, analysis of site data as a function of time can indicate trends from an initial state before contamination.

In this analysis, changes in the distribution of the contaminants with time were used to illustrate the levels of precontamination. Histograms for sulfate concentrations measured in 1977, 1988, and 1994, are presented in Figure 4, page 19. Note that the sulfate concentration in 1988 were as high as 20,000 mg/L, almost 10 times that of the 1977 concentrations. These high concentrations indicate movement of the contaminant plume through the groundwater system. Sulfate concentration measured in 1994 are less than those measured in 1988, yet still greater than the precontaminant levels.

Compliance standards for a case such as this should be based on consideration of the feasibility of further remediation and the risk to the resident population.

**Correlation plots**

The interactions of constituents in soils and groundwater are the primary control on distribution and dissemination of contaminants. The solubility of many metallic and organic species is controlled by the oxidation potential and pH. The transport of species such as uranium may be enhanced by complexation with other constituents such as carbonate.

Generally, the characterization of groundwater and soils often focuses on the concentrations of particular constituents, and does not evaluate their interdependency. The primary contributor to TDS at the uranium mill site is dissolved sulfate. See Figure 5, page 20. This dependence has not changed through time, even as the contaminant plume has moved from the disposal facility.

Upon inspection of the data to evaluate current groundwater concentrations relative to the compliance standard for TDS, it was noted that the compliance standard is exceeded when bicarbonate concentrations in the system are high. To further evaluate this relationship, TDS was plotted as a function of both bicarbonate and sulfate, and the resulting surface was contoured. See Figure 6, page 20. Figure 6 illustrates how TDS concentration reflects changes in both bicarbonate and sulfate. In evaluating this figure, it was determined that the compliance standard for TDS should reflect not only the background concentration determined with the density estimation technique, but also accommodate variations in bicarbonate, a non-regulated and non-toxic constituent.

**Producing conclusions**

This analysis indicates that the
compliance standards established in 1988 for the dissolved constituents nitrate and TDS were significantly less than the naturally occurring concentrations of these constituents. Because compliance standards were based on the mean of the precontamination data, a condition even more restrictive than the 95 percent confidence interval for the mean, they did not fully represent the natural conditions at the site.

Even the estimated mean plus two standard deviations (mean +2σ) falls short of the values determined in this analysis. By setting the background levels for nitrate to the 97.5 quantile of the distribution for the precontaminant nitrate data, the compliance standard must necessarily be changed to a more appropriate and, in this case, achievable level. By changing the compliance standard for TDS to better reflect the precontaminant concentrations and the effects of bicarbonate, the likelihood of successful remediation will be increased.

This approach to analyzing data demonstrates that the use of exploratory data analysis tools enhances the analyst's ability to better evaluate data for regulatory purposes. Because there are myriad statistical techniques and ways of graphically presenting data, these techniques presented should not be considered the best or only approach.

However, the simplicity of the analyses and graphical techniques illustrated here provide for a transparent analysis of environmental data that the general public and stakeholders can easily understand. The robust nature of the nonparametric approach also enables a consistent approach to the data, regardless of the distribution.

Consideration of the interaction of key constituents is essential to

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the quality of an analysis of environmental data. The behavior of many contaminants in natural systems is a function of the soil and groundwater chemistry. To ignore these interactions may leave aspects of the analysis unresolved. In some cases, geochemical modeling should be used to evaluate specific processes that dominate the groundwater or soil chemistry of interest.

Graphical Information Systems (GIS) and 3-D graphical programs such as Earth Vision can be used to evaluate the temporal and spatial variability of contamination throughout a site. With the development of geostatistical techniques, there are seemingly unlimited ways to approach the analysis of data for estimating background concentrations of contaminants in soil and groundwater.

The results of the approach illustrated indicate that estimating background concentrations by a simple formula, such as calculating the mean, may often result in setting background concentrations and compliance standards too low. Attempting to remediate soil and groundwater to conditions where the concentrations of the constituents of interest would be less than naturally occurring is a technological challenge and a questionable use of limited resources.

As the costs of characterization and remediation continue to rise, large savings can be achieved by using an integrated analysis to more accurately estimate background levels. By using a variety of graphical, statistical, and modeling techniques, the analyst can better evaluate the characteristics of a site and thus provide the regulator with a better technical basis for setting compliance standards.  

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Figure 5: Relationship of TDS to sulfate concentrations in 1977.

Figure 6: Total dissolved solids concentrations, or contours, as a function of sulfate and bicarbonate concentrations. If the sulfate compliance standard is 2160, then that for TDS should be about 5000 mg/L to account for bicarbonate concentrations as high as 1500 mg/L.
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Eye on ECOS

States, Department of Defense coordinate military site cleanups

By William Kucharski

Following this opening dialogue is a description of a cooperative program between Department of Defense (DoD) facilities in Pennsylvania and the Pennsylvania Department of Environmental Protection (PaDEP). These organizations are working together to minimize cost and maximize efforts associated with contaminated site cleanup at DoD facilities in the state. One of the best kept secrets in this country is how hard the DoD is working to get their sites cleaned up and how the states have come to recognize that these efforts are sincere.

I was the first chairman of the ECOS Federal Facilities subcommittee; I took on that responsibility because I believed that we, as government agencies, should be a model for cooperation and progressive environmental programs. To have state regulatory agencies and DoD facility representatives locked in court and public relations battles while contaminated sites remained contaminated, because little or no cleanup was occurring, did not seem logical or necessary.

As the chairman of this subcommittee, I brought the existence of ECOS to DoD and to the attention of Sherry Wasserman-Goodman, U.S. deputy under secretary of defense for environmental security. I urged her to become involved with ECOS and she responded with eager enthusiasm. Now four years later, significant progress has been made. Regular meetings are held between DoD representative and state environmental officials. At each annual ECOS meeting, the Federal Facilities subcommittee, now headed by Tom Fitzsimmons of Washington, meets with a federal representative group led by Gary Vest, assistant deputy undersecretary, environmental security.

One of the best kept secrets in this country is how hard the DoD is working to get their sites cleaned up and how the states have come to recognize that these efforts are sincere.

At those meetings, successes and problem areas are discussed. The real lesson associated with these types of regulatory interactions is clear. If the regulatory community and the regulated community want progress to occur, and if a real understanding of the obligations and constraints of both parties can be discussed, costs can be reduced and significant environmental progress can be made.

Jim Seif, commissioner of the PaDEP, is a prime example of the new generation of innovative leaders and champions of change that are leading state regulatory agencies. On the federal side, Wasserman-Goodman has quickly grasped the need for DoD facilities to move forward with improved state relations, carry out responsible cleanups and comply with all of their obligations under the law, all while working with diminishing budget resources.

The concept of partnering between state and federal agencies, such as occurs in Pennsylvania and New
Jersey, seems to be normal and accepted today. This was not always the case. One of the first state/federal partnering activities occurred in Virginia between the Navy, whose champion was Paul Rakowski, of NAVFAC, Norfolk, and local state of Virginia environmental regulators. The communication/cooperation model that came out of that initial partnering exercise has now grown into a national effort.

In Louisiana, I brought all of the Louisiana DoD facility representatives together with LaDEQ mid-level managers to talk. Leading this effort for DoD was Maj. Gen. Eugene Lupia, civil engineer with USAF, and Col. Pat Fink, AFCEE. You might be surprised how many seemingly unsolvable problems can be eliminated in such a setting.

This type of regular meeting between DoD and state environmental representatives has now spread to more than 17 states. As citizens, taxpayers and environmental professional, we should all be proud of the way common sense and a desire to actually accomplish difficult tasks has been pushed by both the DoD and the states. More of these success stories will follow.

States and Department of Defense find success working together toward cleanup goals

By Molly Conrecode

The PaDEP has long been a leader among states in innovative land recycling programs. The PaDEP has been widely recognized, receiving many national awards for its efforts. Its recent agreement to develop programs with the DoD has become a model that other states are following to improve land cleanup efforts.

On July 17, military officials from the DoD and PaDEP signed an agreement to evaluate and clean up the hazardous waste of hundreds of military sites in Pennsylvania by 2010. This agreement, 10 years ahead of the DoD’s schedule calls for all sites to be evaluated and cleanups to begin by Sept. 30, 2010, although long-term monitoring at some sites may continue beyond that date. This first multi-site cleanup agreement in the nation begins a comprehensive effort to assess and eliminate the potential environmental and public health risks at all military sites in the state.

The agreement was signed by Seif and representatives of the Army, Air Force, Navy and Defense Logistics Agency. It incorporates mutual incentives, joint planning, and use of innovative technology, public participation, and sharing of resources to streamline the state/federal relationship and eliminate the potential for uncoordinated activities. The military cleanup programs are based on Pennsylvania’s other successful land recycling initiatives.

Land recycling refers to the cleanup and redevelopment of property that has been contaminated. Such redevelopment is often difficult because the process is caught in bureaucratic chokeholds regarding liability for the original contamination of the land and measures of refurbishment that have to be accomplished on a site. Pennsylvania’s land recycling program is based on a series of laws passed in 1995 by the state’s legislature that make redeveloping brownfields feasible and potentially profitable.

The legislation establishes standards for cleanup, depending on the site and proposed use. Once the site has been cleaned to the agreed-upon standards, owners, developers and all financial backers are cleared of liability from contamination resulting from earlier pollution. The law also allows for a uniform environmental review process with outlined schedules for final approval. In the three years since the program’s creation, 103 sites have been cleaned, more than 200 are in planning stages and 51 of 67 counties are in the process of cleaning sites.

In 1995, DEP signed its first multi-site agreement with Pennsylvania Power and Light (PP&L), which began a 10-year program to clean up 125 sites. A second multi-site agreement was signed with Penn Fuel Gas Inc. in 1996 to clean up 20 former manufactured gas plant (MGP) sites and 340 abandoned natural gas production wells.
Pennsylvania’s Land Recycling Program was one of the winners of the 1997 Innovations in American Government Awards. The program also was named winner of The Council of State Governments’ (CSG) 1997 Innovations Award. The CSG awards program is the only one in the nation to exclusively recognize state programs selected directly by state government leaders.

DEP and the military already have completed a comprehensive inventory of more than 1,000 military sites in Pennsylvania that will serve as the foundation for the future schedule of environmental assessments and cleanups.

“Our first step was to catalogue all military sites in Pennsylvania so they could be addressed under a comprehensive agreement,” Seif said. “This first-in-the-nation achievement has laid the groundwork for dealing with the sites with the greatest potential for environmental problems first.”

Fifty-three sites will be the first to be addressed. Another 364 sites are, or will be, addressed under other programs such as the Base Realignment and Closure program, but are still eligible to participate under the agreement. The remaining 659 sites are considered by DoD to be previously resolved. DEP will conduct a pilot study during the first two years of the agreement of select sites that the military considers resolved to

make sure that no further action is necessary, and to identify any classes of sites that require further evaluation and possible cleanup under state standards. “The state, the branches of the military, and the communities surrounding these sites all will benefit from having a known plan for addressing assessments and cleanups,” Seif said at a signing ceremony at the

“The state, the branches of the military, and the communities surrounding these sites all will benefit from having a known plan for addressing assessments and cleanups.”

Jim Seif
Commissioner, Pennsylvania DEP

Willow Grove Naval Air Station. “The government agencies will be able to manage time and budgets for the projects, and communities will enjoy cleaned up sites that will be available for productive reuse.”

“The agreement between the Defense Department and Pennsylvania demonstrates a strong mutual commitment to using smart business practices to meet our environmental cleanup responsibilities in Pennsylvania,” said Wasserman-Goodman. “Through this dynamic partnership, we can safely accelerate the cleanup of our sites, protect people and the environment, and save federal and state tax dollars. It is a reflection of the central underpinnings of our cleanup program.”

“When we launched our work on a cooperative agreement six months ago, we knew that this project could serve as a model for other states,” Seif said. “Since finalizing our work, we have been contacted by New Jersey and several other states to use our agreement. Now we know it truly is a model for other states.”

New Jersey State Environmental Protection Commissioner Robert Shinn has also signed an agreement with the U.S. military that lays the groundwork for development of a coordinated approach to the cleanup of certain federal installations in New Jersey. The agreement is based on Pennsylvania’s.

“In New Jersey, we are proud when we are first with a good idea, but we are happy to borrow a good idea from a neighbor,” Shinn said. “New Jersey is happy to be the first to learn from Pennsylvania’s example.”
Earlier articles appearing in this column have discussed the utility of high resolution gas chromatography/flame ionization detection (HRGC/FID) techniques such as modified EPA 8015 as a useful means of identifying the nature of fugitive hydro-carbons including many light- and mid-range distillates, residual fuels, crude oils and pyrogenic materials such as creosote and pitch. (See Soil & Groundwater Cleanup, July 1998, pp. 26-28) HRGC/FID is among the best methods for screening environmental samples for the presence and identification of hydrocarbons responsible for contamination in site soils and waters.

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Figure 2: PAH target compound list for forensic investigations. (Abbreviations correspond to Figure 3)
While an extremely useful tool for categorizing the nature of fugitive hydrocarbons, there are clear limitation to HRGC/FID data for forensic purposes. By and large, HRGC/FID is a gross measure of the chemical assemblages that make up hydrocarbon products — such analyses provide a first-level "fingerprint" of a hydrocarbon assemblage, and are useful for determining the nature of in-place contamination, for example, that diesel fuel #2, not fuel oil #6, is the dominant contaminant at a site.

But in many forensic investigations, there is often dispute over the source of a particular contaminant, such as in a due diligence investigation to determine if diesel fuel is from Source A or Source B. Often — for example, in the case of natural resource damage assessment (NRDA) investigations — forensic investigators are asked to track off-site transport of a particular hydrocarbon product, and follow its fate in complex environments where it can become diluted or mixed with confounding signals from other hydrocarbon sources.

Further complicating matters is the fact that hydrocarbons weather, and can quickly lose some or all of the distinguishing features that are visible in the HRGC/FID chromatogram of fresh hydrocarbon products. (See Soil & Groundwater Cleanup, August/Sept. 1998, pp. 29-31.)

Environmental forensic investigators have found that careful analysis of a diagnostic set of polycyclic aromatic hydrocarbons (PAH) that are contained in most hydrocarbon products can be a powerful way of identifying the sources of such materials in complex environmental samples, differentiating among similar

Figure 3: PAH distributions for a variety of hydrocarbon products.
sources of hydrocarbons, and tracking the fate of these materials in the environment long after a useful HRGC/FID signal has been lost. Using more sophisticated gas chromatography-mass spectrometry techniques such as modified EPA 8270, PAH compounds can be accurately and confidently measured in the low parts-per-billion concentration range in a wide variety of environmental matrices. (See Soil & Groundwater Cleanup, May 1998, pp 41-42.)

**Background**
PAH contain multiple 'ring' structures which are aromatic in nature and comprise hydrogen and carbon. See Figure 1, page 25. Other atoms such as oxygen, nitrogen and sulfur can be found in some of these compounds, and are referred to as heteroatomic PAH. The arrangement and number of rings is used to distinguish different PAH. In addition to the rings structures, many PAH contain carbon side-chains of varying numbers, lengths, and locations. Those PAH without any side-chains are considered as "parent" or C₀-PAH. PAH with one, single carbon side chain are said to be C₁-PAH, two additional carbons attached are C₂-PAH, and so on.
For environmental forensic purposes, investigators have developed lists of diagnostic PAH that contain many more compounds than the EPA Priority Pollutant List of 16 PAH. See Figure 2, page 25. Using such an 'extended' list of PAH allows the forensic investigator to better understand the nature of the PAH and, in conjunction with knowledge of the weathering characteristics of PAH, derive chemometric indicators that can be used to differentiate among possible sources of hydrocarbons at complex, contaminated sites.

**PAH distributions for representative products**
Crude oil, almost all its mid-range and residual distillates, and coal-derived liquids such as creosote contain an abundance of 2- to 6-ring PAH compounds. The range of PAH one might find in an hydrocarbon product is a reflection of the distillation cut or pyrogenic processing it had undergone during its production. The distribution and concentration of PAH in a representative crude oil and some refined products are shown in Figure 3, page 26.
Petroleum products are dominated by 2-and 3-ring PAH. There are virtually no 5- or 6-ring PAH in these products. The crude oil contains the broadest range of

Continues on page 28 →

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Environmental forensics,
from page 27

PAH whereas the gaso:ine, the lightest distillate product, contains only the lower boiling 2-ring PAH. Conversely, the residual distillate bunker C fuel contains a relatively higher abundance of heavier PAH. Pyrogenic products such as creosote contain a broad range of PAH and have a large amount of 4-, 5- and 6-ring compounds.

PAH as markers in forensic investigations

Because petroleum products are produced largely on boiling point cuts of crude oil, the gross features of refined products are similar, even from crude stock to crude stock. Hence, HRGC/FID traces of different fuel stocks typically reveal limited evidence to differentiate amongst them.

Consider the forensic investigation of a site contaminated with diesel fuel that potentially arises from two sources, Source A and Source B. A preliminary analysis of source samples and field samples by EPA 8015M confirms that all the samples contain only diesel, but reveal no further useful forensic information about the contribution Sources A and B make to the in-place contamination. Diagnostic PAH analysis using EPA 8270M and the list of target
PAH in Figure 2 of the Source A and Source B diesel fuels reveal that there are differences in the distribution among classes, such as C₀ to C₄ phenanthrenes versus C₀ to C₄ dibenzothiohene and within PAH homologous series, such as the relative amounts of C₀ through C₄ phenanthrenes.

Analyzed in replicate, the cumulative differences between the source signals can clearly be discriminated when using principal component analysis, a multivariate data analysis and visualization technique. See Figure 4, page 28. The factors responsible for pulling these diesel fuel samples into distinct clusters are the previously mentioned subtle differences in PAH composition between the fuels.

Further, analysis of samples from the site shows that the overwhelming number of samples from the free product plume are associated with Source B, while only a small number are related to Source A. Using this information in conjunction with product thickness in wells, product density, and geotechnical analysis, such as soil capillary properties, forensic investigators are able to calculate the volume of the free product plume and the percentage of the plume attributable to Source A and Source B. Such an analysis provides the basis for a negotiated settlement of response and cleanup costs for the site between parties responsible for releases from Sources A and B.

**PAH provide the clues**

PAH are important chemical constituents of almost all crude and refined petroleum and coal-derived liquids. Precise measurements of an extended list of parent and alkyl substituted PAH can often provide a unique forensic "fingerprint" for hydrocarbons products. Such fingerprints can form the basis for tracking the transport of that material in the environment or linking its signature to potential sources. Using such a strategy can be a powerful means to discriminate among sources of otherwise similar fuel at contaminated sites where the source or fate of contamination is in question.

Kevin J. McCarthy, Allen D. Uhler, Ph.D., and Scott A. Stout, Ph.D., are research scientists and consultants with Battelle's Environmental Forensics Investigation Group, Duxbury, Mass. Uhler is also a member of the Soil & Groundwater Cleanup Scientific Advisory Board.
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Training, from page 31
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AS THE PENDULUM SWINGS ...

DNAPL site exemplifies trend away from remediation

By Samuel W. Butcher

Remedial activities at sites with groundwater contamination continue to follow a well-documented trend from active and aggressive remediation to achieve pre-release conditions, toward remediation to achieve a condition of no significant risk. The drinking water standards that were once used widely as regulatory cleanup standards are now being replaced by risk-based standards.

The trend is in response to the realization that removal and treatment of all of an aquifer's contaminants may not be possible, or at least not practical, and that those responsible for cleanup may not have the resources to conduct endless remedial activities. A site in Massachusetts demonstrates how far the risk-based cleanup approach has come. Where a release of dense non-aqueous phase liquid (DNAPL) would have once required a long-term pump and treat solution, a risk-based remedial solution has significantly limited the scope and costs associated with remedial efforts.

Continues on page 34 →
The pendulum continues to swing away from active, complex and costly groundwater remediation solutions toward a less costly risk-based approach. Though contamination at this site included the presence of DNAPL, the risk characterization concluded that for the majority of the plume, a significant risk to public health, safety, welfare and the environment was not present. Though a soil vapor extraction (SVE) system was installed for additional protection against indoor air contamination, the responsible party was able to avoid extremely costly and unnecessary remediation of a bedrock aquifer.

**HISTORICAL PERSPECTIVE OF DEVELOPMENT OF RISK-BASED CLEANUP**

Pre-1980 remediation at disposal sites consisted primarily of pumping and treating groundwater and excavating contaminated soil. Remedial efforts were initiated in an attempt to reduce contaminant concentrations to pre-release conditions or to conservative cleanup standards such as background or drinking water standards. Regulations in some states still reflect this mind set as drinking water standards are the default cleanup standard.

Through the 1980s, however, many consultants, scientists and potentially responsible parties realized that remediation to treat groundwater to nondetectable concentrations was not feasible and in some cases nearly impossible unless unrealistically long remediation scenarios were considered. Editorials espousing a more realistic approach to remedial efforts appeared begging the question “How clean is clean enough?” This discussion focussed primarily on whether continued operation of treatment systems was justified after the contaminants in the groundwater had reached some asymptotically low level. However, it laid the foundation for the discussion of risk-based cleanup.

The 1980s also saw advances in remedial technologies that greatly improved contaminant removal efficiency for groundwater remediation sites. Technologies such as SVE, air sparging, bioremediation, and a multitude of others moved from developmental stages to the mainstream and started to appear at an increasing number of sites. With improvements in the ability to achieve lower cleanup standards, in less time and for less money, remediation became more easily justified.

A risk-based evaluation might be used at sites where contaminant levels were relatively low. But at sites where contaminant levels were high, such as sites with free-phase product, some form of remediation was almost always required regardless of the risk posed by contamination since remediation technologies had made such great strides. To forego remediation of a heavily contaminated aquifers did not pass the “straight face test.”

By the mid-1990s, the American Society for Testing and Materials (ASTM) published a standard for evaluating risk-based corrective action. In addition, just over half of the states incorporated some form of risk-based approach to evaluating cleanup standards and the need to conduct remediation.

While some states simply established separate criteria for residential and industrial settings, others promulgated regulations allowing consultants and responsible parties to conduct risk characterizations wherein site specific contaminant concentrations, exposure pathways and exposure point concentrations are evaluated to derive an overall site risk. Using this approach, the overall risk associated with contaminants in all media is evaluated.

As risk-based corrective action became more widely accepted, so too did natural attenuation as a remedial alternative for sites where contamination decreased over time due to natural chemical, physical and biological processes; where an ongoing source of contamination was not present; and where other forms of remediation were not necessary to reduce risk or contain a contaminant plume. Studies documented the degradation of contaminants in groundwater over time.
and editorials reinforced the opinion that active and aggressive remediation was not the answer to cleaning up contaminated aquifers to pristine conditions.

The USEPA published a Directive regarding the use of natural attenuation as a remedial alternative in 1997. Since that time there has been an apparent increase in acceptance of natural attenuation by regulators.

**CASE STUDY - NEW ENGLAND INDUSTRIAL FACILITY**

A former manufacturer at a New England industrial site used chlorinated solvents including tetrachloroethene (PCE) and trichloroethene (TCE) to clean manufacturing equipment in a manner similar to that which took place at countless other facilities across the country. This manufacturing facility is located in an industrial park situated at the top of a small hill. Geology in the area is dictated by the presence of a fractured igneous bedrock overlain in areas by a thin veneer of soil. Poor storage and handling of these products resulted in periodic spillage and releases to soil and groundwater.

Upon discovery of the contaminant conditions, immediate actions, including the excavation of contaminated soil, were conducted to mitigate potential risks associated with indoor air contamination and direct contact exposure. However, initial assessment activities indicated extensive contamination of soil as well as groundwater in overburden and bedrock. Investigations indicated that total site remediation would not be easily achieved.

Soil, groundwater, and soil gas samples revealed the presence of contamination in the soil, groundwater, and soil gas near the facility building. Oil and hazardous materials (OHMs) at the site consisted primarily of chlorinated volatile organic compounds (VOCs), predominantly PCE, TCE and their breakdown products including vinyl chloride.

Significantly contaminated soil was detected immediately beneath one of the site buildings and in an area where the construction of a new building was proposed. Groundwater observation wells confirmed the presence of DNAPL to a depth of about 30.5 m below grade within the bedrock fractures in the vicinity of the source area. In addition, a dissolved-phase contaminant plume was found to have migrated outward from the source area. Finally, soil gas samples confirmed the presence of unacceptably high concentrations of vinyl chloride in soil gas, due in part to soil contamination and in part to groundwater contamination in the shallow subsurface.

Despite the high contaminant concentrations, a risk characterization demonstrated that no significant risk of harm to human health or the environment for current use and for reasonably foreseeable future uses. This conclusion was based primarily on the absence of complete exposure pathways - the means by which contaminants come in contact with potential receptors, including the public and the environment.

Deeded activity and use limitations were required to assure that future use of the property, specifically the use of site soil, was not inconsistent with the assumptions presented in the risk characterization. Contaminants in groundwater were present, however there were no drinking water wells in the area and no surface water discharge points within a mile downsgradient of the site.

In accordance with applicable regulations an evaluation of remedial alternatives was conducted to determine the feasibility of remediating soil and groundwater to background or pre-release conditions. As part of this study, soil vapor extraction, air sparging, dehalogenation walls, pump and treat technologies, as well as other remedial scenarios, were evaluated. In the final analysis, no remedial technology would sufficiently reduce contaminant concentrations to the point that a restriction on site usage would not be required.

An SVE system was installed primarily as a safety factor to assure that contaminants did not enter indoor air even at acceptably low concentrations. However, because a condition of no significant risk had already been demonstrated, no remediation of the groundwater in overburden or soil was required, despite the presence of DNAPL.

**LESSONS LEARNED**

The assessment and remedial activities presented in this case study exemplify the continued trend away from remediation to achieve pre-release conditions and toward remediation to achieve risk-based clean-up criteria. Where no significant risk is present and remediation is not feasible, remediation is not conducted. Instead, monitoring is performed to assure that a conditions of no significant risk is maintained and to assure that natural attenuation processes continue.

In this case, soil excavation was conducted to eliminate some immediate concerns and an ongoing source of DNAPL to groundwater and an SVE system was installed to mitigate indoor air concerns. Finally, use restrictions were placed on the property to assure that future activities were not inconsistent with the assumptions presented in the risk characterization.

In most states, it would have been inconceivable not to remediate a site where DNAPL was present 20 or even 10 years ago. Now, however, regulatory agencies and consultants alike recognize that if there is no significant risk for current or future use, remediation may not be appropriate.

This continued trend represents a realistic approach to site closure especially where remediation of aquifers has been demonstrated to be impractical and where more attention has been focused of late on preventing releases from occurring in the first place.

Write in 759
It is not difficult to dig up good sources about the science of soil

By Alfred R. Conklin Jr., Ph.D

There are many useful and important information sources about soils. They vary from general to specific. Introductory soils texts give a basic introduction about all aspects of soil. Specific texts about soil formation, soil chemistry, physics, microbiology and biochemistry are also available. There is a soil survey for each county in the United States. This has a great deal of specific information about soils in a county. For even more specific or detailed information about a state or county’s soils, one can contact the Land Grant university in that state or the state soil scientist. Information about soils is readily available if you know where to find it!

Text books are the easiest source of soils information. There are several good texts on the market. Some concentrate on specific types of soils such as tropical, arid or on temperate region soils. For this reason, several basic soils texts may be required.

There are also textbooks that cover specific areas of soils in more detail such as texts devoted to soil formation or soil genesis, soil microbiology, soil chemistry and soil physics. There are also texts covering such specialized topics as soil water relationships and soil plant relationships. These topics are important to those interested in phytoremediation. Other books deal with general topics such as environmental chemistry and biology. Examples of these texts follow:

“Principles of Soil-Plant Interrelationships,” Reading and Taylor, McGraw-Hill.
“Perspectives in Environmental Chemistry,” Macalady, Oxford University Press.

There are also a number of monographs that deal with some particular soil concerns. These cover topics such as soil quality, phosphate and nitrate. Other topics such as soil cleanup and soil environmental problems are also covered. There are books specifically dealing with soil bioremediation and phytoremediation which are interesting and important. However, the more general text should be read before tackling these monographs. They often, rightly, assume that the reader has a basic knowledge of soil and soil terminology.

Every county in the United States has a soil survey. These surveys are included in books, available from the local soil conservation service or local extension agent, which describe the soils and soil characteristics in a county. The information is presented in a written format and includes maps. The

Alfred R. Conklin Jr., Ph.D., is a professor in the agriculture department of Wilmington College, Wilmington, Ohio.
maps, which include a soil’s location and characteristics, are produced by aerial photography. The information included in these county soils books is quite extensive and comprises agriculture, engineering, water, erosion and geological and hydrological characteristics of the soils. These are sources of excellent information about soil that can be used in many different ways. An additional value of the soil survey is that the local soil conservationist will be more than willing to aid in the interpretation of any part of the survey. These conservationists also have access to the latest soil research information relating to the county.

Many states also have publications about specific soil uses. An example would be a state’s book on pond construction. This type of publication would be directly applicable to questions of lagoon construction. It would also be applicable to landfill sites and percolation of water through the soil.

There are also state pamphlets about soil erosion potential. These are appropriate sources of information when a toxic spill has occurred on the soil surface. They provide methods of estimating the potential for pollution due to runoff. Specifically, they answer questions regarding the likelihood of contaminated soil eroding into and polluting nearby water sources.

The most specific and current source of information is the research journal. Two important journals are the Soil Science Society of America Journal (SSSA Journal) and the Journal of Environmental Quality. Both of these are publications of the tri-societies: The Agronomy Society of America (ASA), Crop Society of America (CSA) and the Soil Science Society of America (SSSA). Another good journal is Environmental Science and Technology, published by the American Chemical Society.

A word of caution about journal articles: they are reporting on current research results. In some cases, this work has not been replicated; that is, it has not been done on soils from many different locations. Often additional research is needed before one can be sure that such research results are applicable to the problem at hand.

The tri-societies also have a set of books that describe methods of soil analysis. This set, “Methods of Soil Analysis” has three volumes that deal with the physical, chemical and biological analysis of soils. Even if one does not intend to do soil analysis, this is a valuable set because it explains what can and cannot be learned by various analytical methods.

There are also a number of trade magazines being published. These magazines are particularly valuable in accessing present problems and strategies for dealing with soil solution problems.

Internet access to soil information through two abstract services is available. Perhaps the best is Agricola. It is accessed through First Search under Life Sciences. Interesting and important information can be found using Chemical Abstracts, which is the abstracting service of the American Chemical Society. Chemical Abstracts will be particularly informative if the question is related to the chemistry of a pollutant in soil.

You must subscribe to both these services. Billing for First Search is by the search, so you must choose your search topics carefully. Chemical Abstracts billing is by the hour so planning your search well ahead is important. Both services give references and abstracts for topics searched. A library will still be required to access the original article.

Generally speaking, soils information on the world wide web is surprisingly scarce. The internet is not a place to find reliable soils information.

If seeking information about soils, one should first obtain several basic texts for answering general questions about the characteristics of soils. Then, more specific texts can be used for answering specific questions about specific problems. A soil map, such as those provided in a soil survey, can then be consulted for an area where pollution occurs before bidding on a job or starting a cleanup procedure. If questions about soils then still exist, consult the local soil conservationist.


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■ November 17-19, 1998
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Risk assessment methods can be practical approach for remediation of chemical warfare sites

By T.A. Miller, A. Yaghoobian, G.M. Cross, B.J. Stuckert, J.S. Goudey, and J.M. McAndless

Risk assessments have come a long way since the lengthy and expensive approaches taken in the late 1980s and early 1990s. Using novel screening procedures geared for practical solutions, Golder Associates Limited used advanced techniques to conduct a risk assessment for a site contaminated with chemical warfare agents (CWA) and developed simple, cost-effective remediation strategies.

Golder was contracted by Defence Research Establishment Suffield (DRES) to conduct an ecological risk assessment and develop remediation options for selected sites on the Experimental Proving Ground (EPG) at Canadian Forces Base (CFB) Suffield. DRES is one of several laboratories under the Defence Research and Development Branch of the Department of National Defence (DND) and is responsible for the program in chemical and biological defense.

The DRES EPG occupies about 517 square km of CFB Suffield on the short grass prairie of southeastern Alberta. The EPG was established in 1941 and during World War II was used extensively for the testing of protective equipment and training of personnel in the potential advent of chemical warfare. Following the war, Canada’s production stocks of CWA were shipped to DRES for storage and eventual disposal. From 1989 to 1991, DRES undertook a project to collect and dispose of CWA and related materials. However, areas of residual contamination remained.

In 1995, consistent with DND’s policy of environmental stewardship and to maintain compliance with federal environmental regulations, DRES commissioned an Environmental Baseline Study (EBS) to provide a preliminary assessment of the ecological risks associated with a number of sites. The EBS report recommended that a detailed ecological risk assessment be conducted of EPG selected sites with the overall goal of remediating any sites deemed to have significant ecological risk.

Golder conducted the detailed ecological risk assessment for DRES and developed site-specific remediation options.

Using a risk-based approach

A risk-based approach was used to evaluate the significance of contamination on seven EPG sites. Screening tools including geophysical surveys and indicator analytical chemistry, coupled with a battery of soil bioassays, were used to assess the impacts of contaminants on the environment.

Geophysical survey

Preliminary geophysical reconnaissance was used at three sites to reduce the risk of accidental CWA exposure during subsequent excavations and soil sampling and to identify subsurface sources of chemicals. In particular, a combination of electromagnetic conductivity and magnetic surveys.
were carried out in advance of soil sampling to locate and investigate buried trenches, known to contain chemical munitions, CWA storage containers and other metallic hazards. It was also anticipated that electromagnetic conductivity surveys would detect and delineate zones of chemical contamination by sensing associated soil conductivity anomalies due to chemical enhancement of mobile ion concentrations.

Soil conductivity, corresponding in-phase electromagnetic response and vertical magnetic gradient measurements were acquired on a rectangular grid at a sampling interval of 1.5-2.5 m. Figures 1 and 2, pages 42 and 43, display the geophysical results for two of the investigated sites. Several larger-scale anomalous conductivity zones, incorporating localized metallic (in-phase) signatures, were identified as probable disposal trenches and/or soil and groundwater contamination.

One such geophysical anomaly centered about 27E and 27N (Figure 2) corresponded to an area that was devoid of vegetation as a result of a chemical spill. A number of localized anomalies outside these zones were also identified as potential indicators of buried metal, such as chemical ordnance or canisters. Identified anomalies were ranked for prioritized investigation.

For the first site, a comparison with corresponding soil chemistry and toxicity results indicated that larger-scale conductivity zones are associated with elevated subsurface sulphur concentrations and high toxicity scores. In general, there appears to be a significant direct correlation between apparent soil conductivity and toxicity. These correlations were not confirmed in areas of low electrical conductivity.

Focused ground penetrating radar (GPR) soundings were acquired in an attempt to establish the origin of concentrated tear gas (chloroacetophenone) contamination discovered in connection with an isolated metallic signature (Figure 1, 52E and 193N). No clear source was identified. At another site, high-resolution seismic imaging and GPR techniques were used to pinpoint the location and to guide safe recovery of chemical ordnance encased within a concrete structure.

**Analytical chemistry**

Indicator analytical tests were used to screen soil samples for chemicals at hazardous concentrations. Based on a historical review and information from DRES scientists, mustard and lewisite had been identified as the main contaminants of concern. Additional potential contaminants included nerve agent degradation products and various metals. Indicator analytical tests included sulphur for mustard, arsenic for lewisite, and phosphorous for nerve agent degradation products, metals scans and pH.

A limited number of soil samples were selected for mustard analysis based on the sulphur results and on olfaction. Using this approach, analytical costs were significantly reduced as compared to a traditional, analytical chemistry-based risk assessment by as much as 25 percent to 50 percent.

**Ecological risk assessment**

The risk assessment incorporated a direct measurement of the relationship among contaminant concentration, receptors and exposure pathways through the use of soil bioassays. Soil invertebrates and plants were the main receptors of concern for this remote area of the prairie, and protection of these receptors was determined to be protective of higher trophic levels.

Soil samples were collected focusing on the top 3 m of soil, the biologically active zone. Contamination at depth was considered to be inaccessible to all receptors. Previous hydrogeological investigations conducted on the EPG determined that it would take about 300 years for soil contaminants to migrate to the regional aquifer and several millennia to migrate to the South Saskatchewan River, the closest surface water. Dilution would reduce any contaminants to undetectable concentrations at the point of discharge. Therefore, off-site receptors were not considered further.

The assessment of contaminated soil toxicity was accomplished directly through the use of a battery of six bioassays. Tests and test species were selected in consultation with HydroQual Laboratories Ltd. (HydroQual), a toxicology laboratory in Calgary, Alberta. Toxicity tests were selected to include each trophic level in a soil environment, a mix of indigenous and standard test species, and a range of lethal and sublethal effects.
**FIGURE 1**

The apparent soil conductivity data (Figure A), the in-phase response (Figure B), and the geophysical interpretation with the toxicity results (Figure C) are presented. EM data were acquired in vertical mode at waist level along 3-meter lines with 2.5-meter station intervals. Survey lines and the instrument were aligned in a north–south orientation. Total magnetic data were also acquired over the same survey lines at 0.5-second intervals (approximately 0.5 meters). Most of the indicated metallic anomalies were mapped using the in-phase response and the total magnetic field data. Geophysical data were processed using line based bi-directional gridding software.
FIGURE 2

Apparent soil conductivity data (Figure A) with the geophysical interpretation (Figure B) are presented above. EM data was acquired in vertical mode at waist level along 5 meter lines with 1.5 meter station intervals. Survey lines and the instrument were aligned in an east-west orientation. Areas identified as high apparent conductivity zones indicate trenches and/or chemical contamination. The area identified as Metallic Debris was mapped using the in-phase component of the electromagnetic instrument. Bi-directional gridding was used to process data.
Chemical warfare, from page 43

sublethal endpoints.

Northern wheatgrass, a species indigenous to the short-grass prairie, was used in two soil bioassays — germination and root elongation. Consistent with standard risk assessment practice, most tests were interpreted with regard to potential impacts to populations.

Each test was assigned a relative weight that reflected the relevance of that test to the site, sensitivity of the test and reliability of results when compared to analytical results and other bioassays. See Figure 3, this page. Indigenous species were considered to be the most relevant receptors to the site and were given a relatively high weight.

Bacterial luminescence (Microtox) was given a relatively high weight since it is a sensitive test that is commonly used in contaminated site evaluation. Nematode survival was found to be a relatively unresponsive test in comparison to the other test species and was therefore given a relatively lower weight.

Bacterial counts and soil respiration were used as an evaluation of potential effects to soil bacteria. These tests were given relatively less weight in the final assessment as they are of less value to humans and effects to bacteria would be significant only if they resulted in effects to higher trophic levels, such as plants and invertebrates.

Background samples were also tested to provide a reference of the normal range of response that could be expected for uncontaminated soil from this area. Test results for each sample from a site were then scored out of five and the results for each sample were compared to results for background or ‘reference’ samples. A low score was consistent with low toxicity.

A 20 percent measurement endpoint was used as the acceptable level of effect for all ecological receptors. Therefore, soils having a score of more than 20 percent higher than the range of scores obtained for reference samples were considered to warrant risk management or remediation. The scores for background samples ranged from 1 (lowest possible) to 1.85. Therefore, samples having a toxicity score of less than or equal to 2.2 were considered to be no different from background samples. The results for each soil sample were color-coded according to the following range: green, 1.0 - 2.2; yellow, 2.3 - 3.0; and red, 3.1 - 5.0.

An example of the bioassay results for soil samples collected from the 490 Inner Fence Area is presented in Figure 4, page 45. The 490 Inner Fence Area is a 1.2 x 1.4 km fenced area on the EPG that has been used for blast trials, neutralized mustard hydrolysate land farming, drum disposal in pits created by blast trials, contaminated scrap and equipment storage, neutralization of lewisite and incineration of laboratory chemical waste.

Sixty-three samples from the 490 Inner Fence Area were submitted for toxicity testing. Results for soil samples ranged from no significant toxicity to a strong toxic response. Generally, there was a positive correlation between geophysical anomalies and high concentrations of metals and sulphur and a strong toxic response.

High concentrations (~10,000 to 30,000 mg/kg) of sulphur were associated with a toxic response in some samples but not in others. Generally, the most consistent potentially causal factor associated with samples having high concentrations of sulphur and a strong toxic response was low soil pH, such as < 4.5. The low soil pH was likely due to the degradation of mustard by various processes resulting in the production of \( \text{H}_2\text{SO}_4 \) and \( \text{HCl} \).

Concentrations of arsenic in soil of up to 300 mg/kg were associated with no significant toxicity to the soil-dependent receptors. This concentration is significantly greater than regulatory guidelines for the protection of soil-dependent receptors or concentrations reported as hazardous to these receptors in the scientific literature. Therefore, the use of the bioassays resulted in significantly less remediation than what would have been required using a criteria or even a literature-based assessment approach.

**Recommendations for remediation**

Practical recommendations for risk management or remediation of areas showing a toxic response were provided. For example, recommendations for the 490 Inner Fence Area where shallow soil was associated with a toxicity score of greater than 2.2 were that contaminated soils be excavated to a depth of 0.5 m, re-graded with clean, native soil, contoured and
Figure 4. Defence research establishment, Suffield - EPG, 490 Inner Fence, soil sampling locations and toxicity results.

Seeded with native grassland species. Recommendations also included:

- Contaminated soil from these areas be placed in the blast craters to a minimum depth of 3 m below ground surface (bgs). This depth was chosen based on the biologically active zone. Burrowing animals on this area of the prairie could be expected to burrow to a maximum depth of 3 m.
- Contaminated soil around the perimeter of the blast craters be pushed into the craters to a depth of at least 3 m bgs. Clean fill was recommended for the top 3 m.
- The site of the former craters be contoured and compacted with native soil and seeded with native grassland species. The estimated cost of assessment and remediation for this site was $190,000 ($CA).

Positive results

The results of this study confirm that risk assessment can be a practical tool for assessment and remediation of CWA contaminated sites. To reduce the risk of accidental chemical exposure, preliminary geophysical investigations identified potential subsurface hazards in advance of intrusive soil sampling. Electromagnetic surveys also proved effective for identifying zones of potential chemical contamination by delineating associated electrical conductivity anomalies. However, despite this utility, geophysical methods cannot unambiguously identify the presence of CWA contaminants.

Screening employed for analytical chemistry resulted in significant cost savings while still providing sufficient and, in fact, more suitable information for the assessment. Remediation was based on the direct measure of toxicity provided by a battery of six soil bioassays thereby reducing uncertainty in risk assessment results.

The effective use of the risk assessment process that allowed for screening out of inoperative exposure pathways, such as groundwater, focused the investigation and thus further reduced investigation costs. More importantly, the use of innovative investigation techniques coupled with risk assessment resulted in the development of very cost effective remedial measures that met the DND objective of environmental stewardship by protecting and reestablishing the native ecosystem.
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