



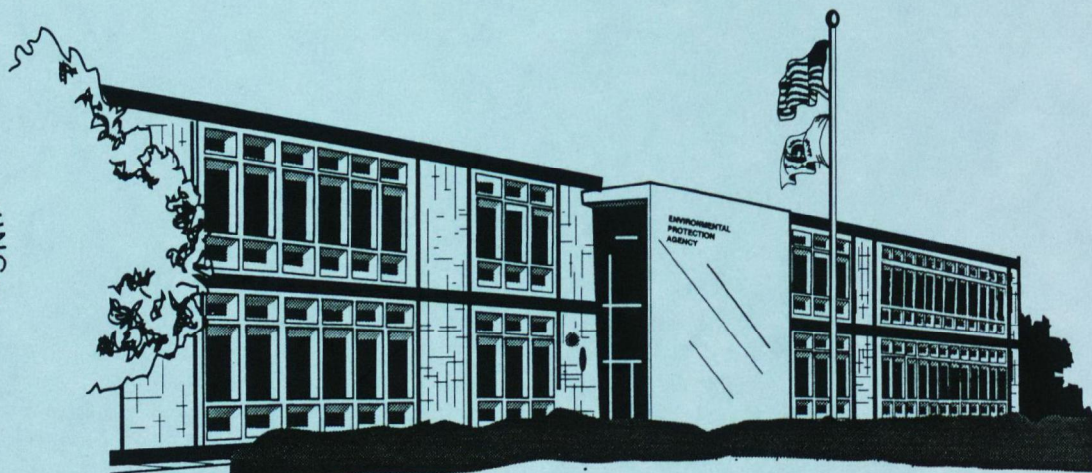
United States  
Environmental Protection  
Agency

National Exposure Research Laboratory  
Characterization Research Division  
P.O. Box 93478  
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December 1995

# National Exposure Research Laboratory Characterization Research Division - Las Vegas

## **Research, Innovation and Technology Support**



*U.S. Environmental Protection Agency, Characterization Research Division - Las Vegas*



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- SITE Program
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- Drinking Water Rad QA

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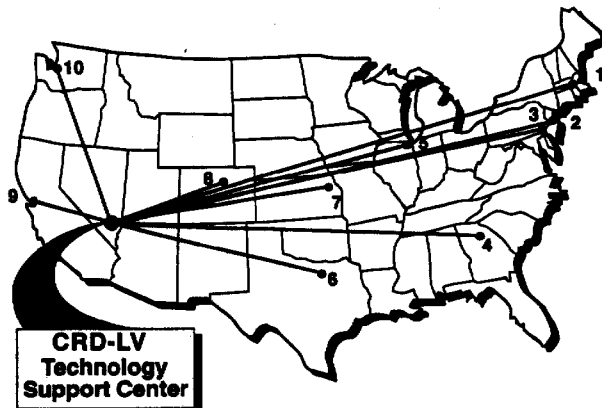
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TECHNOLOGY SUPPORT



# Technology Support Center



## INTRODUCTION

The U.S. EPA maintains Technical Support Centers in laboratories operated by the Office of Research and Development (ORD). These Technical Support Centers are dedicated to serving the EPA Regions by supplying high-quality, quick-response technical services when the scope of work is beyond the technical capabilities of local contractors.

The Characterization Research Division in Las Vegas (CRD-LV) has an active Technical Support Center (TSC) that responds to

requests from the Regions. The TSC began in 1987 and, originally, specialized in Superfund support to Remedial Project Managers (RPMs) and On-Scene Coordinators (OSCs). Since 1991, RCRA technical support is available too.

The CRD-LV TSC specializes in sampling and monitoring technologies, quality assurance, soil and ground water sampling and special analytical services. This diversity of expertise allows the TSC to work with Regional personnel throughout a site character-

ization event, from planning and design to analysis and data interpretation.

In addition to direct technical support, the CRD-LV TSC provides technical communication to the Regions through the Technology Transfer Project. Fact sheets, a bimonthly newsletter entitled "The CRD-LV Bulletin", and various presentations, demonstrations, and poster sessions help to keep Regional personnel up to date with the services available through the TSC.

## REGIONAL REQUESTS

When RPMs/OSC or RCRA Project Officers require assistance through the CRD-LV TSC, they contact the Director by phone or by letter. Before any work is committed, a written request must be made. The TSC Director determines the ability to meet the demands of the request

and contacts the technical staff appropriate to the project.

After the work is done, a report is issued to the requester. Often these reports go beyond the specific needs of a particular site. Technical information gained at

Superfund and RCRA sites form the basis for a growing background literature about the specialized challenges of complex environmental matrices and also serve to validate research-developed procedures, methods, and ideas.

## TECHNICAL FOCUS

The TSC provides support to the Regions in site characterization technologies such as field-portable X-ray fluorescence (FPXRF), soil-gas measurement, geophysics, special analytical services,

quality assurance, chemical analysis, radiochemical analysis, geostatistics, statistical design, GIS, and data interpretation.

When on-site work is required, the TSC mobilizes

specialized teams equipped with portable or deployable instruments to assist the Regions with the screening and site-characterization work that forms the basis for all subsequent work.

## DOCUMENT REVIEWS

In addition to the deployment of field scientists, the TSC helps the Regions evaluate documents that have been

submitted by local contractors. This support is crucial to wise decision-making by the Regions. Team efforts

between the TSC and the Region result in better technology, quicker response, and greater legal defensibility.

## PUBLICATIONS

The TSC Director is a member of various technical forums. This participation often leads to the authorship or coordination of issue papers relating to the use of innovative technologies for monitoring and site characterization.

Technical support projects are documented in reports to the Regions which vary in length and complexity according to the project needs. Projects can identify

areas for further research or develop protocols for experimental or sampling design.

The TSC participates in interagency workshops with the U.S. DOE and U.S. DOD and together these organizations have published guidance documents that address the special challenges of heterogeneous wastes at federal and other facilities.

Through the Technology Transfer Project, the TSC

"markets" its services to the Regions and beyond. Fact Sheets describe dozens of analytical and field technologies that are available through the TSC. Other technology transfer activities include the production of videos outlining various CRD-LV activities and the publication of a bimonthly newsletter, The CRD-LV Bulletin, that is distributed to a growing mailing list of more than 500 interested parties.

## REFERENCES

Included here is a sampling of CRD-LV TSC publications. For a copy of any of these, or for a packet of CRD-LV Fact Sheets, contact the manager of the TSC.

Characterizing Heterogeneous Hazardous Wastes: Methods and Recommendations, EPA/600/R-92/033, (The proceeding of a workshop held at the EMSL-LV and co-sponsored by the U.S. DOE.)

Lewis, T.E., A.B. Crockett, R.L. Siegrist, and K. Zarrabi, "Soil Sampling and Analysis for Volatile Organic Compounds", EPA/540/4-91/001, (A Ground-Water Issue Paper.)

Breckenridge, R. P., J. R. Williams, and J. F. Keck. "Characterizing Soils For Hazardous Waste Site Assessments", EPA/540/4-91/003 (A Ground-Water Issue Paper.)

## FOR FURTHER INFORMATION

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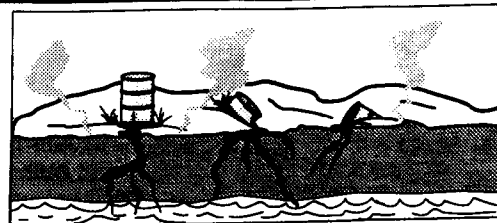
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TECHNOLOGY SUPPORT



# Soil-Gas Measurement



## INTRODUCTION

The term "soil-gas" refers to the atmosphere present in soil pore spaces. Volatile compounds introduced into the subsurface can be present in the gas phase or, more commonly, can undergo a transition from a liquid or sorbed phase (pure product, dissolved, or adsorbed to soil) to become part of the soil atmosphere. Techniques for measuring soil gases were developed early in this century for agricultural studies and for petroleum exploration. Within the last several years, soil-gas measurement has become an accepted environmental site-screening tool. The technique is rapid, low cost, and provides a high yield of information when carefully applied. Because it is an indirect measure of

underlying contamination and because of the potential for false negative results, the technique should be used only for site screening and not for confirmation.

The fate and transport of contaminants and their occurrence and detectability in the soil gases are very compound- and site-specific. Soil-gas technology is most effective in detecting compounds having low molecular weights, high vapor pressures, and low aqueous solubilities. These compounds volatilize readily as a result of their favorable gas/liquid partition coefficients. Once in the gas phase, volatile compounds diffuse vertically and horizontally through the soil toward zones of lower concentration.

Degradation processes (e.g., oxidation or reduction) can eliminate or transform contaminants in the soil atmosphere. The susceptibility of a contaminant to degradation is influenced by such factors as soil moisture content, pH, redox potential, and the presence of microorganisms that can degrade the compound. Other site-specific characteristics affecting results are: soil type, air-filled porosity, depth to the source, barriers to vapor transport, and hydrogeology. Because site-specific factors influence contaminant concentrations detected in the soil gases, a quantitative correlation between soil-gas concentrations and underlying contamination is difficult to generalize.

## APPLICATIONS

Soil-gas surveys can be used to:

- identify contaminants and relative concentrations
- identify sources; indicate extent of contamination
- monitor the progress of cleanups
- guide placement of subsequent confirmatory samples (soil borings, monitoring wells)
- monitor at fixed vapor wells (long-term monitoring)
- detect leaks through use of tracer compounds

Typical primary sources include surface spills, leaking tanks, pipes, trenches, dry wells, or landfills. Contaminants from such sources frequently reach the water table, causing the ground-

water to become a source of contamination to down-gradient sites. The nature of the source will influence the vertical and horizontal dispersion of gas-phase contaminant vapors.

Contaminants detectable in soil gases include many common chlorinated solvents and the lighter fractions of

petroleum products, substances that are widespread environmental contaminants. Of the 25 most commonly encountered contaminants at Superfund sites, 15 are amenable to detection by soil-gas sampling. Inorganic contaminants that can be detected by soil-gas sampling include radon, mercury, and hydrogen sulfide.

### SELECTED COMPOUNDS DETECTABLE IN SOIL GASES

#### Aromatic hydrocarbons:

Benzene, toluene, xylenes, naphthalene

#### Aliphatic hydrocarbons:

C<sub>1</sub> - C<sub>10</sub> (e.g., methane, butane, pentane, iso-octane cyclohexane)

#### Mixtures:

Gasoline, JP-4, various jet fuels

#### Chlorinated hydrocarbons:

Chloromethanes (e.g., chloroform, carbon tetrachloride); chloroethanes; chloroethenes (e.g., vinyl chloride, di-, tri-, and perchloroethene)

#### Other:

CO<sub>2</sub>, CS<sub>2</sub>, H<sub>2</sub>S, NO<sub>x</sub>, radon, mercury compounds

## THE TECHNIQUE

Soil-gas samples can be collected by active or passive methods. For active sampling, a probe is driven into the ground and soil gases are pumped from the subsurface into a sample container (e.g., evacuated canister, tube, glass bulb, gas sample bag, syringe) or through a sorbent medium. For passive sampling, a sampler containing a sorbent with an affinity for the target analytes is placed in the ground for a period of time, and contaminants are collected by virtue of diffusion and adsorption processes. After exposure, the passive sampler is

transported to a laboratory for analysis. The most commonly used technique for analyzing soil-gas samples is gas chromatography (GC) in combination with a detector appropriate to the target analytes. Analyses can be done on- or off-site. Soil-gas samples can also be screened in the field using organic vapor detectors, which provide results expressed as total hydrocarbon concentration relative to a calibration standard.

The design of a soil-gas survey depends on the data required (e.g., identifying and

quantifying specific compounds vs. measuring total hydrocarbon concentration) and the nature of the contamination. A feasibility study is recommended whenever possible, particularly for sites where little information is available. Such a study can be valuable in verifying the effectiveness of the method at the site, selecting the appropriate sampling and analytical methods, choosing the best sampling depth, and optimizing other operational details. Because soil-gas surveying is an intrusive technique, precautions must be taken to avoid buried utility lines, tanks, or other objects.

## DATA QUALITY OBJECTIVES AND QA/QC

Because soil-gas results provide an indirect measure of primary contamination, data quality objective (DQOs) for soil-gas surveys and the Quality Assurance (QA) required need not be as strict as those for confirmatory sampling and analysis of soil or ground water. However,

because most soil-gas survey objectives require comparison of data among points to determine patterns of relative concentration, the investigator must be able to determine whether differences in value are real or merely due to poor method precision. Consistency in procedures is

essential (i.e. collection and analysis of replicate and blank samples) and regular checks of instrument calibration. Materials that come into contact with samples should be inert and easy to decontaminate.

## SUMMARY

Soil-gas measurement can be an effective method for determining the source and extent of volatile contaminants in the subsurface. Because of the many site- and compound-specific factors that can influence results, soil-gas measurement should be done only by experienced field investiga-

tors. With proper QA and judicious data interpretation,

this technique is a useful, low-cost site screening tool.

### SUMMARY OF ADVANTAGES AND LIMITATIONS OF SOIL-GAS MEASUREMENT

#### Advantages

Rapid  
Low cost  
Real-time results  
Minimal disturbance to site

#### Limitations

Indirect measurement  
Interferences (false negatives are a problem)  
Application limited to high volatility/low solubility compounds

## REFERENCE

Mayer, C.L., Soil-Gas Surveys: Planning, Implementation, and Interpretation. EPA/600/X92/065 U.S. EPA. EMSL-LV. Las Vegas, NV. 1992.

## FOR FURTHER INFORMATION

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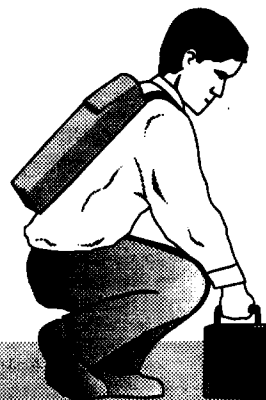




TECHNOLOGY SUPPORT



# Field-Portable X-Ray Fluorescence



## INTRODUCTION

Field-portable X-ray fluorescence (FPXRF) is a site-screening procedure using a small, portable instrument (15 - 25 lbs, or 7-12 Kg) that addresses the need for a *rapid* turnaround, *low-cost* method for the in situ analysis of inorganic contaminants. Traditional Contract Laboratory Program (CLP) methods of analysis may take 20 - 45 days per site to complete and the analysis would cost much more than FPXRF. FPXRF can measure inorganic elements when used with the proper radioisotope source and the appropriate standards. FPXRF is capable of simultaneous analysis of up to six analytes per model. More than one model can be applied to each spectrum obtained. This method is useful at various levels of analysis, with data quality

dependent upon the extensiveness of the survey, the type of standards used, and the reinforcement of data by other corroboratory methods. FPXRF can be used for periodic monitoring as remediation proceeds. The following table includes the elements that are on the EPA's Inorganic Target Analyte List, with asterisks designating the ones quantifiable by FPXRF.

The CRD-LV has been requested to analyze six of these elements to date: arsenic, chromium, copper, iron, lead, and zinc. Though detection limits are highly matrix dependent and site specific, the detection limits for these elements have been in the 100 - 500 mg/Kg range. The instrument used at the CRD-LV is an X-MET 880.

TABLE 1  
INORGANIC TARGET ANALYTE LIST

Aluminum	* Calcium	Magnesium	* Silver
* Antimony	* Chromium	Manganese	Sodium
* Arsenic	* Cobalt	* Mercury	* Thallium
* Barium	* Copper	* Nickel	* Vanadium
Beryllium	* Iron	* Potassium	* Zinc
* Cadmium	* Lead	* Selenium	Cyanide

\* Indicates FPXRF quantifiable analytes.

## THE SURVEY

An FPXRF survey is a combined effort of field scientists and geostatisticians. Ideally, there is a pre-survey aerial photographic evaluation of the site, a screening on-site to collect site-specific calibration standards, an off-site calibration of the instrument, and a final on-site visit for data collection and quality control. Then geostatistical interpretation is done and a site screening report is published.

Typically a field survey is requested by an EPA Region. Remedial Project Managers (RPMs) can contact local contractors with the equipment and expertise to do an FPXRF survey. When special help is needed, the RPM may contact the CRD-LV for expert advice. The team that responds is equipped with an FPXRF instrument and all of the necessary supporting equipment to adequately assess the site. Using the cali-

bration curve that has been generated from site-specific standards, the X-ray responses of the routine samples are regressed against this curve and an analytical result is generated. Geostatistics, an interpretive method which allows for the similarity between neighboring samples, is used to optimize the sampling design prior to the survey. After the sampling, geostatistics is used to analyze the data and to produce concentration isopleth maps.

## INSTRUMENTATION

X-ray fluorescence is based on the fact that atoms fluoresce in a unique and characteristic way. By bombarding a sample with energy, the instrument causes an electronic instability. As the instability relaxes to a more stable energy level, X-ray fluorescence is emitted.

The detector senses and counts this spectrum of radiation which is a fingerprint of the specific analyte and, on this basis, identifies the atom. Quantitation is done against a calibration curve that was generated by the analysis of site-specific standards.

X-ray fluorescence has been a standard laboratory method for years and the recent availability of portable instruments now allows this method to be taken into the field for use at hazardous waste sites.

## HOW A FIELD SURVEY IS CONDUCTED

To effectively use FPXRF, the field scientist must ask a few questions. What is the objective of the survey? What data are needed? What is the most efficient sampling scheme? What are the data quality objectives?

A complete FPXRF analysis is based on calibration of standards that are specific to the site. These standards are collected on the initial site-screening visit and are analyzed by a complete CLP procedure in order to cali-

brate the FPXRF instrument. Numerous in situ measurements are made on the hazardous waste site. QA/QC is integrated into the program. The resulting data are not only quantitative, but of known quality.

## COST

The average cost of in situ FPXRF surveys, based on a wide range of surveys performed by the CRD-LV team has been less than \$50,000. This cost includes

labor, transportation, an aerial photographic pre-survey, analysis of about 15 site-specific standards per analyte, the FPXRF survey of up to 150 measurements

per day, and a final report. A typical survey takes about 3 days. The complete procedure from pre-survey through final report takes about 4-6 weeks.

## ADVANTAGES AND LIMITATIONS

### Advantages

Low cost

Ease of operation - portable, moves to any site

Rapid results - real time  
(once site-specific standards are available)

### Limitations

Complex data interpretation -  
for geostatistical investigations

Matrix variability  
type of soil influences results

Less sensitive than a complete CLP analysis

## REFERENCE

Raab, G. A., R. E. Enwall, W. H. Cole, III, M. L. Faber, and L. A. Eccles, July 1990, X-Ray Fluorescence Field Method for Screening of Inorganic Contaminants at Hazardous Waste Sites. In: *Hazardous Waste Measurements*, M. Simmons, Ed., Lewis Publishers, Chelsea, MI.

## FOR FURTHER INFORMATION

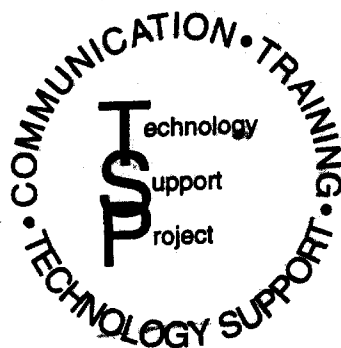
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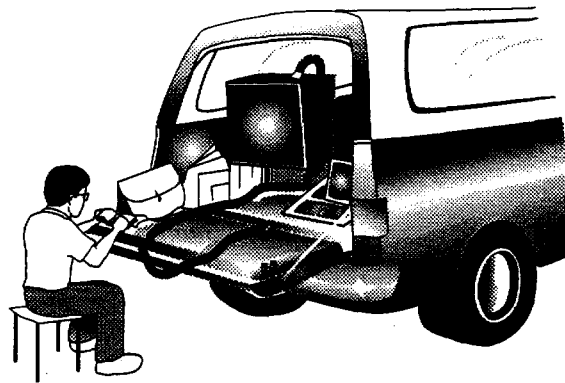


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TECHNOLOGY SUPPORT



# Mobile Mass Spectrometry



## INTRODUCTION

Gas chromatography/mass spectrometry (GC/MS) is the EPA recommended method for the analysis of volatile and semivolatile organic compounds. This proven analytical technique identifies and quantifies organic compounds on the basis of molecular weight, characteristic fragmentation patterns, and retention time. Until recently, it was not feasible to bring a GC/MS instrument to a hazardous waste site because of its size and weight, the need for strict

control of temperature and humidity, and the effect of vibration during transport. With the growing demand for field-portable instrumentation in the environmental area, rugged, smaller units have been developed. Bruker Instruments, Inc. supplied CRD-LV with a complete mobile mass spectrometry system to test under the Superfund Innovative Technology Evaluation (SITE) program. The performance of this system was demonstrated at two Superfund

sites in Region I. The mobile mass spectrometer was used for the analysis of PCBs in soil at the Re-Solve, Inc. Site and for PAHs in soil and VOCs in groundwater at the Westborough Township Site. Because GC/MS is the preferred method for the analysis of volatile and semivolatile organic compounds, mobile GC/MS is anticipated to become the major technology for field analysis of these contaminants in the 1990s.

## INSTRUMENTATION

The Bruker system (specifically the MEM) was considered the most advanced instrument available for this testing and was, therefore, the only one evaluated. When other instruments become available, comparisons will be performed. The Bruker MEM is ca. 22" x 28" x 30" and weighs about 500 pounds. It can be mounted in a four-wheel drive vehicle and taken directly to the site.

This instrument is equipped with built-in power, resistance to shocks, and will operate from -30°C to 50°C with no external cooling or heating requirements. The mass spectrometer has a mass range of 1-400 Daltons which minimizes power consumption. It can operate for 6-8 hours on battery power, or indefinitely using a generator

or conventional AC power. An MS-DOS 386 based data system can be used to acquire, analyze, and archive all GC/MS data. Sampling accessories are available for a wide range of monitoring situations: a "sniffer" with a 3.5 m GC column is used for continuous air monitoring or the thermal desorption of organics from a soil surface. A temperature programmable GC with a capillary column is also available.

The Bruker MEM offers several analysis modes and sample introduction methods which can be chosen based on the data quality objectives (DQO) of the site. Two modes, "rapid screening" and "characterization", were tested in the SITE demonstration. The rapid screening mode allows a quick analysis

for up to ten organic compounds simultaneously. The more accurate characterization mode follows a CLP-type protocol, including an extraction, 5-point calibration, and data acceptance windows. Once the sample is introduced, it passes through a semipermeable membrane into the ionization source where it is fragmented into characteristic ions. These ions are then accelerated, focused, and detected. The resulting mass spectrum is compared against known compounds in the computer's library. The quantitation limits of the MEM vary depending on several factors including:

- analysis mode used
- analytes detected
- matrix analyzed

## SCOPE

The desirability of field-portable GC/MS instrumentation is obvious. The MEM provides the Agency with an instrument for field analysis that is capable of achieving a wide range of DQOs. Because of the proven track record of GC/MS, field GC/MS is a superior choice to other novel techniques which have been proposed for field analysis but lack a basis in routine or special environmental applications. By

replicating the method of choice for organic analysis in a unit that can be deployed to hazardous waste sites, the favored technology is moving on-site. The on-site results can be compared easily with CLP results. Decisions can be made at the site, based on early results, to focus subsequent and intensive sampling in areas of greatest contamination. More than a field screening tool, portable GC/MS provides field scientists

with an instrument of accepted integrity and demonstrated value. It allows field scientists and on-scene decision makers an opportunity to compare field results with historical databases. The development and implementation of these instruments is of great interest to environmental scientists, especially those working within the historical framework of the CLP.

## ADVANTAGES AND LIMITATIONS

These newly tested field methods are capable of improving the overall reliability of organic analysis in field situations. As the technology emerges, further breakthroughs in sensitivity, size, and ruggedness will certainly continue.

This is a system specifically designed for field use not a

laboratory instrument taken to the field.

### Advantages

Simplified operations  
Rapid turnaround  
Unambiguous identification  
Equivalent to EPA method

### Limitations

Complex, requires trained personnel  
Field quality control  
High initial equipment cost

## FUTURE PLANS

Further testing of the Bruker instrument and other manufacturer's equipment is planned. Evaluations of these instruments and comparisons between laboratory and field analysis data will address concerns about volatile loss during

shipment from field to laboratory. More analytes on the hazardous substances list (HSL) will be quantified by portable GC/MS. The use of the system with its ancillary "sniffer" for air testing will be considered. Additional automated sampling devices

will be developed and tested. Computer software will be modified to generate reports in Agency format. Increased demand for this instrumentation will guide research to meet the growing needs of environmental field scientists

## REFERENCES

Project and Quality Assurance Plan For Demonstration of the Bruker Mobile Mass Spectrometer, U.S. EPA Report, September 1990.

Robbat, Jr., A., and G. Xyrafas. "Evaluation of Field Purge and Trap Gas Chromatography Mass Spectrometry," presented at the First International Symposium; Field Screening Methods for Hazardous Waste Site Investigations, Las Vegas, NV, October 1988, proceedings.

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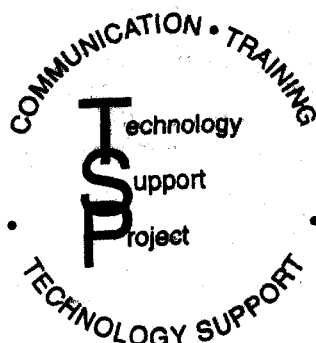
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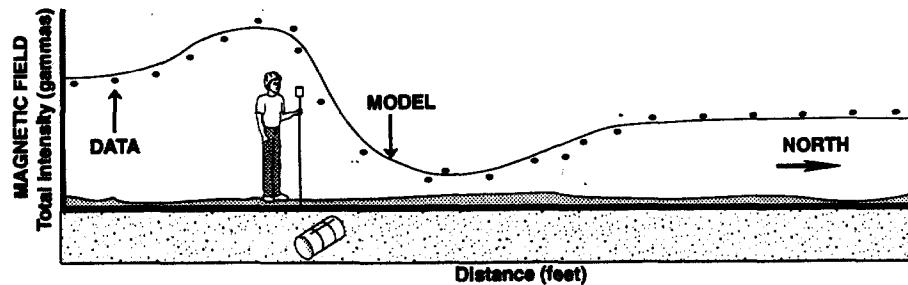




TECHNOLOGY SUPPORT



# Geophysics: A Key Step in Site Characterization



## INTRODUCTION

A frequent problem facing environmental scientists working on the remediation of hazardous waste sites is locating subsurface contamination and delineating features that influence its movement. When a site manager requires information about subsurface characteristics with as little subsurface disturbance as possible,

geophysics offers an array of techniques. Focusing on the location and assessing the extent of contamination can lead to a more clearly defined view of the site that will save time, money and provide a better degree of safety.

Geophysicists at The Characterization Research Division

in Las Vegas (CRD-LV) are experienced in using several geophysical methods that can aid in the detection and definition of contamination. This information can assist the site manager with cost-effective, reasonable options during site characterization.

## METHODOLOGY

All geophysical techniques are based on elements of physics and geology. These methods respond to the physical properties of the subsurface to infer the geological formations and structure, and the presence, location, distribution and size of buried objects.

Generally, the methods fall into six categories:

- seismic (including reflection and refraction)
- electrical methods (including direct current resistivity and

electromagnetic techniques)

- magnetic
- gravity
- radiometric
- ground-penetrating radar

Many of these measurements can be made on the surface of the ground, by airborne methods, or in boreholes. By observing some characteristic of the measured signal, the geophysicist is able to estimate the size, shape, depth, and other characteris-

tics of the subsurface objects. Sophisticated computer algorithms are available that aid the geophysicist in making these interpretations. These usually require some degree of experience and expertise on the part of the geophysicist. Because of ambiguity in the interpretations, usually more than one geophysical method is applied at a site. The equipment used in making geophysical measurements varies but field-deployable units are available in all categories.

## SCOPE

Successful use of information from geophysical measurements for site characterization depends on the investigator's ability to understand and interpret data. Factors include:

- 1) the geologic and hydrogeologic characteristics of the contaminated site.
- 2) physical property differences related to natural geologic occurrences,

such as those at contacts between different kinds of rocks.

- 3) physical property changes produced by contaminants, such as changes in the electrical properties.
- 4) constraints that act within, and on, a system, e.g., the influence of large solution cavities on ground-water movement.
- 5) sources and characteristics of noise that can

obscure the signal and interfere with data interpretation.

The thoughtful use of geophysics in environmental science benefits the site manager in several ways. It provides a reliable 'baseline' characterization of a newly identified site. It helps decision makers to target future characterization and remediation efforts in a focused manner. It aids in

## SCOPE (Continued)

the ongoing monitoring of remediation efforts.

When a site manager first contacts a geophysicist, several questions will arise. Why suspect subsurface contamination? How deep is the buried object or plume? Is historical data available about the site? The Geophysics Advisor Expert System was developed to assist the non-geophysicist managers in evaluating what geophysical techniques may be useful for solving their site-specific problems. It is designed to assist their interactions with

the geophysicists. The geophysicist may also ask for a sample of soil or other material from the area of interest so that physical property variations can be evaluated. Once background work has been completed (searching for historical data, obtaining topographic maps and aerial photographic images, inspecting any other geophysical data that is available), the geophysicist will select the best experimental design to characterize problems at the site. In some cases, a preliminary site visit is made. On the basis of the

background information and the preliminary site visit, the best geophysical methods are chosen and work begins.

Geophysical measurements follow good experimental and sampling design strategies to ensure that the best technical accomplishment is achieved. Following the data gathering, the geophysicist uses computerized modeling algorithms to interpret the data that were generated at the site. Thoughtful data interpretation is fundamental to the success of any geophysical effort.

## ADVANTAGES AND LIMITATIONS

The use of geophysical measurements to determine the location and extent of subsurface contamination is an Agency-accepted method for site characterization. Geophysicists are highly trained and experienced scientists. As more geophysicists enter the environmental workplace, it is expected that the demand for, and the use of, this expertise will increase.

### Advantages

- Surface geophysical techniques provide a good non-intrusive method for characterization of subsurface features
- Better safety considerations due to the non-intrusive aspect
- Cost effective, some methods can be used to initially screen a large area.

### Limitations

- Results require interpretation and can be non-unique
- Some methods require highly trained personnel
- Direct confirmation of results still required

## REFERENCES

### Introductory:

Benson, R. C., R. A. Glaccum, and M. R. Noel, *Geophysical Techniques for Sensing Buried Waste and Waste Migration*, U.S. EPA Environmental Monitoring Systems Laboratory, Las Vegas, 1988.

Olhoeft, G., *Geophysics Advisor Expert System*, EPA Project Report EPA/600/4-89/023, June 1989.

### More Advanced:

Telford, W. M., L. P. Geldart, R. E. Sheriff, and D. A. Keys, *Applied Geophysics*, Cambridge University Press, 1976.

## FOR FURTHER INFORMATION

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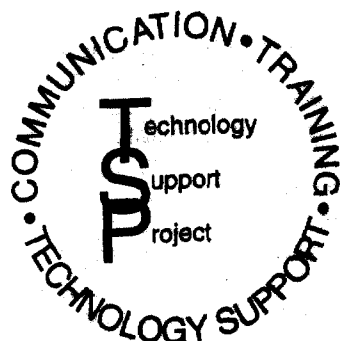
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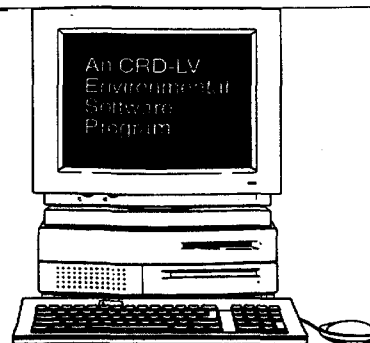
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## TECHNOLOGY SUPPORT

# ASSESS: A Quality Assessment Program



## INTRODUCTION

ASSESS is an interactive program designed to assist the user in statistically determining the quality of data from soil samples taken at a hazardous waste site. CRD-LV scientists have developed this public-domain, user-friendly Fortran program to assess precision and bias in the sampling of soils. The total error in a sampling regimen is the sum of measurement variability

and natural variability of the contamination. It is the field scientist's challenge to mitigate the measurement variability by careful sample-taking, thoughtful sampling design, and the use of recommended quality assessment samples. The greatest potential for error, both random and bias, is in the sampling step. Field conditions, tool contamination, operator differences, all

can affect variability and bias in a sample before it gets to the analytical step.

The value of ASSESS is its ability to detect and isolate error at critical steps in the sampling and measurement function. Installation is simple and is described in the User's Guide referenced at the end of this text.

## FEATURES

ASSESS plots graphics directly on the screen to give the user a quick look at data or results. All graphics can be formatted to give hard copy via pen plotters or other graphics printers.

ASSESS checks for missing data and for data input errors of sufficient magnitude to fall outside numeric parameters that have been previously set.

Reports and plots can be incorporated into WordPerfect.

## SCREENS AND MENUS

After an introduction screen, ASSESS presents screens and menus beginning with the Data Quality Objectives (DQO) Screen. The user inputs known information about the site and sampling method and desired confidence ranges.

Next, the user may choose the Sampling Considerations Screen. This screen allows entry of further specifics about the field sampling, such as, number of samples taken, number of batches analyzed, cost, and batch data.

The next screen is the Historical Assessment Screen that provides options for entry of historical data that

may be critical to the interpretation of this sampling.

A Quality Assessment Data Screen follows that allows the user to view and edit the quality assessment data that are called for in the parent document, *A Rationale for the Assessment of Errors in the Sampling of Soils*, referenced at the end of this fact sheet. These quality assessment samples are fundamental to the successful use of ASSESS. They include samples that will check for and evaluate error in every sampling step. At this point, it is possible to produce scatter plots to visually inspect the contribution to the total error that is made by any particular

quality assessment sample with the confidence in the error estimates being a function of the number of data.

The Transforms Screen follows and it gives the user a method for applying unary or binary operations to the entire data set. For example, the field scientist or data interpreter may wish to truncate the data, view the plot as a log or ln function, or perform a basic mathematical operation on all data.

The Results Screen displays variances for sample collection, batch dissimilarity, subsampling error, and handling differences. This screen also shows the total measurement

## SCREENS AND MENUS (Continued)

error. A report of the results and a list of historical information and the quality assessment data may be saved to a file or printed.

ASSESS is based on the use of field duplicates, splits, and performance evaluation samples that isolate and assess variability throughout the measurement process.

An option is provided for the use of duplicates and splits in the calculation of variability when inadequate types and numbers of performance evaluation samples exist.

## DATA FILES

ASSESS incorporates simple ASCII text files that can be created with any text editor. Two output files can be produced by ASSESS, one of

which can be read as a data file by ASSESS and the other, which is not ASSESS readable, gives a report-like document. A third type is

provided so that the user may edit an input file without entering all the data through ASSESS.

## STATUS

ASSESS is currently available in Version 1.0. This is a prototype environmental software package. Further development is planned and input from field scientists and EPA Regional personnel is

solicited so that the next version may be more tailored to user needs.

ASSESS is based on the EPA publication, *A Rationale for the Assessment of Errors*

*in the Sampling of Soils*, and it is strongly recommended that users familiarize themselves with the concepts in that document before trying to apply ASSESS.

## HARDWARE REQUIREMENTS

*Hardware requirements for using ASSESS are:*

- IBM PC (or compatible)
- 1.2 MB floppy disk drive 5 1/4" (or 3 1/2" DD or HD)
- Minimum graphics hardware is Hercules graphics card, monochrome display with graphics capabilities, CGA and EGA
- Minimum 512 K RAM
- Math coprocessor chip is recommended but not required

## REFERENCES

ASSESS User's Guide, U.S. EPA Report, EMSL-LV, in press.

van Ee, J. J., L. J. Blume, and T. H. Starks, *A Rationale for the Assessment of Errors in the Sampling of Soils*, EPA Report, EPA/600/4-90/013, May 1990.

## FOR FURTHER INFORMATION

*For copies of the ASSESS program, refer to NTIS Order Number PB93-505295, and contact:*

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National Technical Information Service  
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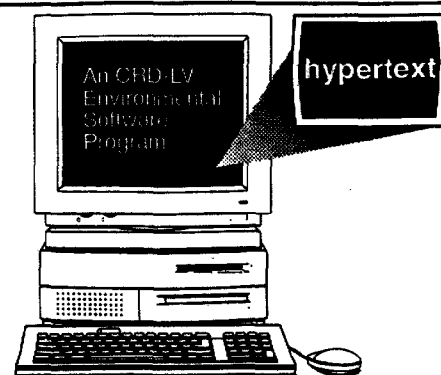
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## TECHNOLOGY SUPPORT

# Hypertext: A Showcase for Environmental Documents



## INTRODUCTION

The amount of "required reading" for those engaged in hazardous waste site remediation is overwhelming. Documents pile up - often leaving the scientist no option but to briefly review the abstract or the executive summary. Fortunately, there exists a computer software tool, hypertext, that allows for documentation on disk that can provide all readers/users with various layers of information. The tiered knowledge in hypertext makes it ideal for experts in the field of the publication who can scan through the general information and concentrate on a particular section. It is also suited to the novice in the document's area who can

access highlighted areas for in-depth definitions of unfamiliar terms, full-screen presentations of tables and figures, and references to ancillary works.

Hypertext is an easy-to-use, timesaving reading tool for the overburdened scientist. The ability to read an electronic book helps each reader optimize the information-time ratio.

Scientists at the CRD-LV have used hypertext on a frequently used document, "A Rationale for the Assessment of Errors in the Sampling of Soils" by J. Jeffrey van Ee, Louis J. Blume, and Thomas H. Starks. The

original hardcopy document is about 60 pages long, and contains 4 figures and 8 tables. The document also contains several formulas that may be unfamiliar to many users. The hypertext version fits on a floppy disk, keeps general information "hidden" unless it's requested by a novice user, and highlights frequently used tables for easy access.

Hypertext can be applied to any document that exists in digital form. The level of hypertext a document needs depends on the complexity and length of the original document and the anticipated expertise of the reading audience.

## THE RATIONALE DOCUMENT

The Rationale mentioned above addresses the complexity of the sampling and analysis of soils for inorganic contaminants from experimental design to the final evaluation of all generated data. Sources of error abound but they can be successfully mitigated by careful planning or isolated by intelligent error assessment. Error can be either biased or random. Biased error is indicative of a sys-

tematic problem that can exist in any sector of soils analysis, from sampling to data analysis. The first step in analysis of variability is to establish a plan that will identify errors, trace them to the step in which they occurred, and account for variabilities to allow direct corrective action to eliminate them.

Error assessment should be understood by the field

scientist and the analyst. To implement the ideas in the Rationale document and aid scientists in the estimation and evaluation of variability, the CRD-LV has developed a computer program called ASSESS. By applying statistical formulas to quality assurance data entered, ASSESS can trace errors to their sources and help scientists plan future studies that avoid the pitfalls of the past.

## HOW HYPERTEXT WORKS

Scientists at the CRD-LV took the disk containing the Rationale document and extracted sections such as the Table of Contents, tables, figures, and certain equations and formulas. These sec-

tions appear separately when selected in the new hypertext version. Then, throughout the document, certain words and phrases were highlighted so definitions can be accessed by a keystroke.

When a reader receives a hypertext document on disk, he or she can look at the Table of Contents and decide which sections to read. By selecting, for example, the section entitled "background",

## HOW HYPERTEXT WORKS (Continued)

the reader can be briefed on the scope of the document. A term within the Background section, e.g., "representative" may be highlighted. Readers

wishing the definition of "representative" as used in this document may get an immediate clarification. In traditional (linear) hardcopy

documents, a reader must either wait for the definition to be clarified in text or seek an external definition through outside reference materials.

## BRIDGE TO ASSESS

The Rationale document is the basis for an CRD-LV environmental software program called ASSESS. The philosophy and statistical background in the document is exercised practically with ASSESS, which is also available on disk. The hypertext version of the Rationale document prepares the reader to use ASSESS

and also serves as a physical link to the program. The last item on the Rationale document hypertext menu is "ASSESS". After becoming familiar with the concepts in the document, the user may select "ASSESS" to begin to use the software.

This hypertext linkage of two or more documents or

programs can simplify and clarify many software applications for novice users. By providing ASSESS users with the technical background in its development and Rationale document readers with a viable program, hypertext serves all levels of users in error-tracing in the complex application of soil sampling.

## ADVANTAGES AND LIMITATIONS

Increased availability of computer workstations and the development of user-friendly programs have made hypertext an almost unqualified bonus to busy readers/users. Hypertext is easily and effectively used for: acronyms and abbreviations, terms and phrases, tables and figures, graphics, formulas and references.

### Advantages

- Streamlined and non-interruptive
- Linkage to other hypertext documents
- Time-saving for expert; instructional for novice

### Limitations

- Availability of computer with appropriate hardware
- Some computer literacy required

## HARDWARE REQUIREMENTS

Hardware requirements for using this hypertext package are:

- IBM PC (or compatible)

- 1.2 MB floppy disk drive, 5 1/4" (or 3 1/2" DD or HD)
- Minimum graphics hardware card, monochrome display with graphics

capabilities, VGA and EGA

- Minimum 640 K RAM
- Math coprocessor chip is recommended but not required

## REFERENCES

*Text, ConText, and HyperText; Writing with and for the Computer*, E. Barrett, ed., The MIT Press, 1988.

van Ee, J. J., L. J. Blume, and T. H. Starks, A Rationale for the Assessment of Errors in the Sampling of Soils, EPA Report, EPA/600/4-90/013, May 1990.

## FOR FURTHER INFORMATION

For more details on Hypertext and the Rationale document, contact:

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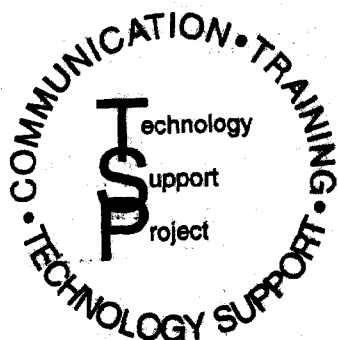
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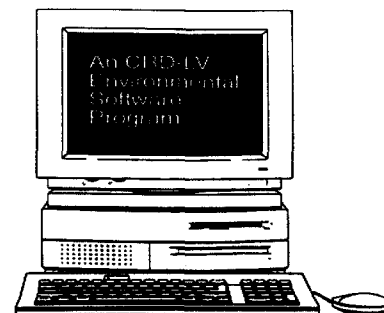
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TECHNOLOGY SUPPORT



# Scout: A Data Analysis Program



## INTRODUCTION

The complexities of correct data interpretation challenge environmental scientists everywhere. Environmental software packages have been developed to address the various needs of data analysts and decision makers. One frequent need is for the reliable determination of outliers in a data set. Scout is a program developed to identify multivariate or

univariate outliers, to test variables for lack of normality, to graph raw data and principal component scores, and to provide output of the results of principal component analysis. Scout provides interactive graphics in two and three dimensions. There are many advantages of a graphical display of data in a multidimensional format: it allows a quick visual

inspection of data, it accentuates obvious outliers, and it provides an easy means of comparing one data set with another. Scout has the flexibility to allow viewing and limited editing of a data set. Scout features on-line help, with a "built-in" users guide. Scout is a valuable addition to the library of environmental software packages available from the CRD-LV.

## FEATURES/ SPECIFICATIONS

Scout is a public domain, Turbo Pascal program that is user friendly and menu driven. Scout reads ASCII data files that are in Geo-EAS format. The first line of a Geo-EAS data file is a comment line, generally used to describe the origin of the data. The second line of the file must contain the number of variables - always a number greater than or equal

to 1 and less than or equal to 48. The next lines contain variable names in the first 10 columns and the associated values in the next 10 columns. Scout is compatible with most IBM personal computers that have an EGA, VGA, or Hercules graphics system. Scout will run with or without a math co-processor, but this feature is preferred for handling floating point

calculations. A fixed disk drive is strongly recommended because Scout performs many transfers between memory and disk during execution. On-line help is available throughout Scout and the user can access it by selecting the "System" option in the main menu and then selecting "Information".

## MENUS

There are five menus in Scout: file management, data management, outliers, principal components analysis, and graphics.

After the introduction screen, the user should choose the "File Management" option on the main menu. This option allows the user to load the Scout data file or read an ASCII data file and to access various subdirectories of data. Scout saves data files in two formats: binary and the Geo-EAS ASCII format. Scout has the ability to search for file names, includ-

ing wild cards. The current search string is printed at the top of the window. Other options in this area include "Write ASCII Data File" for saving the Scout file and "Merge Two Data Files" for combining two files into one.

The second menu is "Data Management" which includes options for editing data, variables, and observations. This menu also displays summary statistics, such as mean, standard deviation, and variance. Additionally, there is a "Transform" option which allows the user to test

each variable for lack of normality, based on the Kolmogorov-Smirnov test at the five percent significance level. The critical value, test statistic, and apparent conclusion are displayed. The Anderson-Darling test is also performed and a horizontal histogram is displayed at the bottom of the screen.

Menu three is "Outliers", which applies two powerful tests for discordancy to the data: the (Mahalanobis) generalized distance, and the

(Continued)

## MENUS (Cont.)

Mardia's multivariate kurtosis test. After selecting "Outliers", the user can tell Scout which variables to test, or use the default wherein Scout tests all variables. The user must then decide to use the generalized distance test or Mardia's kurtosis. If a large proportion of the data is identified as discordant, the user should be cautious that the problem may be due to lack of multinormality. The outlier report may be displayed, sent to a file, or printed. By selecting "Causal Variables" the user can test each variable for its contribution to the discordant nature of the outlier. This option can trace some independent errors, such as typographical or transcription errors.

The fourth menu is "Principal Component Analysis" which

allows the user to select the variables to be used and to display covariance or correlation. By choosing the "View Components" option, the user can view the eigenvectors and eigenvalues of the PCA. Scout will prompt the user to specify whether or not to include previously determined outliers. The user can graph the component scores, which are products of the eigenvectors and the standardized observation vectors. A "Transform Data" option is available to change the data in memory from observations to component scores.

The fifth, and final, menu is "Graphics" which features two graphics systems: two-dimensional and three-dimensional. The two-dimensional system is used to display scatter plots and

x-y plots. The three-dimensional system is used to display three variable plots, which can be rotated to illustrate the added dimension. The user can modify graph colors and shapes. Graphics screens may be saved by writing to a file on disk. The user can change the size of the graph by zooming in or out using the "+" or "-" keys. The four arrow keys are used to rotate the graph. The left and right arrows rotate the graph around the Z axis. The up and down arrows rotate the graph around an imaginary horizontal axis that passes through the origin. Another feature, "Search Observation Mode", is available and allows users to identify the individual observations shown on the graph.

## REFERENCES

Chemometrics: A Textbook, Massart, D. L., B. G. M. Vandeginste, S. N. Deming, Y. Michotte, and L. Kaufman, Volume 2 in the Series "Data Handling in Science and Technology", B. G. M. Vandeginste and L. Kaufman, eds., Elsevier, Amsterdam, the Netherlands, 1988.

Garner, F. C., M. A. Stapanian, and K. E. Fitzgerald, Finding Causes of Outliers in Multivariate Data, J. Chemometrics, in press.

## FOR FURTHER INFORMATION

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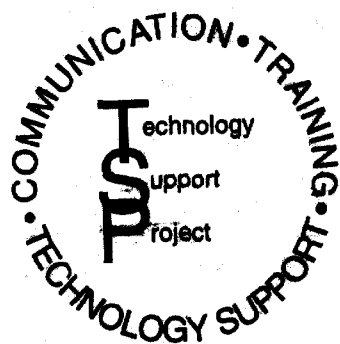
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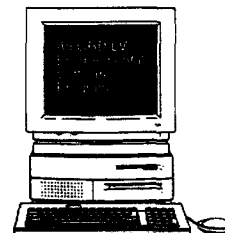






## TECHNOLOGY SUPPORT

# Geo-EAS: Software for Geostatistics



## INTRODUCTION

The Characterization Research Division in Las Vegas (CRD-LV) can meet the needs of scientists who work with spatially distributed data. The complexity of contaminant distribution and migration at hazardous waste sites requires a mathematical method that is capable of interpreting raw data and converting them to useful

information. Geostatistics began in the mining industry and has grown to include applications ranging from microbiology to air monitoring.

Though the application of geostatistics is crucial to the delineation of buried contaminants, not every field scientist can be expected to develop customized geostatistical

algorithms for individual sites. Geostatisticians at the CRD-LV developed a software package, Geo-EAS in 1988. The current version, Geo-EAS 1.2.1, was released in 1990. This program offers the environmental scientist an interactive tool for performing two-dimensional geostatistical analyses of spatially distributed data.

## THE METHODOLOGY

Geostatistical methods are useful for site assessment and monitoring where data are collected on a spatial network of sampling locations. Examples of environmental applications include lead and cadmium concentrations in soils surrounding smelters, and sulfate deposition in rainfall. Kriging is a weighted moving average method used to interpolate values from a data set onto a contouring grid. The kriging weights are computed from a variogram, which measures the correlation among sample values as a function of the distance and direction between samples.

Kriging has a number of

advantages over other interpolation methods:

### Smoothing

Kriging regresses estimates based on the proportion of total sample variance accounted for by random noise. The noisier the data set, the less representative the samples and the more they are smoothed.

### Declustering

The kriging weight assigned to a sample is lowered to the degree that its information is duplicated by highly correlated samples. This helps mitigate the impact of oversampling hot spots.

### Anisotropy

When samples are highly

correlated in one direction, kriging weights will be greater for samples in that direction.

### Precision

Given a variogram representative of the area to be estimated, kriging will compute the most precise estimates from the data.

Estimation of the variogram from sample data is a critical part of a geostatistical study. Geo-EAS is designed to make it easy for the novice to use geostatistical methods and to learn by doing. It also provides sufficient power and flexibility for the experienced user to solve practical problems.

## EQUIPMENT REQUIREMENTS

Geo-EAS was designed to run under DOS on an IBM, PC, XT, AT, PS2, or compatible computer. Graphics support is provided for Hercules, CGA, and EGA. At least 512 Kb of RAM is required, but 640 Kb is recommended. An arithmetic co-processor chip is strongly recommended due to the computationally intensive nature of the programs, but is not required. Programs

may be run from floppy disk but a fixed disk is required to use the programs from the system menu. The system storage requirement is approximately three megabytes. For hardcopy, a graphic printer is required. Support is provided for most plotters. Design features such as simple ASCII file formats and standardized menu screens, give Geo-EAS flexibility for

future expansion. It is anticipated that Geo-EAS will become a significant technology transfer mechanism for more advanced methods resulting from the CRD-LV research and development programs.

Geo-EAS software and documentation are public domain, and may be copied and distributed freely.

## MAPS AND MENUS

The Geo-EAS programs use an ASCII file structure for input. The files contain a header record, the number of variables, a list of variable names and units, and a numeric data table.

All Geo-EAS programs are controlled interactively through menu screens which permit the user to select options and enter control parameters. The programs are structured to avoid a "black box" approach to data analysis. Several of the more complex programs permit the user to save and read parameter files, making it easy to rerun a program.

The programs DATAPREP and TRANS provide capability for manipulating Geo-EAS files. Files can be appended or merged, and variables can be created, transformed, or deleted. Transformation operations include natural log, square root, rank order, indicator, and arithmetic operations.

POSTPLOT creates a map of a data variable in a Geo-EAS data file. Symbols representing the quartiles of the data values or the values themselves are plotted at the sample locations.

STAT1 computes univariate statistics, such as mean and standard deviation, for variables in a Geo-EAS data file, and creates histograms and probability plots.

SCATTER and XYGRAPH both create x-y plots with optional linear regression for any two variables in a Geo-EAS file. SCATTER is useful for quick exploratory data analysis, while XYGRAPH provides additional capabilities such as multiple "y" variables, and scaling options.

PREVAR creates an intermediate binary file of data pairs for use in VARIO, which computes and displays plots of variograms for specified distance and directional limits.

Variogram models can be interactively fitted to the experimental points. The fitted model may be the sum of up to five independent components, which can be any combination of nugget, linear, spherical, exponential, or Gaussian models. XVALID is a cross-validation program which can test a variogram model by estimating values at sampled locations from surrounding data and comparing the estimates with known values.

KRIGE provides kriged estimates for a two-dimensional grid of points. A shaded map of estimated values is displayed and a Geo-EAS file of kriged grid results is generated.

CONREC generates contour maps from a gridded Geo-EAS data file, usually the output from KRIGE. Options are provided for contour intervals and labels and degree of contour line smoothing.

## REFERENCE:

Isaaks, E. H. and R. M. Srivastava, *An Introduction to Applied Geostatistics*, Oxford University Press, New York, 1989.

## AVAILABILITY:

For copies of Geo-EAS, refer to NTIS Order Number PB93-504967, and contact:

United States Department of Commerce  
Technology Administration  
National Technical Information Service  
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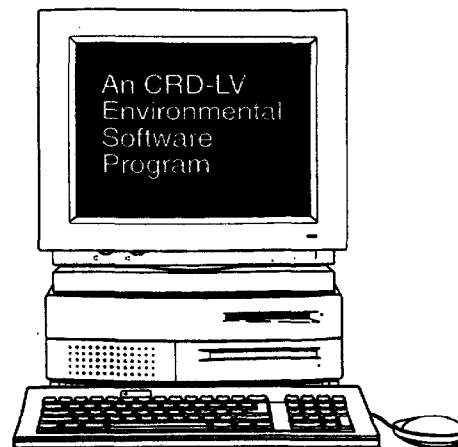


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TECHNOLOGY SUPPORT



# Geophysics Advisor Expert System



## INTRODUCTION

The Characterization Research Division in Las Vegas (CRD-LV) is concerned with the selection of correct monitoring methods. Sometimes the best technique is not easily discernible. This is particularly a problem in sampling and monitoring complex matrices, like soil and sediment, and when buried structures and plumes are hidden from sight. The characterization and remediation of a hazardous waste site involves several disciplines, from experimental design to analytical protocol.

Individuals who decide upon methods and who are responsible for approving contractor suggestions need an easy-to-use text or computer program that will guide them in expensive and decisive actions.

The decision to use geophysical methods and which geophysical method to use is a challenge to site managers. The CRD-LV, in cooperation with the U.S. Geological Survey, has developed an expert system, Geophysics Advisor, to aid these person-

nel in critical decisions about geophysical methods that may impact the quality and reliability of their data. This program is built on a foundation of expertise in applying geophysical methods to complex hazardous waste sites. The current version, Geophysics Advisor 1.0, is designed to meet the needs of non-geophysicists to assist and educate them in their interaction with geophysicists. It is not intended to replace the expert advice of competent geophysicists.

## THE PROGRAM

Geophysics Advisor 1.0 asks questions about the site, cultural noise, and the contamination problem. The program builds upon the user's answers to early questions and poses subsequent questions on this basis. At the end of the run, the program will indicate any inconsistencies in the user's responses. The user may then return to specific questions and consider changing the answer.

The program considers several geophysical methods:

- electromagnetic induction
- resistivity

- ground-penetrating radar
- magnetic
- seismic
- soil gas
- gravity
- radiometric

Geophysics Advisor recommends the type or types of geophysics that will most likely fit the site requirements for determining the location of contamination and providing site characterization.

The program will also tell the user if the use of geophysics is not suitable for the site. A

relative numerical ranking of the various methods is shown on screen, indicating the degree of superiority of one method over another. Methods are also categorized as "recommended," "not recommended," or "uncertain of effectiveness."

Additionally, Geophysics Advisor tells the user why the various methods will or will not work at the site.

Geophysics Advisor allows the user to make soft responses such as "maybe" and "don't know" so novice

(Continued)

## THE PROGRAM (Continued)

users or those lacking specific knowledge about the site can access some of the power of the program. The user will be asked about soil type, cultural noise, contami-

nant identity and level, the presence of underground tanks or drums, and the distance between various buried items.

If a site is extremely complex, it is recommended that the user divide the site into several subsite problems. The program can be run for each subsite.

## AVAILABILITY

Geophysics Advisor is a public domain program written to run on any IBM-PC-DOS compatible computer. It is written in True Basic and requires 512 K memory when the operating system is included.

Geophysics Advisor is available to all Agency users, free of charge, upon receipt of a pre-formatted 3 1/2" or 5 1/4" floppy disk. For copies of Geophysics Advisor, or for consultation with an CRD-LV geophysicist, contact:

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Las Vegas, NV 89193-3478

(702) 798-2254

## REFERENCES

### Introductory:

Benson, R. C., R. A. Glaccum, and M. R. Noel, Environmental Monitoring Systems Laboratory, Las Vegas. Geophysical Techniques for Sensing Buried Wastes and Waste Migration, U.S. EPA. 1982.

### More Advanced:

Telford, W. M., L. P. Geldart, R. E. Sheriff, and D. A. Keys, Applied Geophysics, Cambridge University Press, 1976.

### User's Guide:

Olhoeft, G., Geophysics Advisor Expert System, EPA Project Report EPA/600/4-89/023, 1989

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*For copies of Geophysics Advisor Expert System, refer to NTIS Order Number PB93-505162 and contact:*

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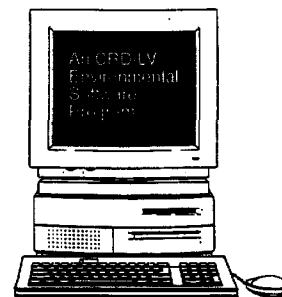


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TECHNOLOGY SUPPORT



# CADRE: A Data Validation Program



## INTRODUCTION

The Characterization Research Division in Las Vegas (CRD-LV) has developed a computer software system to aid environmental scientists and data analysts in the evaluation of data generated by the Contract Laboratory Program (CLP). This system, CADRE (Computer-Aided Data Review and Evaluation) assists in the validation of results from various CLP methods.

CADRE provides data analysts with a quick and reliable method for examining data that will be used for decision making at hazardous waste sites. The program automates the phases of data validation that involve electronic-format data. The data validation process involves comparison of quality control (QC) indicators used in the analysis with pre-established data quality

criteria. Non-compliant data are qualified with appropriate codes to indicate the severity of the defect. The final assessment of the data is made by the data reviewer, using the information provided by CADRE.

Examples of QC parameters that are checked by CADRE are: holding time, blanks, calibration, and precision.

## FEATURES

CADRE can read data in several CLP electronic formats. It checks for data completeness, and allow the user to edit data. After the validation is complete, CADRE reports the results.

CADRE can be customized by the user to validate data collected using several methods in the CLP. Users can configure CADRE to examine different compounds, alternate quantitation limits, or varying QC parameters.

Another customization of CADRE involves changing data validation criteria to meet the needs of a modified method. The user can choose, for example, to allow a longer holding time if the compound of interest is unlikely to volatilize or degrade. The ability to modify CADRE's specific data quality codes provides the user with greater flexibility and responsibility.

To protect the data from tampering and from human

error, a layered security system allows each user access to the program features he or she needs.

The program blends ease of use with a sophisticated screen system. Knowledge of data validation rationale and microcomputer operation are recommended for the effective use of CADRE. A user's guide, training courses, and technical user support are available from the CRD-LV.

## CLP ORGANIC VERSION

The CLP ORGANIC version of CADRE evaluates data from CLP analysis of volatile, semivolatile, and pesticide compounds. Volatile and semivolatile organic compounds are analyzed by gas chromatography/ mass spectrometry (GC/MS). Pesticide analysis is a GC method.

CLP ORGANIC CADRE can be customized to evaluate modified versions of these routine analyses. It can use alternate data validation criteria selected by the user.

Data can be read by CLP ORGANIC CADRE from the CLP Analytical Results Database (CARD) or from Agency standard format files.

Checks performed by CADRE include:

- quantitation limits
- holding time
- GC/MS tuning
- calibration
- internal standards
- system performance
- surrogate recovery
- matrix spike recovery
- precision of duplicates
- contamination of blanks

## QUICK TURNAROUND METHOD VERSION

The Quick Turnaround Method (QTM) version of CADRE reviews data obtained by the QTM methods. There are QTM methods available for VOC, PAH, phenols, pesticides, and PCB. These methods are based on the need for fast

extraction and chromatographic analysis within 2 days. For speed and simplicity, QTM CADRE works in conjunction with other software for electronic data transmission from the laboratory to the user through

the Agency communications network.

QTM CADRE is completely automated. The data reviewer needs only to set up the system and interpret the reports.

## ADVANTAGES AND LIMITATIONS

The use of computerized data evaluation is changing the workplace for many data reviewers. The automation of routine checks will give the individual more time to thoughtfully interpret the results.

It is anticipated that increased accessibility of computer hardware to personnel will lead to greater demand for programs like CADRE that will streamline routine work. Currently, CADRE is being developed for inorganic methods.

### Advantages

- Fast, complete, and consistent data validation
- Easy customization for modified methods
- Reduction of human error
- Automated report generation

### Limitations

- Requires availability of powerful computer for efficient use
- Reviewer judgement needed for some decisions
- Available for CLP organic and QTM methods only
- Needs complete data set in electronic format

## HARDWARE REQUIREMENTS

Hardware requirements for using CADRE are:

- IBM PC (or compatible)
- MS-DOS (or equivalent)

- Hard disk drive
- 640 K RAM

A math coprocessor chip is recommended but not

required. For easy use, a mouse pointer is recommended.

## REFERENCE

Simon, A. W., J. A. Borsack, S. A. Paulson, B. A. Deason, and R. A. Olivero, Computer-Aided Data Review and Evaluation: CADRE CLP Organic User's Guide, U.S. EPA, June 1991.

## FOR FURTHER INFORMATION

For further information on CADRE, contact:

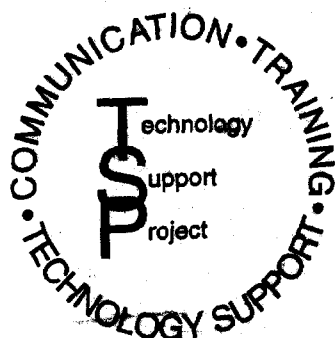
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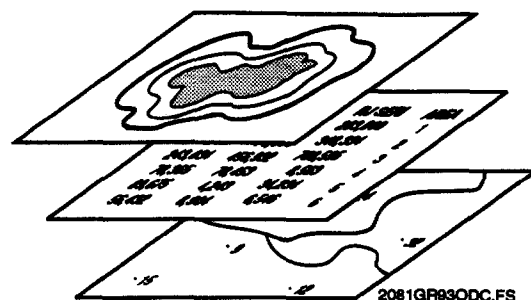


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TECHNOLOGY SUPPORT



# ARC/INFO Concepts and Terminology



## Introduction

The U.S. EPA uses geographic information systems (GIS) technology to obtain reliable spatial information from layers of descriptive data. GIS provides methods for the management, display, manipulation, and analysis of geographic data, such as topological information, transportation routes, geopolitical boundaries, and waterways.

The Characterization Research Division in Las Vegas (CRD-LV) is the EPA's center for research and development for GIS technology. As such, it demonstrates the applicability of GIS to various environmental scenarios, including Superfund and RCRA site characterization and the Environmental Monitoring and Assessment Program (EMAP).

Currently, the EPA uses ARC/INFO, a full-featured GIS software that follows a geographic toolbox approach. There are distinct tools for modeling and feature manipulation for each type of geo-dataset. Some tools operate on entire databases, others on entire geo-datasets, and others on individual features (1).

## The Architecture

Map library tools define and manage entire GIS databases centrally. These tools control the access, modification, and update of each theme within a map library. Geo-dataset tools operate on entire datasets and can be categorized as translation, edit, analysis, and query/display tools.

Digital dataset conversion into an ARC/INFO geo-dataset is handled by a large set of translation tools. Digitize/edit tools support creation of new geo-datasets including topology, locational data, attribute entry, and data verification. Analysis tools perform spatial analysis functions on one or more datasets. Examples of these analysis tools are:

- Coverage overlay
- Thiessen polygon generation
- Surface and contour generation
- Buffer zone generation
- Network allocation
- Map projection and coordinate transformation
- Rubber sheeting
- Feature generalization
- Feature selection and aggregation
- Arithmetic and logical attribute combination
- Proximity and dispersion analysis

The query/display tools scale and position map data,

associate cartographic symbols to map features, and display, identify, and control map features based on their attributes. Feature-level tools operate on individual features within a coverage.

ARC/INFO is structured so that similar types of tools are organized within software modules that perform similar sets of functions. Table 1 lists the main functions of each subsystem of ARC/INFO.

ARC/INFO has an embedded language processor that is machine independent, providing a consistent way to control the user environment, command processing, and application development.



Table 1. ARC/INFO Subsystems

Module Name	Main Function
Arc	Start other modules, data conversion, analysis and manipulation, coordinate transformation, topology generation, attribute <i>automation</i> , database construction, plotting, coverage and workspace management
Arcplot	Vector and raster data display and query. Spatial analysis
Arcedit	Vector data editing and manipulation
COGO	Coordinate geometry
TIN	Surface generation
Grid	Raster processing and modeling
Librarian	Centralized spatial database management
Network	Linear modeling and distribution analysis

## Geographic Concepts in GIS

There are six for concepts that are pertinent to the application of GIS technology to environmental studies:

- Geographic data representation
- Topology
- Maps as the basis for GIS data input and output
- Data resolution
- User interface
- Relational database management systems

The basic unit of data management in ARC/INFO is the geo-dataset, which includes the coverage, grid, and triangulated integrated network (TIN). Each geo-dataset uses an associated data model to define locational and thematic attributes for map features. The data model (vector or raster based) has its own set of geo-processing and modeling tools.

Polygons, lines, points, nodes, and annotations are

features which, when associated with thematic and locational attributes, can be used to represent many types of mapped information.

The integration of various data types is the strength of GIS technology. Using layers of data, researchers are able to generate information that realistically defines conditions at a site. This information is a key to correct decision making at Superfund and RCRA sites.

## REFERENCES

- (1) Morehouse, S. The Architecture of ARC/INFO, ARC News, 12 (2). 1990

## FOR FURTHER INFORMATION

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TECHNOLOGY SUPPORT

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# Accessing Geographic Information Systems Technology



## Introduction

Geographic Information Systems (GIS) technology has been used by the U.S. Geological Survey and by state and municipal governments for years. Recently, its application to environmental studies has become apparent and growing numbers of environmental scientists are able to access the power of GIS.

The user is able to analyze data, query the system for more information, and obtain detailed databases upon which accurate site assessments can be made. Questions about the destination of effluents, the location of population groups, and other environmental impact determinations can be made.

Its power is in its ability to relate attribute data to cartographic features. This allows data analysis that can be used by decision-makers to guide the course of an investigation. This strength makes it particularly applicable to environmental investigations, where decisions must be based on

complexities of source, extent, and matrix.

GIS can incorporate databases from the U.S. Geological Survey, aerial photographic information, measurement results, and data from municipalities and utilities. Further, it can incorporate historical databases for comparisons. By overlaying the digitized information, GIS scientists can produce accurate and informative maps of a location. GIS represents data as points, lines, or polygons. Types of data input include transportation features, geopolitical boundaries, streams, and topography. This integrated approach is particularly pertinent to the characterization of hazardous waste sites. Man-made structures can be superimposed upon natural features to provide the investigator with a complete picture of an area of environmental interest. By using GIS, scientists can identify areas that require closer screening for hazardous components.

The Characterization Research Division in Las Vegas (CRD-LV) was the first EPA laboratory to use GIS technology in environmental applications. Now, CRD-LV is a center for GIS research and development and customizes GIS use to the needs of the EPA Regions and Program Offices. There is a GIS applications center in each Region with in-house experts to help Remedial Project Managers, Site Assessment Managers, and On-Scene Coordinators.

The power of GIS technology enhances the ability of environmental decision-makers to assess the extent of contamination. GIS uses an increasing amount of information that is pertinent to the characterization and remediation of hazardous waste sites.

The reverse side of this Technology Support Center Fact Sheet gives GIS contacts at the CRD-LV and at each of the Regions.

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## REFERENCE

### FOR FURTHER INFORMATION

A summary of GIS Support to Superfund, a U.S. EPA, EMSL-LV report, EPA/600/X-93/062, 1993.

EMSL-LV publications Tech Memos 1-5

*For information about the CRD-LV GIS Center for Research and Development and for copies of the documents listed above: write to:*

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Region 4	James Bricker	404-347-3402
Region 5	Noel Kohl	312-886-6224
Region 6	David Parrish	214-655-8352
Region 7	R. Lynn Kring	913-551-7456
Region 8	Bill Murray	303-294-1994
Region 9	Mark Henry	415-744-1803
Region 10	Ray Peterson	206-553-1682



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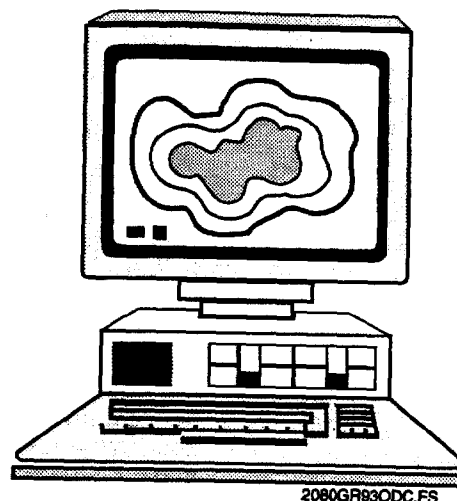
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TECHNOLOGY SUPPORT



# Geographic Information Systems: An Overview



## Introduction

The U.S. EPA is interested in the development and utilization of sophisticated tools for the measurement and analysis of contamination at Superfund and RCRA sites. Geographic Information Systems (GIS) are systems where geographic data describing the earth's surface are managed, displayed, manipulated, and analyzed (1). GIS is able to analyze spatial data, making it a powerful tool for the analysis of the source, extent, and transport of various types of contamination.

The Characterization Research Division in Las Vegas (CRD-LV) is the Agency's

Center for Research and Development in GIS technology. Work is underway on the application of GIS to site characterization at various Superfund and RCRA sites.

The ability to analyze complex, spatial data makes GIS technology interesting to a growing user community within environmental science. Applications include environmental monitoring, modeling non-point runoff, and landscape ecology. The EPA's Environmental Monitoring and Assessment Program (EMAP) is tapping into the many capabilities of GIS technology as it begins its

long-term evaluation of ecological trends.

The heavy emphasis on analytical manipulation of spatial data is the main characteristic that distinguishes GIS from other technologies like computer-aided design and electronic mapping systems. Using GIS, an analyst is able to present a complete picture of a site location, tiering maps of streams, geo-political boundaries, transportation routes, and topographic information.

## Data Analysis

The power of GIS to generate highly specialized informational maps makes it an effective method for presenting information to decision makers and to the public. GIS is capable of much more than generating maps and presenting data.

Environmental studies produce complex data that are difficult to represent verbally or visually. Using GIS, environmental scientists are able to interpret spatial data, manage complex databases, and use layers of information from various

sources. Based on GIS, analysts can produce a realistic and understandable visual analysis of a hazardous waste site.

## Hardware, Software, and People

GIS systems rely on a relational database management system to provide the ability to query, manipulate, and extract geographic reference and attribute data. This approach permits standard statistical manipulations of attribute data, as well as logical and boolean queries based on GIS feature characteristics (2). Some common analysis capabilities include measurements, attribute reclassification, topological overlay, connectivity operations, coordinate transformations, and surface analysis.

GIS hardware includes the computer platform and peripherals. Components

include a terminal to display graphics, a central processing unit, a digitizer to manually trace data from maps, a plotter to write cartographic output, and a tape drive to save and export information. Other GIS peripherals include scanners, optical drives, and image recorders. The trend is toward workstations and personal computers that provide the power and performance required by GIS.

User interface functions such as menus, scrolling lists, and other graphic user interface (GUI) building tools may be supported by the language processor.

Applications can be built to simplify complex tasks, providing decision support tools to novice users. Some GIS language processors have the ability to access other programs written in higher language systems such as Fortran and C, using embedded routines to access common blocks of computer memory.

There is a growing need for spatial analysis to be an integral part of routine data analysis and decision-making. To meet this need, GIS technology is migrating to the desktops of applied technologists in fields like biology, economics, and environmental science.

## Reliability

Digitized data and the informational maps that result from GIS applications are only as reliable as the quality of the data that is input.

Whenever GIS is used for decision-making, it is important to state the confidence levels of the information. Some research effort is

underway to represent the reliability of the data by subtle differences in the display characteristics.

## REFERENCE

1. Understanding GIS: The Arc/Info Method. Environmental Systems Research Institute, Inc., Redlands, CA. 1990.
2. Geographic Information Systems (GIS) Guidelines Document. Office of Information Resources Management. U.S. EPA. 1988.

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## TECHNOLOGY SUPPORT

# The GIS Planning Process



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## Introduction

Planning is an important step in the characterization of contamination at hazardous waste sites. Thoughtful planning early in the process can save time and money as the characterization progresses. The use of geographic information systems (GIS) technology can provide the analyst with valuable information about a site. Because so much information is available, it is important that the analyst ask the right questions and access pertinent databases.

GIS is a complex tool that requires planning in many areas to avoid problems that can affect the project's outcome. Scientists at The Characterization Research Division in Las Vegas (CRD-LV) have isolated six areas essential to the GIS project planning life cycle.

They are:

- Define project objectives
- Identify analytical requirements

- Define data and hardware requirements
- Determine data availability
- Resolve data development issues
- Implement project plan

As with any analytical process, the quality of the result is dependent upon the recognition of the exact problem and the implementation of the correct steps in addressing it. The GIS software used by the U.S. EPA is ARC/INFO.

## Project Objectives

Defining specific project objectives reduces wasted time and effort in the project planning lifecycle. Project objectives should encompass every aspect of the project, from data collection and manipulation to data display

and archival. Not all aspects of a project are known in their entirety at the onset of a project, of course, so project objectives should be flexible enough to be customized as more knowledge of the study becomes available.

Sometimes very little is known about the project at the beginning of the study and a preplanning data gathering effort is necessary to establish the facts.

## Analytical Requirements

The next step in planning is the identification of analytical requirements. The defined analytical requirement will be used to specify more exact standards for database data quality, resolution, and scale.

This stage of the GIS planning process requires the

input of project staff and GIS specialists. It is important that the project staff communicate their exact needs to the GIS experts. After the requirements are established, program management staff should prioritize the needs and establish measur-

able data quality objectives to meet them.

GIS systems are used to organize field data in a spatial context that allows decision makers to make informed choices as the study progresses.

## Data and Hardware Requirements

After the analytical requirements are established, it is possible to compile a detailed list of data and hardware needs. A data matrix of needs and sources is helpful in this planning step. At this stage it is useful to consider the attribute information

required for analysis, minimum data resolution and scale, data input and output formats.

Hardware requirements should be specified at this point. Some key considerations are the integration of data from other sources,

data display needs, and the types and functions of the user interface. ARC/INFO supports many different types of graphic terminals and their plotters. Data visualization is affected by the sensitivity and resolution of graphics terminals and printers.

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**Data Availability**

The project's analysis objectives can only be met if the data is available. The degree to which GIS data are available is related to the resolution, scale, and compi-

lation date required by the study. Another availability factor is cost. Data may be available in the sense of existing but may be beyond the cost restrictions of the

particular project. The data needed for a project will fall into one of three categories: data you have, data someone else has, and data no one has.

**Data Development Issues**

Data development may be required to address the data quality objectives of the project. At this point, data must be assessed to ascertain their adequacy. Project deadlines and data quality objectives (DQOs) should be reviewed at this time. The personnel responsible for

critical decisions should be involved in this adequacy review. Key questions should be asked. Are the data adequate to meet the DQOs of the project? Can defensible decisions be made based on the data at hand? Is the data quality sufficient? Is there enough time to

gather additional data if necessary?

All aspects of the information should be evaluated for cost impact. Cost considerations may include the acquisition of data, travel costs, quality assurance, contractor fees, and all project management costs.

**Implementation**

The GIS project implementation phase carries out the database development and analysis objectives. The database design defines the database structure, its characteristics, coverage attribute coding scheme, data models, and automation methods. The resulting design document should

determine if the GIS database meets the project's analytical objectives. The data capture and automation phase carries out the database design through data acquisition and integration of data into the GIS system. The database design includes digitizing analog maps, converting digital data

into GIS format, and correcting and coding data.

Once the database is complete, a test of the GIS analysis functions is performed. When the staff are satisfied with the system's ability to meet the analytical requirements of the project, database production can begin.

---

**REFERENCE**

GIS Technical Memorandum 1; GIS Planning and Data Set Selection, U.S. EPA, EMSL-LV.

**FOR FURTHER INFORMATION**

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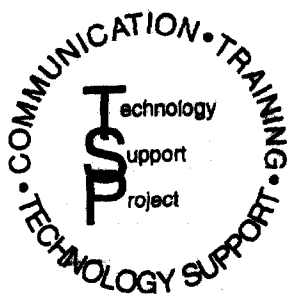
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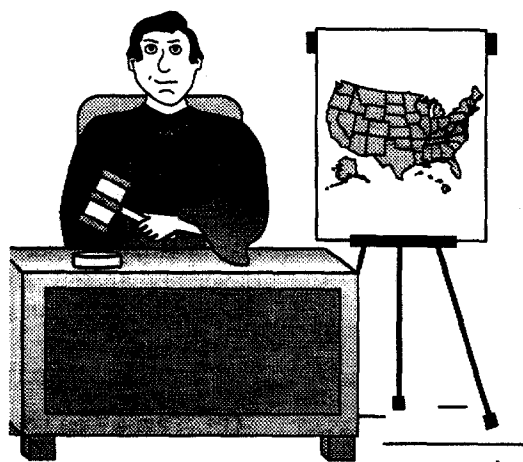
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TECHNOLOGY SUPPORT



# Remote Sensing in Environmental Enforcement Actions



## CAPABILITIES

The Characterization Research Division in Las Vegas (CRD-LV) and its Environmental Photographic Interpretation Center (EPIC) support EPA litigation actions through remote sensing technology. In the course of conducting environmental analyses EPIC has acquired:

**1) a large library of remote sensing and resource documentation derived from archival sources nationwide.** The library collection includes more than 150,000 frames of imagery dating from the late 1930s to the present, covering areas

throughout the United States. In addition to the imagery, completed remote sensing reports and other resource data such as maps, soil surveys and cartographic data are available for documentation in legal proceedings.

**2) a technical staff experienced in the analysis of imagery in a number of discipline areas: wetlands, geology, environmental site analysis, as well as photogrammetry.** Over the years the technical staff has gained substantial experience in the analysis of imagery and its

interpretation using modern computer technology.

**3) a modern integrated system of imagery collection and analysis equipment.** EPIC has a computer driven analytical stereo plotter and a digital video plotter, both of which enhance accurate photogrammetric measurements of environmentally significant features. Additionally, geographic information systems (GIS) capabilities permit highly accurate integration of both spatial and positional data that can bear legal scrutiny.

## APPLICATIONS TO EPA ENFORCEMENT ACTIONS

CRD-LV has provided vital technical support to a variety of EPA mandated cases. They include civil and criminal actions brought by EPA Regional offices, the National Enforcement Investigations Center (NEIC), and the Offices of Inspectors General.

EPIC has supported general counsels of various EPA Regions, U.S. Department of Justice attorneys, and state attorney generals offices. Specific cases have involved prosecutions brought under CERCLA, RCRA, Clean Water Act, and National

Environmental Policy Act. In almost all instances, the actions culminated in outcomes favorable to EPA interests. The penalties have included cost recoveries in civil proceedings, corporate fines, and fines and prison sentences to individuals in criminal proceedings.

## SERVICES

EPA/CRD-LV facilities - EPIC East and West — operate under conditions of continuous security. Both facilities are vaulted, and 24-hour round-the-clock protection is maintained at each location. The following are some of the services provided and procedures observed in supporting environmental enforcement actions.

- Acquisition, indexing and archiving of imagery, topographic maps and all photo-derived documents.
- Chain-of-custody documentation of imagery, which records the handling of the imagery from supplier, through shipper and in-house handling, to customer receipt.
- Certified authenticity of imagery and product documents used in courtroom testimony.
- Depositions or affidavits by expert witnesses, trained and experienced in environmental disciplines.

## PRODUCTS

The products provided in supporting environmental enforcement actions include: historical and current imagery, enlarged photographs, digital and analog remote sensing products, environ-

mental reports, and mounted graphical exhibits for courtroom display. The preparation of photographic and graphic courtroom exhibits is under controlled laboratory conditions and careful

supervision. All graphical displays can be easily annotated for full visual effect in the various litigation or testimonial forums.

## REFERENCES

Remote Sensing in Hazardous Waste Site Investigations and Litigation TS-AMD-86724; December 1988 (Revised).

## FOR FURTHER INFORMATION

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TECHNOLOGY SUPPORT



# Topographic Mapping for Environmental Assessment



## INTRODUCTION

The location, extent, and historical change in the nature of hazardous waste sites is of great importance to the Environmental Protection Agency, and can be documented through the creation of topographic maps. The Characterization Research

Division in Las Vegas (CRD-LV) is the Agency's center for mapping and related remote sensing technologies. Topographic (elevation) maps are simple, effective, and graphic tools for recording the quantitative and qualitative characteristics of

hazardous waste sites. These maps are most often created from aerial photographs and, since national archives of coverage date back more than fifty years, maps can be created that reflect historical site conditions.

## TECHNIQUE

A typical topographic mapping project begins with a request from an RPM to the CRD-LV Technology Support Center. The CRD-LV provides a cost estimate and arranges for all necessary geodetic surveys, aerial photographic overflights, and map production. No permission is needed for a flyover,

so aerial photography is of particular value in situations where uncooperative owners deny intrusive sampling. A specially calibrated aerial camera is used to insure accurate photography for later use in the map production process. Once the film is developed, it is placed in a special instrument

(stereoplotter) which creates a model of the terrain to produce a contour map. The map may be generated as hardcopy, or in digital form for later use with Geographic Information Systems (GIS). The same aerial photographs can be interpreted to assess the remediation actions at the site.

## SCOPE

In addition to basic positional information about ground elevation and locations of objects, maps can serve as the base for a targeted sampling grid, or for recording specialized information such as land disposal activity, population distribution, geologic fractures, vegetation communities, wetlands delineation, and land use.

When compared with historical aerial photographs these maps can provide both qualitative and quantitative information on changes in volume and elevation (e.g., last year there was a mound three times larger than the present one; or, between 1988 and 1990, there were 100,000 cubic yards of material placed in the land-

fill). Topographic information is entered into ARC/INFO (the GIS software currently used by the EPA) for future referral. The information on these maps can provide answers to critical environmental questions such as the probable sources of contamination and the ultimate destiny of discharges.

## ADVANTAGES AND LIMITATIONS

Topographic mapping is a mature technology that is expanding to meet the needs of the environmental community. Advances in computer technology and optical sciences have enhanced remote sensing capabilities over the years - and continue to do so.

### Advantages

Legally defensible data  
Permanent historical record  
Digital or analog format  
Geographic relationships are clearly demonstrated  
Quantitative measurements can be made

### Limitations

Seasonal and weather restrictions  
Complexity of technology

## FUTURE PLANS

Remote sensing and mapping technologies continue to develop and hold great promise for practical environmental usage. The basic topographic mapping process is being augmented by a series of related monitoring techniques that will provide

new thematic mapping products. Among these are: the use of orthophotography which is hard-copy imagery corrected to map-quality standards; land use/land cover mapping from satellite data; and the development of various digital products in a

Geographic Information Systems format.

The increased need for accurate information will continue to drive remote sensing and topographic mapping growth in the 1990s

## REFERENCES

U.S. Environmental Protection Agency. Photogrammetric Mapping Program for Hazardous Waste Sites. An EMSL-LV publication. 1984.

Remote Sensing and Interpretation, Lillesand, T. M., and R. W. Kieffer, especially Chapter 5. John Wiley and Sons, 1979.

## FOR FURTHER INFORMATION

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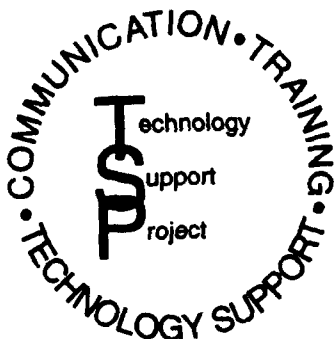
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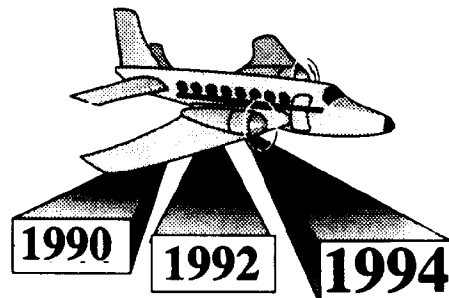


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TECHNOLOGY SUPPORT



# Remote Sensing Support for RCRA



## INTRODUCTION

Since the passage of the Resource Conservation and Recovery Act (RCRA), the U.S. EPA has employed aerial remote sensing techniques to assess the suitability of sites for disposal of hazardous wastes. Remote sensing (interpreted aerial imagery) provides key information necessary for RCRA personnel to respond to problems at waste disposal sites, to assess the risks of those sites to their neighboring communities, and to evaluate new sites proposed for the disposal of hazardous waste. Aerial photography and other sensor imagery are the most economic source of information that is required by Agency officials for permit reviews, litigation support, site operations monitoring, and general environmental assessments. Acquisition and interpretation of aerial

imagery data for this and other Agency programs are conducted by the Characterization Research Division in Las Vegas (CRD-LV).

The CRD-LV provides aerial imagery acquisition and interpretation support for hazardous waste site analysis to the Regional offices and to the Office of Solid Waste and Emergency Response (OSWER). Typical OSWER activities that have been supported include emergency response to hazardous materials release situations, current site condition assessments, historical reviews of site development, waste site inventories for large geographical areas, topographic mapping of sites, and criminal and civil litigation under RCRA. The remote sensing support provided is typically

paid for by reimbursable funding from the office supported.

Remote sensing is a key tool for addressing RCRA enforcement and response issues. The Environmental Photographic Interpretation Center (EPIC), at CRD-LV, provides:

- A team of scientists with the critical skills that are required for unique environmental/enforcement issues;
- The applications research that is necessary to keep the Agency at the state-of-the-art and a capability to transfer this technology to the Regions; and,
- The ability to respond quickly to emergency spills of hazardous materials.

## ENFORCEMENT REQUIREMENTS

The CRD-LV program also supports special enforcement requirements. Once a site analysis is completed by CRD-LV and a final report is produced, it may be several years before the associated RCRA case comes up for litigation. For more than 17 years, the CRD-LV has contributed to the production and maintenance of hazardous waste disposal site image analysis reports and records. The CRD-LV program thus provides a

team with an institutional memory that offers reliable and consistent support to enforcement cases throughout extended litigation under RCRA. In this role, the CRD-LV provides support to EPA's National Enforcement Investigations Center (NEIC), to Regional Offices of Criminal Investigation (OCI's), and to the Department of Justice.

EPA's attorneys prefer using a centralized EPA remote sensing program for criminal

prosecutions. In their opinion, such a program is sensitive to the security requirements of enforcement cases, is involved in fewer conflicts of interest, uses proper chain-of-custody procedures for handling cameras, film, and photographs, and develops long-term working relationships with the EPA attorneys.

## TECHNOLOGY TRANSFER ACTIVITIES

The CRD-LV also provides technology transfer support to EPA Headquarters and Regional program offices in the form of RCRA training workshops and technical advice. This includes send-

ing CRD-LV scientific staff to the Regions to demonstrate the use of interpreted aerial imagery in addressing RCRA requirements in the Region. This is an on-going activity conducted on a regular basis

to ensure that new RCRA staff are properly informed and current staff are kept up-to-date with the technologies

## EMERGENCY RESPONSE CAPABILITY

EPIC also uses the capability of the CRD-LV to respond to emergency requests, usually in response to hazardous material release or other emergencies at waste sites. These actions provide quick pictorial information on conditions at the site. Information on the extent and location of visible spillage,

vegetation damage, and threats to natural drainage and human welfare are typical of the types of information gathered during emergency response activities.

EPIC, through its fully operational photo processing and image analysis facilities in Warrenton, VA, and

Las Vegas, NV, is on call to respond to emergency situations and prepared to work around the clock to process aerial photography, analyze the film, document the analysis results, and ship the results to the requester as soon as possible.

## ENFORCEMENT

The Agency has special enforcement requirements for civil and criminal litigation and many of these requirements have direct policy implications. For example,

there are specific security requirements of EPA criminal cases, as outlined in the Federal Rule of Criminal Procedure 6(e), which requires protection of grand

jury material. CRD-LV provides protection of these materials through the use of proper chain-of-custody procedures which is crucial to the success of EPA cases.

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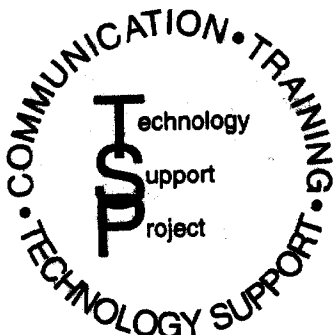
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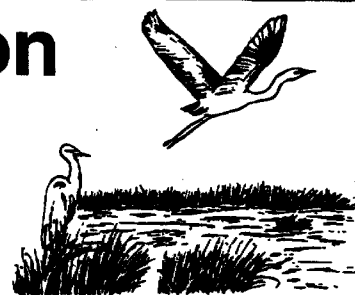
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TECHNOLOGY SUPPORT



# Wetlands Delineation for Environmental Assessment



## INTRODUCTION

The Environmental Photographic Interpretation Center (EPIC) at The Characterization Research Division in Las Vegas (CRD-LV) provides current and historical wetlands analyses that locate, characterize, and document historical dredge or fill activities in wetlands.

Aerial photographs offer a synoptic view of wetlands and their surrounding environments and form a permanent record of present and past conditions. Precise quantitative measurements can be derived from aerial

photos that aid field work by displaying relationships not readily apparent on the ground. Uses for extracted data range from general regional planning to legally defensible presentation of data.

EPIC wetlands analysts tap years of experience in photointerpretation of varied wetlands habitats. Collateral information on soils, local hydrology, and vegetation is always utilized to ensure the accuracy of the delineations. Field verification may be used to enhance the accu-

racy of the delineations. Aerial measurements of data can determine loss of wetland habitat, length of constructed drainage channels, or other pertinent information.

Various levels and formats of wetlands delineations are available as dictated by the needs of the requester. Overlays to either aerial photos or topographic maps may be produced, or the data can be converted to digital form for use within a Geographic Information System (GIS).

## SCOPE

### Wetland/Upland Boundary Analysis

Determination of a wetland/upland boundary is the simplest analysis. This level of analysis is used to locate wetlands and off-site drainage patterns. It is typically requested for a specific area surrounding sites and usually involves the most current year of photography, but multiple years can be analyzed if change detection is needed.

### Detailed Analysis

A detailed wetlands analysis is requested when information is needed on vegetation types in the wetlands and deepwater habitats classification system developed by Cowardin et al. (1979) for the U.S. Fish and Wildlife Service. Analyses of single or multiple years of coverage are performed.

### Section 404 Support

Section 404 of the Clean Water Act protects wetlands from unpermitted dredge and fill activities. Analyses involve field work using jurisdictional delineation procedures. Wetlands are classified using the full Cowardin et al. (1979) classification system. Two types of analyses are used in support of this program.

### Enforcement

Court support can be provided for enforcement cases where wetlands have been dredged or filled and no permit had been issued. Using historical photographs and field verification, reference wetlands having the same photographic signature, soils, and hydrology as the dredged or filled wetlands are used to confirm the classification of the filled or dredged

wetlands. Current overflights of the site are generally acquired to ascertain current conditions. To detect change, at least 2 years of photography are analyzed. Area measurements of wetlands loss and change by type are calculated using Geographic Information Systems software. Should legal proceedings be required, graphic displays and expert witness testimony are provided.

### Advance Identification

In support of the Advance Identification process of 404, delineation of wetlands on overlays of current photographs or base maps are available. These studies are a cost-effective way to identify wetland habitat in advance of permit application and evaluation.



## ADVANTAGES AND LIMITATIONS

Historical aerial photographs are often the only means of establishing the prior existence of wetlands for sites that have been dredged or filled. Progress in computer technology has enhanced the accuracy of both presentation and measurement of wetland change detection data and subsequent transfer to maps.

### Advantages

- More cost effective than intense field sampling
- Legally defensible
- Verifies existence of current or historical wetlands
- Detection of change
- Photo coverage of critical years

### Limitations

- Visibility obscured by snow cloud cover, and leaf-on conditions
- Available photography may exhibit extremes in hydrology (drought and flood)
- Lack of photo coverage for critical years

## FUTURE PLANS

Remote sensing for wetlands delineation and mapping is an expanding field. Improvements in the resolution of aerial photography and associated technologies will expedite the delineation

process. With the introduction of photogrammetric instruments into this mapping discipline, precise planimetric and volumetric measurements can be performed in support of EPA needs. By

converting photointerpreted data into digital format, they can be combined with data from diverse sources resulting in spatial information useful for environmental decision making.

## REFERENCES

Cowardin, L. M., V. Carter, F. C. Golet, and E. T. LaRoe. Classification of Wetlands and Deepwater Habitats of the United States, U.S. Department of the Interior, Fish, and Wildlife Service, FWS/OBS-79/31, 1979.

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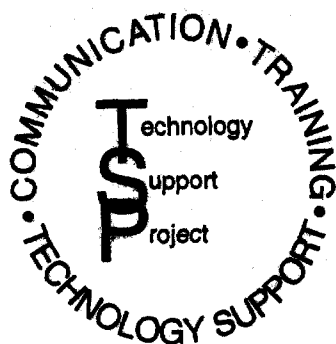
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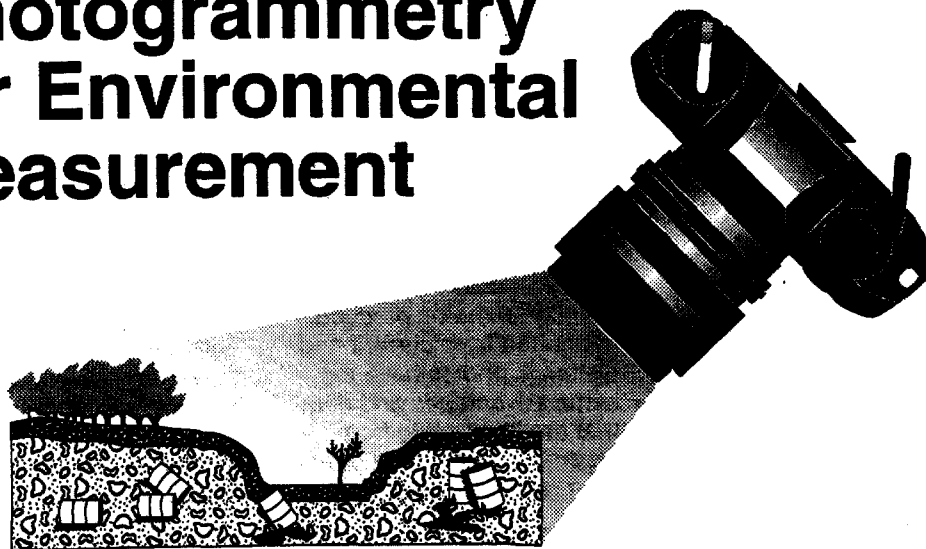


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## TECHNOLOGY SUPPORT

# Photogrammetry for Environmental Measurement



## INTRODUCTION

The Characterization Research Division in Las Vegas (CRD-LV) has an active remote sensing department, capable of responding to all Regional requests for obtaining and interpreting aerial photography. Photogrammetry is defined as the "art and science of obtaining reliable measurements from photographs" (American Society for Photogrammetry and Remote Sensing, 1991).

Most small and medium scale maps are made from aerial photographs, and photogrammetric sciences are a fundamental part of modern map making. The aerial photographic holdings in the EPA and other agencies of the federal government are a wealth of spatial and temporal data about environmental conditions and processes. CRD-LV currently provides qualitative information that is

interpreted from aerial photographs to characterize hazardous waste sites, analyze wetlands, identify ecological resources and to meet a number of environmental monitoring needs. CRD-LV has now acquired the capability to supply highly accurate measurement information for similar applications.

## TECHNIQUE

Photogrammetric data are produced on very precise photo-measurement devices called analytical stereoplotters. These devices, typically calibrated to the micron level, enable

the scientist to create complex mathematical models that correct for known distortions in the photographs. From these three-dimensional photo models, highly accurate measure-

ments and positional data can be derived for mapping and analytical purposes. These data can be produced in digital format directly for input in a Geographic Information System (GIS).

## THEMATIC MAP PRODUCTS

Cartographic information can be produced from aerial photographs to meet National Map Accuracy Standards. The information can be traditional map features such as roads and hydrology or special map layers such as

historical hazardous waste site activity and fractures in the bedrock. Any information that can be derived from the aerial photo can be accurately mapped in a digital format. Once the photo model is established, the-

matic information represented by points, lines, and polygons can be input directly in digital format without transfer to a hard-copy map and digitizing from the map base. This saves time and reduces errors.

## MENSURATION PRODUCTS

Exact measurements can be accomplished on an analytical stereoplotter to help characterize activity of environmental interest. For

example, in studying hazardous waste sites, the volume of waste accumulation and changes in this volume are needed to evaluate remedial

options. Also, precise distance and area measurements can be utilized for risk assessment and other site characterization activities.

---

**PRECISE LOCATION OF FEATURES**

Any feature that is observable on an aerial photograph can be accurately referenced to a coordinate system. Photogrammetry can be extremely useful for collecting and recording the coordinate data that are required by the EPA Locational Data Policy. Information that is not readily

visible on photographs, such as property boundaries or pipelines locations, can be superimposed digitally onto the photo model for special mapping or interpretive purposes.

Cartographic information that depicts the elevation of the

land surface, such as the contour map or the digital elevation model, can be produced by photogrammetric techniques. The resolution of this data can be tailored to the specific needs of the project.

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**ADVANTAGES**

Photogrammetric products generated from current and historical photos have the same advantages and data that are interpreted from air photos: they form a permanent record of present and

past conditions, they are defensible in court, and they serve as valuable aids to site-specific field work. The ability to provide quantitative measurements as a supplement to qualitative

photointerpretation products will significantly enhance the products and services available to the EPA community.

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**FUTURE PLANS**

More of the basic photogrammetry and photointerpretation products will become available in digital, GIS formats.

Also, the use of digital imagery in the photogrammetric process is currently being researched and will be

incorporated into future products as will the use of digital photography in the GIS environment.

---

**REFERENCE**

American Society of Photogrammetry, Manual of Photogrammetry, 4th Edition, Chester C. Slama, Editor-in-Chief, American Society of Photogrammetry, Falls Church, VA. 1980.

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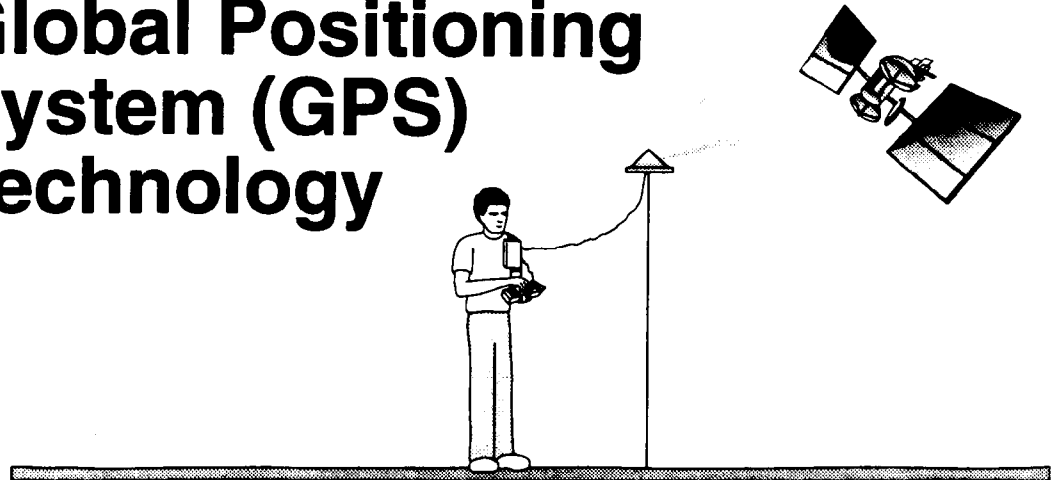
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TECHNOLOGY SUPPORT



# Global Positioning System (GPS) Technology



## INTRODUCTION

Global positioning system (GPS) technology is a satellite-based radio positioning and time-transfer system that can provide accurate, three-dimensional geographic positioning anywhere on the

earth's surface. Developed by the Department of Defense, this technology was designed primarily for military navigational systems, but there are numerous geocoding applications in the

field of environmental science. GPS is an emerging technology in geodesy, geography, surveying, and environmental monitoring and analysis.

## THE EPA LOCATIONAL DATA POLICY

Data collection in environmental monitoring is affected by spatial considerations. With the Agency's widespread use of geographic information systems (GIS) for environmental analyses, the quality of the geographic reference of database items

becomes central to the quality of the overall scientific analyses.

In May 1990, after Agency-wide review, the EPA adopted the Locational Data Policy (LDP) with the purpose of ensuring the collection of accu-

rate, fully documented latitude/longitude coordinates as part of all Agency-sponsored data collection activities. The EPA accuracy goal has been established at 25 meters and the best collection method is currently considered to be GPS (EPA 1991).

## THE SCIENCE OF SATELLITE POSITIONING

By using radio signals from a constellation of earth-orbiting satellites, earth-based receivers can compute highly accurate three-dimensional geographic coordinate positions. Terrestrial positions can be determined using different instruments. GPS utilizes satellite tracking and ranging to determine a point's three-dimensional geocentric coordinates.

If data on the satellite geometry, position, and movement (called ephemeris data) are known, the distance to an earth-based receiver can be geometrically calculated by measuring the time it takes for the radio signal to reach the receiver. This type of positioning is only possible because of the accuracy and speed of modern clocks and computers. Ephemeris data are constantly monitored by a

network of earth tracking stations and relayed back to the satellite where they are included in the transmitting signal and tracked by the GPS receiver. If this ranging process is repeated constantly from several satellites, and known errors caused by clock timing and atmospheric effects are modeled, a precise position can be calculated and referenced to a known datum and coordinate system (Wells et al., 1986).

## HOW ACCURATE IS IT?

Accuracy depends on several factors including the design of the receiver. There are two general classes of GPS receivers: navigation and

geodetic. By employing two or more GPS receivers with another that is located over a known geodetic control point, navigation grade instruments

can routinely yield accuracies in the 2-5 meter range. The geodetic quality units can compute coordinates with millimeter level accuracy.

## APPLICATIONS

Apart from the traditional types of geocoding, surveying, and the collection of accurate latitude/longitude coordinates, one of the main applications of this technology is in the area of GIS. GPS technology provides a means of evaluating and quantifying the spatial accuracy of digital map data as well as creating digital cartographic data structures. Potential products and application areas include:

- Direct Digital Mapping - Portable GPSs can be hand-carried or mounted on vehicles to create digital data structures that can be used as direct input into GIS systems. The system is used to update existing map data, provide highly accurate subsections, or create entirely new map products.
- Field Navigation - Field sampling teams can use GPS to easily and accurately record the location of specific sampling locations or to navigate back to a previous sampling point even when surface markers have been disturbed or are no longer present.
- Quality Control - A carefully planned GPS survey can provide first order control locations which can then be utilized to assess the spatial quality of other thematic overlays that have been developed for the database or to geo-reference raw data layers, such as satellite or aerial images.
- Network Modeling - Kinematic (mobile) positioning techniques can be used to create network structures with much greater accuracy and precision than is currently possible. Spatial variations in movement and rate, and time series analysis can be acquired at greater data resolutions.
- Photogrammetric Control - Photogrammetry and cartography often remain the most cost-effective methods of creating thematic maps. The ease of establishing a control configuration for existing aerial photographs with GPS technology as opposed to traditional surveying methods can result in significant savings in cost, time, and manpower.

## REFERENCES

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U.S. Environmental Protection Agency, Locational Data Policy Implementation Guidance - Draft. Office of Information Resources Management, Washington, D.C. 20460, 1991.

## FOR FURTHER INFORMATION

For further information about GPS systems or applications to a specific environmental application, contact Terrence Slonecker or Mason Hewitt.

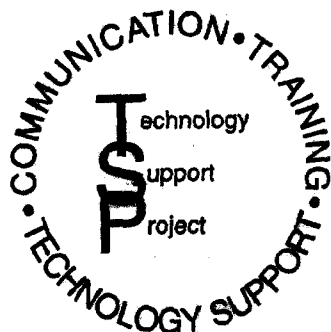
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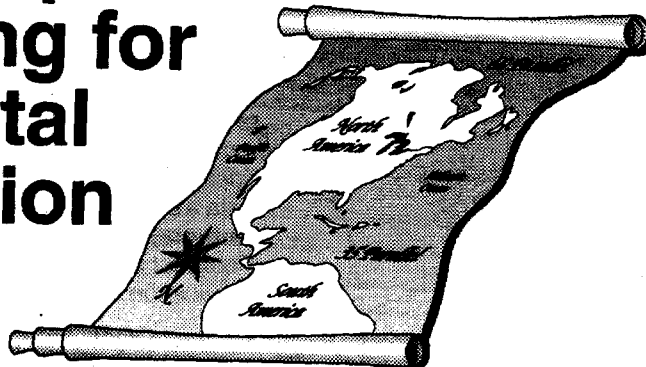


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## TECHNOLOGY SUPPORT

# Historical Maps and Archiving for Environmental Documentation



## INTRODUCTION

The location, extent and history of activities at hazardous waste sites is of great interest to the U.S. Environmental Protection Agency and can be documented through the analysis of historical records such as aerial imagery, historical and thematic maps and other cartographic data. Since its

inception, the Characterization Research Division in Las Vegas (CRD-LV) and Warrenton, Virginia field station has been collecting and analyzing these data sources for environmental site analyses and civil and criminal actions. Cases are brought by the Department of Justice, FBI, and National

Enforcement Investigations Center. Prosecutions related to CERCLA, RCRA, National Environmental Policy Act, and Clean Water Act violations serve as support for EPA Regional offices' investigations at hazardous waste sites across the country.

## DATA SOURCES

Aerial imagery is the cornerstone data source used by CRD-LV during the completion of environmental site analysis. Historical aerial photography records the evidence of past commercial or industrial activities as well as changes in topography, hydrology and vegetation brought about by industrial development. Aerial photographic coverage dating back to the late 1920s is available for portions of the industrial-

ized U.S. Other types of aerial imagery used at CRD-LV include color infrared photographs (useful in detecting vegetation stress) and thermal infrared imagery which records qualitative variations in surface temperatures and can be used to identify leachate discharge points, past disposal activities, and subsurface pipelines. Historical maps date back to the mid 1850s and consist of U.S. General Land

Office land surveys, U.S. Army Corps of Engineers river and harbor charts, fire insurance maps and early U.S. Geological Survey topographic maps (late 1880s). Thematic maps such as soil surveys and bedrock or surficial geology maps date back to the turn of the century and can provide information on the subsurface environment which may in turn measure the migration of contaminants in ground water.

## ACQUISITION AND ARCHIVING

Historical aerial photographs are available from federal agencies (such as USDA, USGS, NOAA, and USEPA), state agencies, and private vendors responsible for their production. Archival aerial photographs from some federal agencies are stored at the National Archives in Washington, D.C. Aerial photographs acquired from the above sources are indexed and added to CRD-LV's film archive, which currently includes over

150,000 frames of imagery. When current photography is required, CRD-LV initiates an overflight of the site being studied. These overflight photographs are indexed in the CRD-LV film archive. Historical maps are available through a number of sources such as the National Archives, Library of Congress, state libraries, university libraries, and state and county offices. Thematic maps are available from the agency responsible for their

production, e.g., USDA SCS Soil Surveys, USGS Geologic Quadrangle Maps. These maps are acquired and cataloged as collateral data and remain with the CRD-LV library-filed project folder. Historical land use data including census tracts are available at the National Archives, as well as state or university libraries, and can be acquired to support land-use mapping.

## APPLICATIONS

Apart from the traditional types of geocoding, surveying, and the collection of accurate latitude/longitude coordinates, one of the main applications of this technology is in the area of GIS. GPS technology provides a means of evaluating and quantifying the spatial accuracy of digital map data as well as creating digital cartographic data structures. Potential products and application areas include:

- Direct Digital Mapping - Portable GPSs can be hand-carried or mounted on vehicles to create digital data structures that can be used as direct input into GIS systems. The system is used to update existing map data, provide highly accurate subsections, or create entirely new map products.

- Field Navigation - Field sampling teams can use GPS to easily and accurately record the location of specific sampling locations or to navigate back to a previous sampling point even when surface markers have been disturbed or are no longer present.
- Quality Control - A carefully planned GPS survey can provide first order control locations which can then be utilized to assess the spatial quality of other thematic overlays that have been developed for the database or to geo-reference raw data layers, such as satellite or aerial images.
- Network Modeling - Kinematic (mobile) positioning

techniques can be used to create network structures with much greater accuracy and precision than is currently possible. Spatial variations in movement and rate, and time series analysis can be acquired at greater data resolutions.

- Photogrammetric Control - Photogrammetry and cartography often remain the most cost-effective methods of creating thematic maps. The ease of establishing a control configuration for existing aerial photographs with GPS technology as opposed to traditional surveying methods can result in significant saving in cost, time, and manpower.

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U.S. Environmental Protection Agency, Locational Data Policy Implementation Guidance - Draft. Office of Information Resources Management, Washington, D.C. 20460, 1991.

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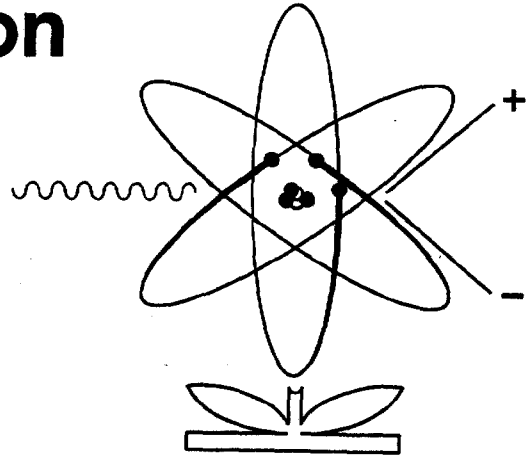
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TECHNOLOGY SUPPORT

# Field Screening Methods for Radioactive Contamination



## INTRODUCTION

The complexity of hazardous waste sites presents a challenge to field scientists and decision makers in the remediation process. There is growing concern in the technical and secular communities about the likelihood of radioactive contaminants at sites previously thought to contain only organic or inorganic material. Hazardous waste site problems can be described broadly as:

- Low level without radioactive contamination

- High level without radioactive contamination
- Low level with low level radioactive contamination
- Low level with high level radioactive contamination
- High level with low level radioactive contamination
- Radioactive contamination only
- High level with high level radioactive contamination

Surveys are recommended for sites that are suspected of

containing radioactive waste. This cautionary measure can identify problems early in the site characterization procedure and can isolate areas that require special care in the remediation program.

Portable instruments are available that will determine the presence of radioactive hot spots in a quick, semi-quantitative manner. These instruments are not isotope specific, but do identify the source as an alpha, beta, or gamma ray emitter.

## INSTRUMENTATION

Several portable instruments are commercially available that can detect alpha, beta, and gamma radiation. The alpha counter is a separate unit from the beta/gamma counter. Each is battery operated, smaller than a shoebox, and easily managed by one field scientist. The beta/gamma counter operates in two modes: with the shield closed, it detects

gamma rays; with the shield open, it detects beta plus gamma rays. The amount of beta radiation can be determined by the subtraction of gamma from beta plus gamma. The readings are displayed on an analog meter in millirems/hour or counts/minute.

Another device that is amenable to field survey use

is the portable ion chamber. It is a hand-held instrument with charged gas in a chamber and is useful for the detection of gamma radiation.

A "pancake" detector is often used for quick screening of clothing and flat surfaces. It is sensitive to beta and gamma radiation and gets its name from its flat round shape.

## FIELD USE

Portable radiation survey instruments are calibrated with laboratory sources placed at various distances from the detectors before the site survey. A sampling grid is established following data quality objective goals. Once the instruments are ready and all health and safety precautions have been addressed by the field team,

the survey can begin. A typical approach may consist of two field personnel, one with an alpha counter and the other with a beta/gamma (also known as Geiger) counter. Each sampler would have a log book in which to record the readings at the pre-ordained locations on the grid. Due to the character of gamma radiation, gamma

signals will be detected and counted. It is important that the sampler hold the counter just above the ground surface consistently through the study. For screening purposes, it is essential that any radiation greater than background level be investigated further to assure a thorough knowledge of the radioactive character of the site.

## ADVANTAGES AND LIMITATIONS

Commercially available detectors are generally reliable, consistent and easy to use. The strong advantage of knowing the radioactive character of a hazardous waste site is obvious. It allows future characterization and remediation to be performed intelligently and safely.

When combined with a carefully planned laboratory confirmation, field screening

can be a quick and effective method for assessing the extent and location of radioactive contamination. Liquid scintillation methods, alpha/beta counting, alpha spec-

troscopy, and high resolution gamma spectroscopic methods can identify the isotopes and better quantify the radioactivity at the site.

### Advantages

- Rapid, real-time results
- Low cost (compared with full laboratory analysis)
- Easy to use

### Limitations

- Inability to probe beneath surface
- Doesn't reveal specific isotope identity
- Difficulty detecting tritium

## FUTURE WORK

A low-energy photon detector system (LEPS) is being investigated for use at mixed-waste sites. Using germanium diodes with a high

sensitivity to gamma-and x-ray energies, this detector can be encased in a water-tight container and used above ground or lowered into

a drilled borehole. This technology promises remote sensing of radiation by the employment of rugged, submersible detectors.

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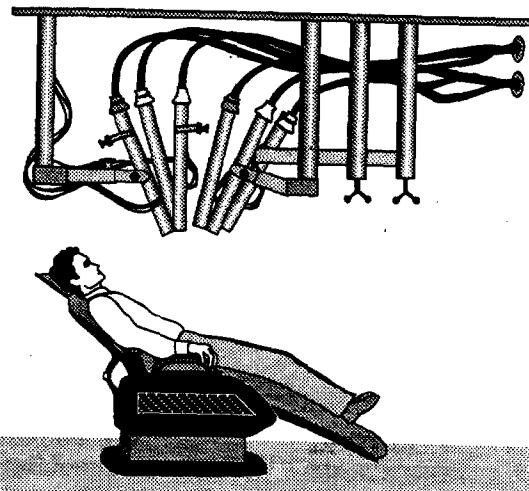


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TECHNOLOGY SUPPORT

# Internal Dosimetry for Radionuclides in Humans



## INTRODUCTION

Monitoring human exposure to radionuclides is an integral component of EPA's mission to protect the health of the public. State-of-the-science equipment and a rigorous quality assurance program provide scientists with accurate information.

Whole body counting is an internal dosimetry method that uses gamma spectrometry to identify radionuclides and to measure their concentration and distribution in a human body.

Lung counting detects inhaled radionuclides which are deposited in the lungs. Counting of areas of the body such as the skull, the liver, or other organs where specific radionuclides may concentrate provides additional information necessary to calculate internal radiation dose. The germanium detectors used in both the whole body and lung counter are passive devices, i.e., they detect emitted radiation but

do not emit any radiation themselves.

Bioassay for tritium, strontium, and other radionuclides which are not detectable with gamma spectroscopy is performed, when necessary.

The Office of Radiation and Indoor Air (ORIA-LV) in Las Vegas maintains a whole body counting facility.

## THE FACILITY AND EQUIPMENT

Two counting vaults, shielded with 6-inch thick, pre-World War II steel walls, provide a low background area for counting. One vault, used for whole body counting, is equipped with a high purity germanium detector positioned over an adjustable chair in which the subject reclines during the count. High energy gamma-emitting radionuclides, with energies ranging from 60 keV to 2.0 MeV (such as cesium and cobalt) can be identified and measured with this system.

The second vault contains an adjustable chair with six state-of-the-art, high-purity

germanium semi-planar detectors mounted above it. These detectors, fitted with very thin "windows" to admit very low energy radiations, are designed for detection of low energy gamma and X-ray emitting radionuclides (such as americium and plutonium). Detected energies range from 10 to 300 keV. Lung, liver, skull, and other specific organ or bone counting is done here.

Both counting vaults have anticlaustrophobic measures. One wall of each vault is covered with a mural to provide a less institutional

feeling, and the subject may watch TV or read.

Data acquisition and processing equipment includes a gamma spectroscopy system which detects the radiation, amplifies and shapes the detector signals, stores and displays data, and analyzes the data to identify radionuclides. A fully-integrated computer/multichannel analyzer system is used, and the software, including data acquisition and analysis, data base management, word processing, and statistical analysis, is tailored for whole body counting needs.

## QUALITY ASSURANCE

The efficiency of the detection system is determined by comparing the amount of radiation measured by the counting system to the known amount in a sample - in this case, a polyethylene bottle "phantom" called the "BOMAB." Its shape and volume is equal to a "standard man." Lung and thyroid phantoms are also used for efficiency calibration.

An energy calibration is done daily to correct for the inherent drift properties of detectors.

Calibration results are tracked with a quality assurance software package. Daily and monthly quality assurance reports and plots are generated. Internal and external audits are routinely conducted, and permanent

records are kept of quality assurance and personnel counting data. This facility participates in intercalibration studies with other whole body counting facilities in the United States to check on both efficiency and energy calibration status.

## COUNTING PROGRAM

Civilian government, Department of Defense, commercial power plant, fuel fabrication plant, and contractor personnel who have a potential for exposure to radionuclides are counted routinely. Any person who feels they may have been exposed to radionuclides may make an appointment for a count.

A program to assess levels of radionuclides in members of some of the families residing in communities and ranches surrounding the Nevada Test Site was initiated in December 1970. The Community Monitoring Station Network, a joint endeavor among Department of Energy, Environmental Protection Agency, and the Desert

Research Institute of the University of Nevada, was established in 1981. The station managers of this network, who are generally science teachers in their communities, and their families, entered the counting program at this time. The families who participate in this program are located in Nevada, California, and Utah.

## SUMMARY

The internal dosimetry program and the networks maintained by ORIA-LV around the Nevada Test Site and in the states west of the Mississippi River provide for

the monitoring of human exposure to radionuclides. Whole body counting is provided free of charge, by appointment only, to EPA Regional personnel and their

contractors who are involved with radioactive or mixed waste cleanup programs and other work involving exposure to radionuclides.

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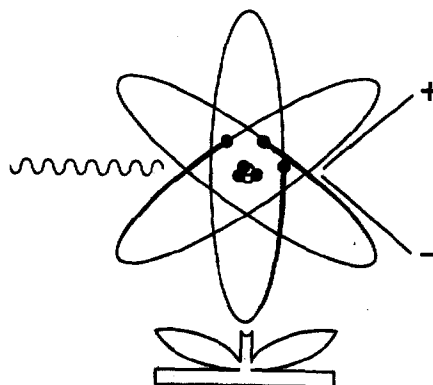


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TECHNOLOGY SUPPORT

# Ambient Gamma Radiation Monitoring



## Introduction

Environmental radiation can be analyzed from two perspectives: impact on environmental systems and impact on biological systems. Dose measurement is the analysis of the amount of energy deposited in matter or tissue and its damaging effect (usually on humans). Exposure measurement is the measurement of environmental radiation, especially X-rays and gamma rays, below 3 MeV in air.

The Office of Radiation and Indoor Air (ORIA-LV) is a national authority on the moni-

toring of environmental radiation. This analytical expertise includes the measurement of ambient gamma radiation, tritium, and noble gases.

The measurement of exposure rate is currently done by pressurized ion chamber (PIC) technology. Six field-portable PICs are currently available through the ORIA-LV. They can provide real-time monitoring for any releases of radiological material. Instruments at the

ORIA-LV were able to detect radioactivity from the Chernobyl accident in 1988. These instruments are so sensitive that readings vary with altitude (cosmic radiation) and with radioactivity in the soil (terrestrial radiation). Integrated ambient gamma exposures over extended periods of time are also measured using thermoluminescent dosimeter (TLD) technology.

## Pressurized Ion Chambers

The PIC is a spherical shell filled with argon gas to a pressure of 25 atmospheres. In the center of the chamber is a spherical electrode with a charge that is opposite to the outer shell. When gamma radiation penetrates the sphere, ionization of the gas occurs and the ions are collected by the center electrode. The electrical current generated is directly proportional to the amount of energy deposited in the chamber, and thus to the ambient gamma radiation exposure level at the monitoring location.

The PIC network continuously measures ambient gamma radiation exposure rates. Because of its sensitivity, the network detects low-level exposure rates and changes that might not be seen by other monitoring methods. The primary function of the PIC network is to detect changes in ambient gamma radiation levels. These changes can be caused by barometric

pressure shifts and from other meteorological changes as well as from the presence of sources of ionizing radiation. The PIC network is capable of providing near real-time documentation of radioactive cloud passage as might result from an unplanned release from nuclear testing operations.

A total of 27 PIC stations have been established in communities around the Nevada Test Site (NTS). These communities are located in Nevada, Utah, and California. In routine operation, equipment installed at each station continuously measures observed ambient gamma radiation levels. Every five minutes the equipment automatically calculates and stores the minimum, maximum, and average observed ambient gamma radiation levels for the previ-

ous five minute period. Every four hours stored data is transmitted via satellite telemetry using the Geostationary Operational Environmental satellite (GOES) directly to a receiver earth station at the NTS and then to ORIA-LV via a dedicated telephone line.

Because of the sensitivity of the equipment, site-specific limits for "natural background" have been established. If the established threshold is exceeded for two consecutive five minute samples, the system automatically switches into an "alarm" mode and transmits data more frequently. The location, operational status, and most recently transmitted data for each station may be shown on computer graphic displays in the nuclear test operations control room at the NTS and at ORIA-LV.

(Continued)

**Pressurized Ion Chambers**  
cont'd.

All data collected by the PIC are stored on magnetic tape or solid state removable recording devices installed at each station. The stored data is manually retrieved and processed on a weekly basis to confirm the accuracy of satellite transmissions.

In addition to satellite telemetry and on-station magnetic or solid state recording, data are recorded on strip charts. The strip chart recording is visible at the station location. Each station also includes a

liquid crystal display. The combination of strip chart and liquid crystal display allows an interested individual to monitor real-time readings and readings recorded over the previous 24 - 48 hours.

**Thermoluminescent Dosimetry**

Thermoluminescent dosimeters (TLDs) can be used to measure environmental gamma radiation exposures integrated over extended periods of time. The exposure integration period for environmental applications normally approximates a calendar quarter. In this context TLDs are fundamentally different from PICs, which can provide near real-time highly detailed measures of plume passage. Environmental TLDs monitor accumulated, long-term exposure in areas surrounding the

NTS. Each environmental TLD contains 3 simultaneously exposed and identically filtered  $\text{CaSO}_4:\text{Tm}$  phosphors. Two TLDs are deployed at each monitoring location, thereby providing up to 6 replicate data points. This phosphor-filtration combination provides excellent sensitivity at the low levels encountered in environmental monitoring situations. The phosphor is not directly tissue equivalent, so no attempt is made to express results in

units descriptive of an absorbed dose equivalent in humans. TLDs used to monitor personnel use a combination of phosphors and filtrations. Evaluating the ratios of the phosphor-filtration responses from personnel TLDs permits an estimation of the radiation type and energy to which the dosimeter was exposed, thereby providing a mechanism for assessing the absorbed dose equivalent.

**Data Interpretation**

The data are evaluated weekly by ORIA-LV personnel. Trends and anomalies are identified and investigated. Equipment problems are referred to field personnel for correction. Weekly PIC averages are compiled from the periodic telemetry data and from the 5-minute averages recorded on the removable storage devices. Computer-generated reports of the PIC weekly

average data are issued for posting at each station. These reports show the reporting week's average gamma exposure rate, in units of microRoentgens per hour ( $\mu\text{R/hr}$ ). In addition, the reports include the average observed in the previous week, the average over the previous year, and the range (minimum and maximum) of

natural background radiation levels for the United States. Results obtained from reading environmental TLDs are reported in units of  $\text{mR/deployment period}$ . The result reported is the mean measurement obtained from 3 - 6 simultaneously exposed and identically filtered  $\text{CaSO}_4:\text{Tm}$  phosphors.

**Applications**

Whenever measurement of low levels of ambient gamma radiation is of concern, it is appropriate to consider a monitoring program that includes using PICs. Following mobilization of the response team and placement

of PICs, monitoring ambient gamma radiation levels in the environment is a matter of collecting and evaluating data. The experts at the ORIA-LV are ready to work

with Regional personnel to assure the appropriate use of and to provide experienced data interpretation for results obtained using these sensitive technologies.

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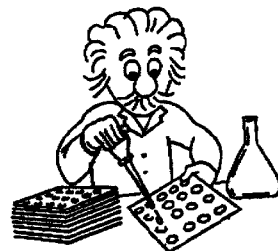
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## TECHNOLOGY SUPPORT

# Immunochemistry for Environmental Monitoring



## INTRODUCTION

The Characterization Research Division in Las Vegas (CRD-LV) is pioneering an investigation into the usefulness of several immunochemical techniques for monitoring the extent of contamination in various environmental and biological matrices. Immunochemistry includes all methods of sample preparation and analysis that incorporate antibodies that have been developed for specific analytes

or groups of analytes. Enzyme-based immunochemical techniques have been in use since the '70s and more recent efforts have focused on their applicability to the complex matrices that face environmental scientists. The CRD-LV has developed and demonstrated several immunochemical techniques and believes that these methods hold great promise for the quantitative analysis

of target analytes for use in ground-water surveillance, *in situ* hazardous waste site monitoring, and assessment of human exposure. Current work involves the analysis of chemicals, like PCBs, nitroaromatics, and certain pesticides, that are difficult to analyze by other analytical methods.

## BACKGROUND

Immunochemistry includes techniques such as immunoaffinity and immunoassay. Immunoaffinity is a sample preparation procedure that takes advantage of the attraction between an antibody and a specific analyte. Immunoaffinity preparations have great potential for cleanup of complex samples like dioxins. By rinsing a sample over an antibody-treated surface, scientists can isolate particular compounds in the sample

that adhere to the antibody. The isolated compound is then eluted from the immobilized antibody and is ready for analysis by chromatography or immunoassay. One common immunoassay is the enzyme-linked immunosorbent assay (ELISA). The specificity of the antibody for the analyte and the resultant immune complex is the basis for the specificity of immunoassays. Most field immunoassays are colorimetric analytical methods that

quantify compounds of interest. A sample is spiked with a known amount of a labelled analyte. The label is typically an enzyme. A chromogenic substrate is added to serve as an indicator of compound concentration in the sample. Laboratory-based immunoassays include fluorescent and radioactive methods that have greater sensitivity but are less portable.

## FIELD USE

Immunoassays are portable, rugged, and inexpensive. Their use at hazardous waste sites has been investigated by the CRD-LV. The results of Superfund Innovative Technology Evaluation (SITE) studies indicate a strong correlation between field immunoassays, laboratory immunoassays, and gas chromatography/mass spectrometry. The only equipment needed is a spectrophotometer, various microtiter plates or test tubes, precision pipets, and immunologic reagents. The 96-well

microtiter plate is approximately 3" x 6" and has 96 depressions, each capable of holding about 250  $\mu$ L liquid. Smaller microtiter strips are available that can be assembled to form modular sections for individual analytes. These plates and test tubes are available pre-coated with the antibody base.

Another field use of immunochemistry is being explored at the CRD-LV. This use may revolutionize safety and exposure precautions used

by workers who deal with hazardous chemicals. Dosimeter badges with an immunochemical twist are available for pentachlorophenol and nitroaromatics. These personal exposure monitors (PEMs) are lightweight, inexpensive, can be analyzed quickly, and provide real time indication of exposure. These badges employ a microdialysis tubing containing an immobilized antibody phase. Immediate identification of high exposure levels is critical to the conduct of safe site characterization.

## ADVANTAGES AND LIMITATIONS

The use of immunochemical techniques is gaining acceptance in the area of environmental science. One need that is being addressed is that of specificity. Frequently, immunoassays are available for a class, like PCBs. Specific quantitation for each component would be difficult.

PEMs are available for pentachlorophenol and are being developed for parathion and chlorpyrifos. The development of PEMs must address the question of

### Advantages

- Field portable
- User friendly
- Quick and inexpensive
- Potential for wide range of analytes
- Useful for many matrices
- Low detection limits

### Limitations

- Separate immunoassay needed for each analyte
- More complex analysis required for quantitation of specific analytes
- Long development time for new antibodies and methods

diffusion of chemicals through the dialysis tubing, the optimum concentration of the antibody, detection limits and quantitation of the

badge, the efficiency of the antibody in capturing the analyte, and the capacity of the device.

## FUTURE

The CRD-LV is active in the development of all immunochemical methods that have potential for Agency use. One new avenue of investigation is the use of antibody-coated fiber optic immuno-sensors. Another application is the integration of robotics capability for high sample throughput and a tiered

analytical approach, i.e., biological and environmental samples, biomarkers, target analytes, and degradation products. This system of analytical procedures will enable scientists to measure contamination at the source, follow the fate and transport of residual amounts, and assess human exposure.

Multi-analyte immunoassays that can identify several analytes simultaneously are expected to expand the desirability of immunoassay technology for environmental use. Work in this area is already underway at the CRD-LV.

## REFERENCE

*Immunochemical Methods for Environmental Analysis*, J. M. Van Emon and Mumma, R. O., eds., ACS Symposium Series 442, ACS, Washington, DC, 229pp. 1990.

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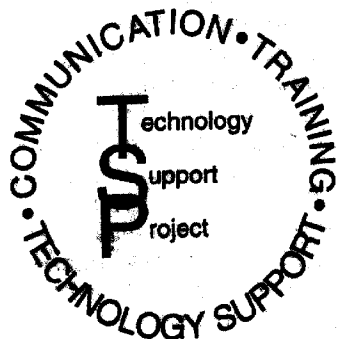
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TECHNOLOGY SUPPORT



# High Resolution Mass Spectrometry



## INTRODUCTION

The identification and quantitation of organic compounds is a fundamental goal of both CERCLA and RCRA. When the identity of the organic compound is known, the formal CLP methods are generally able to address the quantitation needs. Often, however, the exact identity of an organic contaminant is not obvious and is intractable to the commonly used low resolution mass spectrometer. In these cases, a little chemical detective work is needed! Many thousands of pollutants exist, but only a few hundred

matching standards are available, predominantly for the Target Compound List (TCL) pollutants. High resolution mass spectrometers (HRMS) have been developed to provide a closer reading of the fingerprint of a molecule or element. With HRMS it is possible to isolate specific characteristic ions, determine their accurate mass, and thus assign the correct elemental composition without reference standards. Thus, HRMS is a valuable tool for structure determination, and has largely replaced other

techniques such as elemental analysis for structure verification. Data interpretation is complex, as is the instrumentation. Expert analysts must combine their knowledge of chemical interactions with super-sleuthing capabilities to effect a complete and successful identification. The Characterization Research Division in Las Vegas (CRD-LV) has the analytical expertise and instrumentation necessary to provide answers to the most difficult problems of environmental analysis.

## INSTRUMENTATION

Mass spectrometry is a three-phase analytical procedure consisting of ionization, separation, and detection. High resolution mass spectrometry differs from other techniques primarily in the separation capability. High resolution instruments are able to separate ions having the same nominal mass but differing in specific elemental composition and hence in accurate mass, because each element varies from integral mass slightly and differently (except carbon, set

at 12.0000). HRMS has been applied to organic and inorganic identification at ultratrace levels. For example, minor organic contaminants, rare earth elements, and lead isotope ratios can be identified and used for site-specific fingerprinting. The high resolution instrument is much larger and more expensive than the commonly used quadrupole mass spectrometer. It contains a large magnet and an electrostatic sector to provide a focused beam of

ions for determinations of mass that are accurate to 1/1000 of a mass unit. This ability to separate compounds having the same integer mass number is a great advantage to the analyst who is faced with a particularly difficult mass assignment. High resolution mass spectrometers are equipped with special inlet, ionization, and computer systems to maximize their capabilities.

## INTERPRETATION

The interpretation of high resolution mass spectral data is a complex procedure. A skillful and experienced spectroscopist incorporates several areas of expertise into a thoughtful reading of the experimental data. The analyst uses historical information about the site and its contamination, early

results from low resolution mass spectrometry, knowledge of the probable chemical reactions, precursors, by-products, and experience in recognizing the statistical significance of a measurement that borders between two interpretations. Sometimes the particular component of interest has been

depleted or altered by biodegradation, photodegradation, or another agent. The mass spectral analysis must then be thoughtfully focused upon chemical precursors or by-products of the original compound.

## ADVANTAGES AND LIMITATIONS

The complexity of high resolution mass spectrometry interpretation demands considerable interpretive expertise. This level of effort is justified for identification of unknown toxic contaminants during site characterization and remediation. It can also allow the unambiguous correlation of off-site contamination to a specific site.

### Advantages

**Dependable, high sensitivity detection**

**Legally defensible determinations**

**Ability to identify previously unlisted compounds**

**Site fingerprinting**

### Limitations

**Costly instrumentation**

**Expert interpretation is needed**

## REFERENCES

The Wiley/NBS Registry of Mass Spectral Data, F. W. McLafferty and D. B. Stauffer, eds., 1967  
Interpretation of Mass Spectra, 3rd Edition, F. W. McLafferty, University Science Books, 1980

## FOR FURTHER INFORMATION

The CRD-LV will support the Regions in the determination of the identity of compounds that are intractable to routine analysis. This assistance can aid in the identification of the Potentially Responsible Party (PRP).

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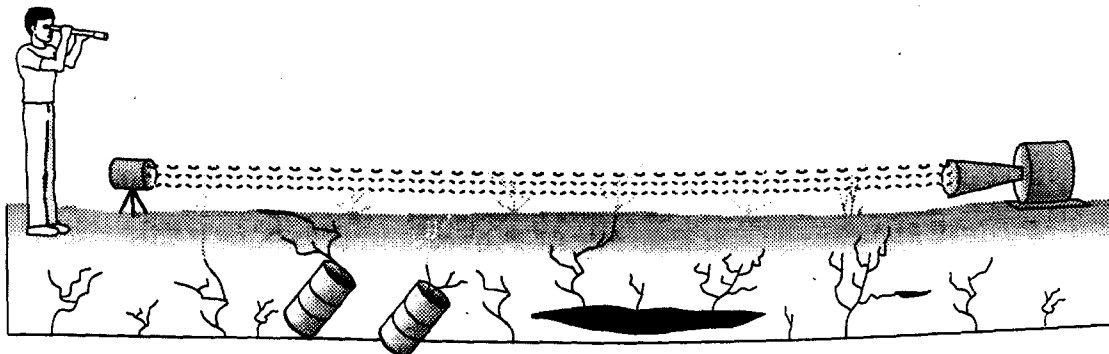


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TECHNOLOGY SUPPORT



# Open Path FT-IR Use in Environmental Monitoring



## INTRODUCTION

A major environmental concern is the identification, location, and extent of volatile organic compound (VOC) contamination in the air at hazardous waste sites. Open path (or long path) FT-IR was adapted to environmental use to address the need for information about VOC levels and to improve upon costlier and more time-consuming

current methods. Open path FT-IR is useful at many stages of screening and remediation because VOC contamination can result from many sources, including underground storage tank leaks, chemical spills, and off-gassing at air stripping plants. A mobile system has been developed at Kansas State University through a coopera-

tive agreement with CRD-LV and Region 7. The mobile laboratory set-up provides an on-site, quick turnaround means of obtaining data that can guide remediation decisions. The outlook for expanded use of open path FT-IR is excellent, with research in the area responding to the needs of field scientists and Agency personnel.

## INSTRUMENTATION

The FT-IR spectrometer being used for developmental work is a Bomem DAO2 system equipped with a KBr/Ge beam splitter, a mercury-cadmium-telluride detector that is liquid nitrogen cooled, an adjustable tripod, and a collection telescope (10-inch Cassegrainian). The source is an air cooled and quartz shielded Nernst glower operating at 2,000 Kelvin. This source is located at the focal point of a 20-inch Newtonian telescope in order to generate a collimated beam of infrared radiation.

The mobile laboratory is driven to one side of the site to be surveyed and the FT-IR spectrometer with its collection telescope is set up adjacent to the station. The IR source and its collimating telescope are positioned on the opposite side of the site to be surveyed so that the collimated beam of infrared radiation may be sent across to the collection telescope of the FT-IR spectrometer. A laboratory calibration is usually sufficient for field sampling.

An alternative arrangement is to place both the source and the spectrometer adjacent to the laboratory station. Then a reflector is placed on the opposite side of the site so the collimated beam of infrared radiation is sent across the site to the reflector and bounced back to the spectrometer. In either arrangement, the IR absorption spectrum of the atmosphere above the site is used to identify any VOC present in the path of the beam.

## SCOPE

Open path FT-IR is useful for the qualitative and quantitative measurement of VOC and low-boiling semivolatile compounds. To date, the spectral database contains 35 VOC files, with a total of 70 compounds expected to be included by the end of

1990. The instruments can be positioned at varying heights above the soil by using tripods. Though this technology is sensitive to meteorological factors such as wind, particulate matter, and rain, most of these affect point sampling by

canister as well. Open path FT-IR is faster and cheaper than the canister methods while providing a greater likelihood of locating the pollutant plume and should be the favored technique when time and budgetary constraints are considerations.

## ADVANTAGES AND LIMITATIONS

Using open path FT-IR to analyze the atmospheric concentration of VOC and solvents is a newly developed and emerging technology. It has many advantages and some limitations that are presented here as an aid to methodology decision-making.

It is obvious that the Data Quality Objectives (DQO) of a site must drive the decisions

### Advantages

Low analysis cost  
Computerized operation  
Rapid results

### Limitations

In development stage  
Equipment is customized  
Sensitive to meteorological changes  
Provides average concentration along pathway

on instrumentation so that the necessary data are not compromised. As with any new method, specialized

equipment and expert advice is fundamental to the site-specific applicability of the technique.

## FUTURE PLANS

As open path FT-IR gains stature as an environmental screening tool, work will be underway to refine its capabilities in quantitation. A growing database that will include more VOC and some semivolatile compounds will increase the usefulness of this method. The anticipated

demand for instrumentation will result in the development of more sensitive, integrated systems. Better computerized formats may enable extrapolation from atmospheric to subsurface concentration. The first two limitations listed above are not intrinsic to the method

and will be solved with the advent of commercially available systems. In general, the outlook is very positive for increased need for screening technologies such as FT-IR, and the demand is expected to guide researchers to promising refinements of these techniques.

## REFERENCES

Fateley, W. G., R. M. Hammaker, D. F. Gurka, Field Demonstration for Mobile FT-IR for Detection of Volatile Organic Chemicals, EPA Report 600/4-90/008, March 1990.

Spartz, M. L., M. R. Witkowski, J. H. Fateley, J. M. Jarvis, J. S. White, J. V. Paukstelis, R. M. Hammaker, W. G. Fateley, R. E. Carter, M. Thomas, D. D. Lane, G. A. Marotz, B. J. Fairless, T. Holloway, J. L. Hudson, and D. F. Gurka, Evaluation of a Mobile FT-IR System for Rapid VOC Determination, Part 1: Preliminary Qualitative and Quantitative Calibration Results, Am. Envir. Laboratory, November 1989, pp 15-30.

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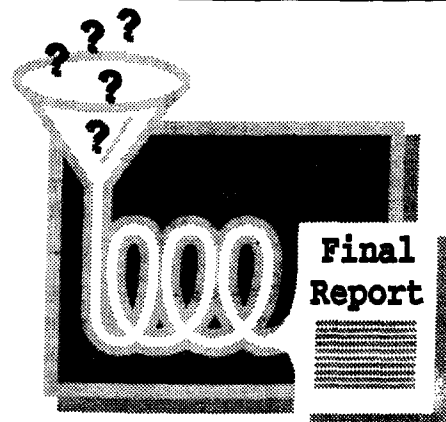
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TECHNOLOGY SUPPORT



# Continuous Monitoring with Purge-and-Trap Gas Chromatography



## INTRODUCTION

Preliminary site assessment and monitoring of remediation efforts rely upon timely and accurate information. Various methods exist for the continuous monitoring of water and air samples. Their value lies in the elimination of labor-intensive sample collection, handling, and analytical procedures. The generation of real-time data permits treatment systems to operate in a true process control mode. Additionally, data quality may be better since samples are never subjected to the packaging and transport needed for conventional laboratory analysis.

The Characterization Research Division in Las Vegas (CRD-LV) is interested in the application of continuous monitoring technologies that will reduce the time-in-field

for environmental scientists working at Superfund and RCRA sites.

A system developed by Analytic and Remedial Technology, Inc. was evaluated for the on-line monitoring of volatile organic compounds (VOCs) in a ground-water treatment process. This monitoring system, Automated Volatile Organic Analytical System (AVOAS), consists of a sampling manifold, a purge-and-trap unit coupled to a gas chromatograph (GC) equipped with an electrolytic conductivity (or Hall) detector and a computer system. The innovative components of this system are:

(1) the sampling manifold, which allows for direct, on-line intake of samples from different collection points or treatment streams.

(2) the injector, which allows direct injection of the sample into the GC without the handling and preparation steps often associated with VOC loss due to volatilization.

(3) the computer software that is customized for the analysis system.

The AVOAS was tested at a Superfund site in Region 1 under the Superfund Innovative Technology Evaluation (SITE) program. Under the conditions of this study, the CRD-LV found this system to be reliable and easy to use. Comparisons of data from the AVOAS study with standard analytical laboratory results from sample splits indicate a strong correlation. The AVOAS results were consistently higher, perhaps reflecting differences due to sample loss during transport.

## DEMONSTRATION

The evaluation was conducted at the Wells G&H Site in Woburn, MA, U.S. EPA Region 1. Ground water at the site is known to be contaminated with VOCs. Remedial action required treatment of the ground water to remove the VOC contamination. As a result, a pilot-

scale operation of a ground-water extraction and treatment system was conducted to evaluate the relative merits of three treatment processes: an ultraviolet/chemical oxidation process, a carbon adsorption process, and an experimental dehalogenation process.

Six sampling points in the treatment train were selected to monitor the efficiency of the individual methods for reducing VOC content. These discrete samples were sent off-site for standard analyses using a purge and trap GC/MS method. This

(Continued)

## DEMONSTRATION (CONTINUED)

treatment study presented an excellent opportunity to demonstrate and evaluate the AVOAS as an application of the principles of process analytical chemistry during a remediation activity. The AVOAS was programmed to

collect and analyze samples at six collection points. In addition to the GC/MS samples, matching samples were taken and shipped to the CRD-LV for analysis by EPA GC Method 502.2. The AVOAS GC analysis is

similar to Method 502.2, making direct comparison allowable. A variety of QA/QC samples were also analyzed under each protocol, consistent with the requirements of the study design.

## ADVANTAGES AND LIMITATIONS

The use of continuous monitoring devices holds great promise for enhancing the characterization and remediation activities at a hazardous waste site. The increasing number of these devices coming into the environmental market puts a burden of evaluation upon both manufacturer and consumer. There is no gain in sacrificing data reliability for ease of use. The CRD-LV will continue to evaluate the performance of demonstrated technologies, like the AVOAS, for applications where a need is indicated.

### Advantages

- Eliminates problems associated with standard VOC sampling and transport
- Allows selection of sampling point, frequency, intervals
- Reduces labor costs
- Provides real-time, in-situ data
- Minimizes exposure of field personnel

### Limitations

- Initial hardware cost
- Problems associated with long-term operation need to be identified
- Availability of equipment
- Application to other situations must be explored

## REFERENCES

Volatile Organic Compounds in Water by Purge and Trap Capillary Column Gas Chromatography with Photoionization and Electrolytic Conductivity Detectors in Series, Method 502.2, U.S. EPA, Cincinnati, 1986.

Methods for the Determination of Organic Compounds in Water, U.S. EPA, Office of Research and Development, Cincinnati, 1986.

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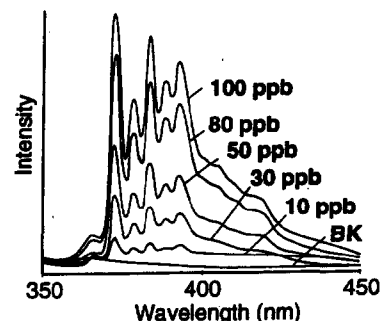


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TECHNOLOGY SUPPORT



# UV-Vis Luminescence in Field Screening and Monitoring



## INTRODUCTION

Ultraviolet-visible photoluminescence techniques (including fluorescence and phosphorescence) are gaining recognition as useful methods for monitoring Superfund, RCRA, and other hazardous waste sites. The Characterization Research Division in Las Vegas (CRD-LV) is active in the research, development, and application of these methods. This document will focus on fluorescence spectroscopy. One application of this method uses a fixed wavelength excitation and records

the fluorescence emission spectrum of the sample. Another application, synchronous fluorescence spectroscopy scans both excitation and emission monochromators to produce a simplified spectrum, typically with one peak per compound. This allows polyaromatic hydrocarbons (PAHs) to be separated roughly into classes according to the number of fused rings. Both techniques hold great promise as field methods that are suitable to the screening, characterization, and monitoring of

contaminants at hazardous waste sites. Although mostly used for PAHs, phenols, and pesticides, luminescence techniques are also available for metal chelates and uranium.

With the emergence of field-deployable, field-portable instruments, and fluorescence sensors, luminescence spectroscopy is joining the list of easy-to-use, inexpensive methods for evaluation of contamination at hazardous waste sites.

## INSTRUMENTATION

Luminescence techniques are mostly used for the analysis of aqueous samples, though soil extracts may also be used. The most frequently used source is a pulsed or continuous xenon lamp which disperses light through a grating. Alternative light sources include mercury lamps and lasers with either fixed or tunable wavelengths. For scanning spectrofluorometers, the continuous spectrum of the light source is dispersed by an excitation monochromator, which can

be scanned mechanically to select a bandpass. Then, the emitted light at each wavelength is detected (usually at right angles to the exciting light) by an emission monochromator coupled to a detector. For quantification, the fluorescence intensity is compared to the response from standards at various levels on a calibration curve.

Identification, classification, and quantification can be performed by either fluorescence emission or synchro-

nous fluorescence spectroscopy. The generated spectra are simplified cross-sections of excitation-emission arrays.

Both emission and synchronous luminescence methods are useful for characterizing the source and concentration of various polyaromatic compounds. Current work on PCBs and PAHs demonstrates the usefulness and sensitivity of luminescence methods.

## FIELD USE

The applicability of luminescence methods to environmental work is increasing with greater availability of compact instruments. The CRDLV has field-deployable fluorescence instruments. In addition, a prototype of a

portable synchronous spectrofluorometer with a fiber optic probe is being developed for the CRD-LV through an interagency agreement with the DOE at Oak Ridge National Laboratory. Using these instruments, scientists

are able to identify and quantify total PAHs and PCBs. These methods are particularly good for environmental samples requiring relatively simple sample preparation. Field use is simple for this non-destructive

(Continued)

## FIELD USE (Continued)

tive technique. A typical field instrument has two parts - the spectrofluorometer and the controlling computer. Each of

these units is portable and suitcase-sized. The ease of use and lack of elaborate preparation steps makes UV-

vis luminescence an excellent choice for many hazardous waste sites.

## ADVANTAGES AND LIMITATIONS

UV-vis luminescence compares very favorably with many field techniques because it has high sensitivity, is non-destructive, and can analyze thermally labile samples or heavy compounds like tars and polar compounds like phenols.

This technology has a proven track record with the U.S. Coast Guard where it is used for oil spill identification. Extending this application into various environmental areas is the next step. The

### Advantages

- Very sensitive for aromatic and polyaromatic analytes
- Inexpensive
- Water is not an interferent
- Non-aromatic analytes usually do not interfere
- Little or no pretreatment required
- Simple microextraction procedure

### Limitations

- Needs derivatives for most non-aromatic analytes
- Interpretation may require special training
- Fluorescence yields vary

CRD-LV is committed to the careful application of existing

technologies to novel uses in environmental monitoring.

## FUTURE

Current research should lead to UV-vis fluorescence instruments that are smaller, cheaper, and more sensitive to a wider range of analytes. The development of reason-

ably priced small lasers may eventually replace xenon lamp sources. Rugged, tunable lasers in the UV range are being investigated. Some monitoring can be

done with a filter fluorometer saving the cost of the scanning step. The most versatile applications remain in the area of emission and synchronous luminescence methods.

## REFERENCE

Eastwood, D. and Vo-Dinh, T., *Molecular Optical Spectroscopic Techniques for Hazardous Waste Site Screening*, EPA 600/4-91/011, U.S. EPA, Environmental Monitoring Systems Laboratory - Las Vegas, 1991

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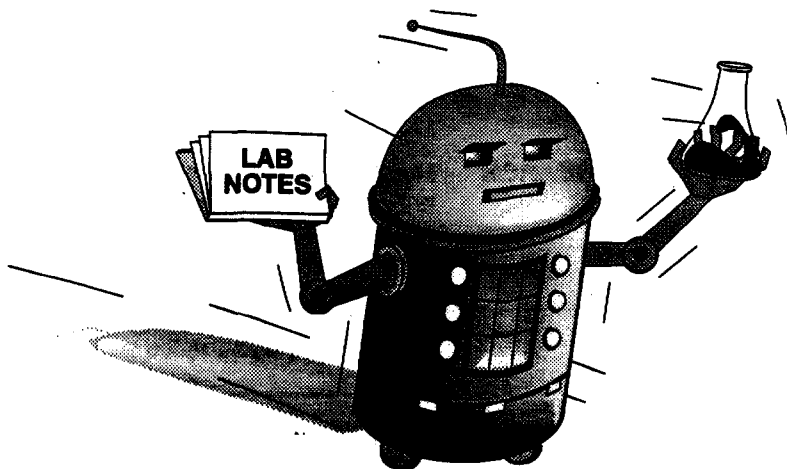
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TECHNOLOGY SUPPORT



# Robotics Technology in Environmental Sample Preparation



## INTRODUCTION

The Characterization Research Division in Las Vegas (CRD-LV) is supporting the use of robotics technology for routine analyses of environmental samples. The CRD-LV currently uses two robotics systems for inorganic analyses. Robotics minimizes the incidence of operator error and provides legally defensible documentation following chain-of-custody requirements.

Increasingly sophisticated robotics technology coupled with software that is user-friendly makes robotics attractive to laboratories that are concerned about the number of samples that can be analyzed with consistently high precision and improved accuracy.

The CRD-LV will provide technical document review and consultation to EPA

Regions who are considering the purchase of a robotics system. Evaluations of manufacturers bids and demonstrations of the CRD-LV systems are available through the Technology Support Center at the CRD-LV. This technology has increased the Laboratory's ability to perform quick-turnaround analyses that are backed up by strong documentation.

## HARDWARE

In a sense, robotics hardware is really analytical laboratory hardware. When the robot is used to weigh, dilute, and prepare samples for chromatographic analysis, for example, the hardware is a table, a rack of sample jars, an analytical balance, a solvent vessel, a shaker, and various arms and pipets that allow the work to progress. When a robotics network is being designed, it is important to consider parallel uses

that might be added for little extra expense. This design stage is critical in the cost effectiveness of the system. Scientists at the CRD-LV worked with manufacturers to ensure that the instruments were customized for particular uses, but were not confined to a single application.

An operator still weighs out the samples for analysis because environmental samples are too complex for

the robot to judiciously segregate. For a soil sample containing fines, coarse gravel, and a few miscellaneous twigs, human oversight is needed. The analytical balance, however, is tied into the robotics network so that transcription errors are eliminated. Therefore, robotics reduces human error but does not eliminate human intervention.

## SOFTWARE

Robotics systems come with easily modified software packages. Solvent amounts, volume of internal standards and surrogates, and time on the shaker can be adjusted easily. Software allows the robot to recognize bar codes, and to stop operation if a sample is dropped or broken.

A strong round robin study can be done when several laboratories use the same

robotics software. The elimination of operator bias gives a better indication of the true sources of variance in any investigation. The correct robotics system provides chain-of-custody records, fraud detection, simpler analytical QA, and round-the-clock performance.

The robotics system can be described as a computer - with arms. As such, it is no

smarter than the designers and operators of the system. The robot is not foolproof but merely fool-resistant. It will follow orders, add solvents, and shake samples. It cannot differentiate between HPLC grade and less pure methylene chloride, for example. The responsibility for good laboratory practice remains with the analyst.

## FUTURE RESEARCH

Robotics usage will be enhanced with increased ability for error recovery, allowing the system to know when samples have been switched, for example, and to correctly match samples with

their weights. Artificial intelligence and expert system technology might be coupled with robotics to give users systems that are capable of more intricate sample handling and decision

making. Microwave digestion applications and complex extraction procedures may soon be programmable at the robotics workstation.

## REFERENCES

Hillman, D. C., P. Nowinski, M. A. Stapanian, J. E. Teberg, and L. C. Butler, "A Single Laboratory Evaluation of a Robotic Microwave Digestive System", EMSL-LV, 1992.

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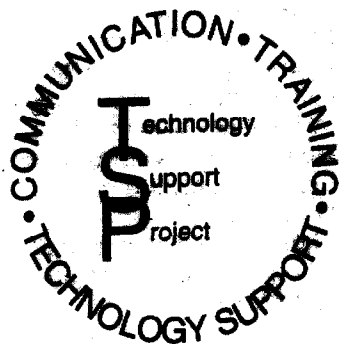
A copy of a video illustrating the CRD-LV robot in action is available free to Agency users from L. Butler.

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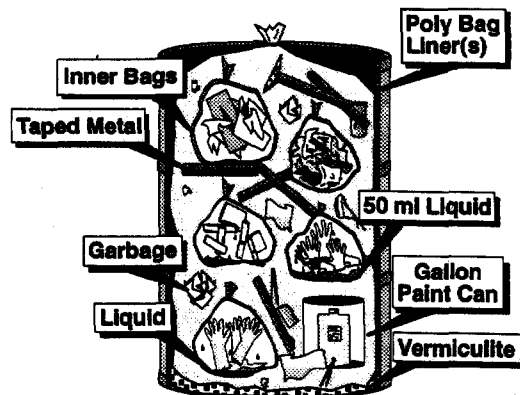
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TECHNOLOGY SUPPORT



# Guidance for Characterizing Heterogeneous Hazardous Wastes



## INTRODUCTION

The U.S. EPA and the U.S. DOE are interested in addressing the special problems presented in sampling heterogeneous hazardous waste ranging from physically diverse samples from landfills to chemically mixed waste found at many sites. This area of sampling and analysis poses problems to field and laboratory personnel engaged in the identification, classification, and quantitation of

potentially hazardous materials.

A recent workshop cosponsored by the DOE Office of Technology Development and the Characterization Research Division in Las Vegas (CRD-LV) resulted in a document that provides guidance for scientists working in this challenging area. *Characterizing Heterogeneous Hazardous Wastes:*

*Methods and Recommendations* (EPA 600/R-92/033) is available to Agency personnel through CERL. This document contains valuable information about proven protocols as well as innovative technologies and recommendations for further research. It presents a typical case study and a survey of the statistics involved in design and analysis.

## PLANNING THE STUDY

This chapter establishes a rational diagram to follow in the sampling and analysis scheme. It is a five-step process: preliminary planning, DQO process, sampling and analysis design, sample collection and analysis, and data assessment. Sampling heterogeneous matrices is

complex and presents a challenge to those planning the study.

Particular stress is placed on asking the right questions at the beginning of a study, searching for any pertinent historical data, and establishing DQOs that are realistic.

Examples are provided that prompt readers to look for potential pitfalls in a sampling scheme. Guidance is provided for the use of non-traditional statistical sampling plans and recommendations are made for the establishment of appropriate confidence intervals.

## QA/QC AND DATA QUALITY ASSESSMENT

In this chapter, the focus is on quality assessment strategies that can be used in the sampling of heterogeneous matrices and in the analysis of the subsequent data. The importance of a *priori* knowledge is stressed. An effective quality assessment process will provide useable data without stipulating onerous procedures upon

the already overworked sampling expert. The correct use of QA/QC samples such as replicates, duplicates, and co-located samples is discussed. Field evaluation samples and field matrix spikes are recommended. Even in unconventional methods, the use of well-planned QA/QC practices can identify random or biased

error and trace the error to its source.

The reader is referred to the document *A Rationale for the Assessment of Errors in the Sampling of Soils* (EPA/600/4-90/013) and to the software package, ASSESS, available through CERL to Agency users.

## SAMPLE ACQUISITION

This chapter specifies sampling procedures that should be followed when sampling heterogeneous hazardous waste – whether contained or uncontained. Contained waste is that found in drums or boxes. Uncontained waste is landfill litter and debris piles that exist at some sites. The monitoring of regulated landfills is required by law. Sometimes state monitoring requirements are more rigorous than federal guidelines.

Several questions arise when sampling heterogeneous

waste. Is it possible to obtain a sample of sufficient representativeness that the resultant data will truly reflect the type and level of contamination at the site? Is it correct to physically separate samples before analysis? Should this separation be based on physical characteristics or on contamination type? How can health risks be fairly evaluated when the contamination varies in level from trace to high percentages? Can homogenization steps be taken without compromising the quality of the data?

These questions are addressed and guidance is given in technologies ranging from soil-gas measurement and open-path FTIR to geophysical methods and aerial photography. Particular emphasis is placed on sample collection procedures and on handling steps. Field screening methods are discussed; X-ray fluorescence, vapor analyzers, and various spectroscopic techniques. Additional discussion focuses on radiography, gamma ray assay, and neutron assay methods.

## ANALYTICAL LABORATORY REQUIREMENTS

This chapter deals with the analysis of the samples as they are received by the analytical laboratory. If the sample arrives as a multiphase liquid or as a collection of various solids, decisions must be made about the analysis. It is crucial that any segregation or homogenization of samples be discussed with the decision makers. The DQOs should be consulted again and, as always, QA/QC plays a vital role in the generation of useable data.

A flow chart is provided to lead the reader through

several phases of the laboratory procedure. The consideration of *a priori* knowledge is important in the laboratory, too.

Fusion methods are discussed for use in the analysis of inorganic contaminants. Neutron activation analysis is suggested for some analyses of radioactive samples. Guidance is provided on the choice of sample size and the consideration of particle size. A table compares various radiation screening devices.

A section on the special requirements of mixed waste

samples documents the need for further refinement of analytical methods and the need for proper safety precautions. Waste disposal at the analytical laboratory is discussed and the reader is reminded that help exists in this area from the American Chemical Society's Task Force on RCRA.

The importance of proper reporting is stressed because the need for understanding reporting requirements in advance is often critical in the success of a study.

## FOR FURTHER INFORMATION

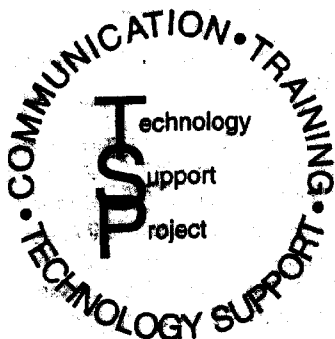
For further information about the document, *Characterizing Heterogeneous Hazardous Waste: Methods and Recommendations* (EPA/600/R-92/003) or to obtain a copy, contact:

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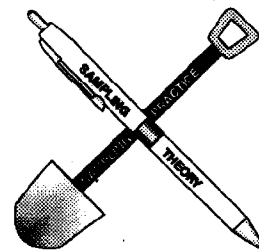


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TECHNOLOGY SUPPORT



# Correct Sampling Using the Theories of Pierre Gy



## INTRODUCTION

The Characterization Research Division in Las Vegas (CRD-LV) is interested in the optimization of sampling protocol, sampling tools, subsampling techniques, and sample analysis. The importance of obtaining representative samples in the field and retaining their integrity throughout the analytical procedures is fundamental to the generation of meaningful data. Because sampling correctness and representativeness is critical to the collection and handling of environmental samples, the CRD-LV has hosted short courses presented by M. Francis Pitard to explain and enforce the theories of Pierre Gy relating to sampling practice. The inherent heterogeneity of

soils presents a particular challenge to field personnel who are responsible for sampling hazardous waste sites. This heterogeneity is also a factor that must be addressed by statisticians, geostatisticians, and chemometricians as they develop sampling plans for the location and frequency of sampling. It affects the manner in which analytical chemists subsample in the laboratory. Finally, heterogeneity influences the interpretation of data and the decisions made about the actions taken to remediate contamination at a site. The theories of Pierre Gy present practical sampling and subsampling methods that can be applied for little or no added expense. Careful attention to these

techniques can result in samples that better represent the site and data that more truly represent the sample.

True and complete homogeneity is impossible to achieve because many factors, including gravity, work against it. But the extent of heterogeneity and its effect on environmental sampling can be minimized. Established methods from the mining industry are applicable to the sampling of soils. The work of George Matheron, father of geostatistics, and Pierre Gy, sampling expert, can provide useful insights for environmental scientists who are faced with sampling a complex matrix for trace contaminants.

## TYPES OF ERROR

Pierre Gy's theory addresses seven types of sampling error and offers proven techniques for their minimization. The seven major categories of sampling error cover differences within samples. Other differences can exist, such as, within space (covered by geostatistics) and within time (covered by chronostatistics.) The internal sample errors are:

**Fundamental Error:** This is loss of precision inherent in the sample and includes particle size distribution. It is circumstantial error. It can be reduced by decreasing the diameter of the largest particles or by increasing the sample volume.

**Grouping and Segregation Error:** Error due to non-random distribution of particles, usually by gravity. It can be minimized by compositing an analytical sample from many randomly selected increments or by properly homogenizing and splitting the sample.

**Long-range Heterogeneity Error:** This is fluctuating and non-random. It is spatial and may be identified by variographic experiments and can be reduced by taking many increments to form the sample.

**Periodic Heterogeneity Error:** This fluctuation error is temporal in character and

can be minimized by compositing samples correctly.

**Increment Delimitation Error:** Error tied to inappropriate sampling design and the wrong choice of equipment.

**Increment Extraction Error:** This error occurs when the sampling procedure fails to precisely extract the intended increment. Well-designed sampling equipment and good protocols are crucial.

**Preparation Error:** This error is the expression of loss, contamination, and alteration of a sample or subsample. Field and laboratory techniques exist to address this problem.

## SAMPLE INTEGRITY

To truly represent a lot (or a hazardous waste site) a sample must be both accurate and precise. Obviously, 100% accuracy and precision cannot be obtained. It is important to minimize the error that is introduced in that sample-taking and in the subsequent handling, subsampling, and preparation. If large-scale heterogeneity is ignored in a sampling design, data generated from the preferentially sampled

material will never truly reflect the character of the site.

Some sampling devices and protocols preselect fines or coarses. This error is very serious in environmental work where concentration is fundamental to decision making. For example, if the action level for compound X is 100 micrograms/kilogram, a sample containing very fine particles coated with compound X would exceed action

levels but a large rock of the same sample weight would not. But both samples came from the same site, in fact, from the same cubic meter of soil. If samples spanning all particle sizes are sent to the analytical laboratory, a very confusing picture of the site will emerge. When decisions are made based on the ensuing data, they will be incorrectly made (or made correctly by accident!)

## DEVICES

Correct sampling devices are essential to good sampling protocol and to good laboratory practice. Pierre Gy recommends scoops and spatulas that are flat, not spoon-shaped, to avoid the preferential sampling of coarse particles. Additional

care must be taken at the analytical laboratory, where error can be introduced by poorly designed riffle splitters, spatulas, and vibrating tools. It is recommended that the sample be subsampled using a system of alternate shovelling wherein a large

sample is "dealt out" into several smaller piles. One of these subsamples is chosen for the analysis. This method avoids preferential sampling by saving the subsample selection until last.

## SUMMARY

Methods developed for the mining industry can provide environmental scientists with guidance for the correct sampling and subsampling of soils. The sampling theories

of Pierre Gy are applicable to most sampling events at hazardous waste sites and to the successful subsampling of those samples at the analytical laboratory. Greater

sample volume yields data that better represent the site. Careful use of practices suggested by Pierre Gy will result in higher quality data for little or no added expense.

## REFERENCES

Pitard, F. F., *Pierre Gy's Sampling Theory and Sampling Practice*, 2 Volumes, CRC Press, Inc., Boca Raton, Florida. 1989.

## FOR FURTHER INFORMATION

For more information about the application of Pierre Gy's theories to environmental sampling, contact:

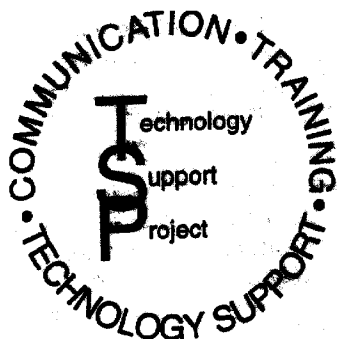
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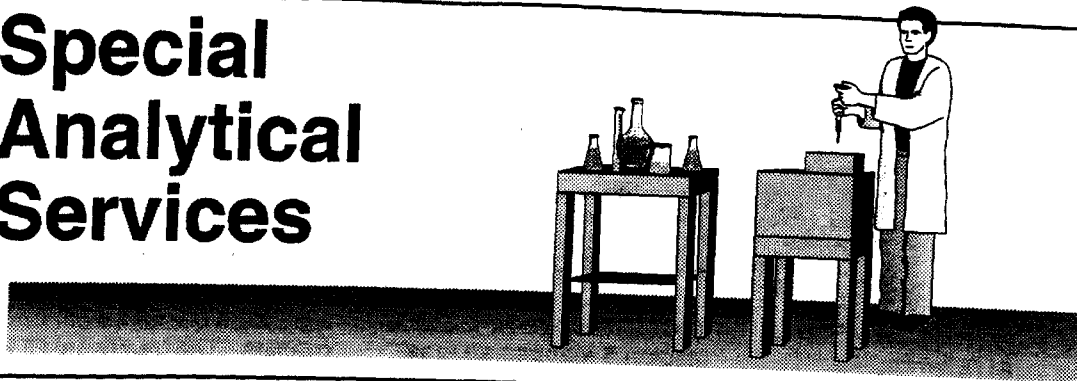
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TECHNOLOGY SUPPORT

# Special Analytical Services



## INTRODUCTION

The Characterization Research Division in Las Vegas (CRD-LV) has an excellent background in the preparation and analysis of non-typical samples that require special care, in-depth knowledge, and high-tech instrumentation. The EPA Regions are welcome to submit

special samples to the CRD-LV through the Technology Support Center.

Representative sampling and subsampling present challenges to field and laboratory personnel. The CRD-LV has experience and expertise in the handling of complex and

heterogeneous matrices and in the interpretation of results from non-routine samples.

The following examples illustrate the wide range of capabilities and analytical services available through the CRD-LV.

## DOUBLE EAGLE, 4TH ST. NPL SITES

At the request of Region 6, the CRD-LV analyzed complex mixtures of tar, asphalt, oily soil, sludge, and water samples from the Double Eagle and 4th St. NPL Waste Oil Sites. One main goal was to use various organic and inorganic markers to allow source identification between the two sites. Despite severe sample heterogeneity problems and matrix inconsistencies within

each site, numerous organic and inorganic markers were identified using ICP-MS and GC/high resolution MS. This allowed unambiguous source identification of samples from either of the two sites. It was then possible to correlate off-site wastes to one of the two sites.

A decision to use complete sample dissolution in closed high-pressure digestion

vessels for the inorganic indicator parameters paid off because volatile osmium was detected. This rarely detected analyte would not have been noticed if conventional methods of sample preparation had been used. The expertise gained in sampling, extraction, digestion, and analyses of these complex samples adds to the existing experience at the CRD-LV.

## JACK'S CREEK NPL SITE

The CRD-LV received unusual soil samples from Region 3's Jack's Creek NPL Site. The samples contained "an unknown purple compound". This compound was highly soluble in ethanol and other organic solvents but not in water. Ethanol extracts were analyzed by ICP-MS with a focus on compounds that could impart a purple color (such as chromium, nickel, and iodine). Iodine was detected in significant quantities and was verified in

several qualitative wet chemistry tests as complexed iodine. GC/MS analysis of a methylene chloride extract of the compound produced two identifiable peaks. The most likely match was leuco crystal violet, a reduced form of the aniline dye known as crystal violet. The presence of complexed iodine further confirmed this identification as developed leuco crystal violet. Through this series of analytical deductions, multidisciplinary scientists at the CRD-LV were able to

identify the mystery compound from the Jack's Creek Site.

The Jack's Creek Site also required analyses for chlorinated dibenzofurans. These compounds were successfully quantified in the presence of chlorinated diphenylether interferences by careful deconvolution of the GC/high resolution MS results. Quantification of these furans has not traditionally been attempted under such conditions.

## INDIANA HARBOR RCRA SITE

Indiana Harbor is a RCRA facility in Region 5. The Region needs to classify the sediments in the harbor to decide on the eventual disposal of dredged material. Oily sediment samples had

been analyzed previously by a CLP laboratory but the results were inconsistent between the total analyses and the toxicity characteristic leaching procedure (TCLP).

By using extra care in sampling and homogenization techniques, as well as use of excellent laboratory practices (ELP), CRD-LV scientists were able to provide the Region with consistent results.

## NORTH DRIVE NPL SITE

The North Drive NPL Site in Region 5 features an area contaminated with Prussian blue (ferrous and ferric cyanide compounds). Again, routine CLP analyses had yielded unsatisfactory results. The Prussian blue compounds at the site were found to be mixed with sulfides which distill along with

significant quantities of cyanide. The traditional CLP cyanide methods are inaccurate in the presence of sulfide interference.

CRD-LV scientists researched alternate cyanide methods that are less affected by sulfide interferences. The ASTM method for weak-acid dissociable

(WAD) cyanide gave results that were consistent when synthetic iron cyanide solutions containing sulfide interferences were analyzed. The North Drive Site samples are now being analyzed with the method which is easier to use and holds promise for all high-sulfide samples requiring cyanide analysis.

## INNOVATIVE METHODS

The CRD-LV is proud to maintain the instrumentation and personnel necessary to perform innovative analysis of difficult and unusual

samples. Teaming state-of-the-art equipment with highly specialized, multidisciplinary technical staff enables the Laboratory to provide high quality service to the EPA

Regions. The staff at CRD-LV is keeping current with the analytical demands of an increasingly complex environment.

## REFERENCES

Report on the Identification and Analysis of Potential Indicator Parameters for Sourcing Off-Site Contamination (Double Eagle and 4th Street Refinery NPL Sites), EMSL-LV TSC-17, July 1992.

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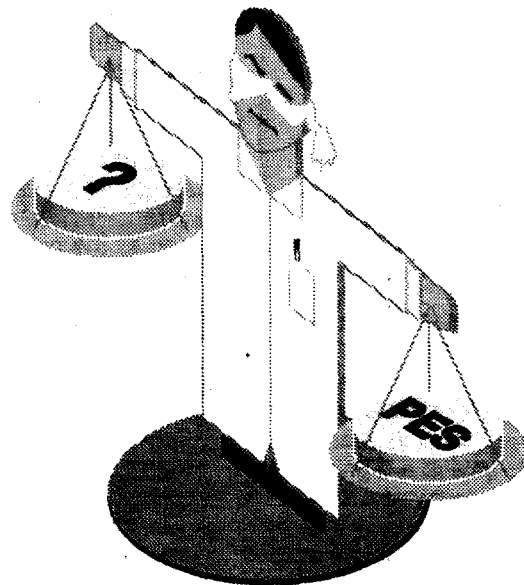




TECHNOLOGY SUPPORT



# Performance Evaluation Samples



## INTRODUCTION

Quality assurance (QA) and quality control (QC) are integral features of the Agency's programs for the detection and measurement of contaminants in the environment. QA monitors the planning, implementation and completion of sample collection and data analysis activities. The Characterization Research Division in Las Vegas (CRD-LV) has considerable experience in the design of effective QA programs. The Analytical Operations Center (AOC) of the Office of Emergency and Remedial Response has been preparing Performance Evaluation Samples (PES) with advice from the CRD-LV. AOC uses a Quality Assurance Technical Support

(QATS) contractor also located in Las Vegas to prepare the PES. The incorporation of PESs of known concentrations into a study is useful for evaluating the accuracy of the analytical procedures for real samples. The AOC is responsible for the production and distribution of PESs; the Office of Research and Development (ORD) provides technical direction and independent oversight.

Through the QATS program, the CRD-LV is assisting in the development, testing and distribution of PESs. PESs are available from QATS for a wide range of contaminants in various matrices. The most frequently requested

PESs are water and soil matrices with contaminants that are encountered in the contract laboratory program (CLP). The CLP is also managed by AOC.

PESs can be zero blind, single blind, or double blind. When the analyst knows that a sample is a PES and also knows the identity and concentration of the analytes of interest, the sample is zero blind. Zero-blind PESs are often called laboratory control samples (LCS). When the sample is known to be a PES but the identity and concentration of the analytes are not known, the sample is single blind. When the analyst is not aware that the sample is a PES, it is double blind.

## THE PES INVENTORY

Complex PESs for a variety of Superfund needs are provided by the AOC through QATS with oversight and technical direction from the CRD-LV. These samples are usually single blind because the physical appearance probably alerts the analyst to the fact that they are PESs but the identity and concentration of the analytes are not known.

The inventory of PESs available from the QATS includes low/medium organic compounds in water and in soil, low/medium inorganic compounds in water and in soil, chlorinated dioxins or dioxins/furans in soil and in sediments, low concentration organic and inorganic compounds in water, high concentration inorganic compounds in soil, soil/oil, oil,

and oil/water, and individual aromatics in soil.

The inventory is growing as new methods are developed for the preparation and preservation of PESs. Requests for site-specific PESs are filled if the requirement is general and is typical of several site categories. The development of site-specific PESs for a single site is too expensive.

## PES BY SITE CATEGORY

The National Priority List (NPL) recognizes more than 20 industrial site categories, ranging from battery acid sites to gasoline stations. The similarity of contaminants within these site categories is sufficient to warrant PES batches that address the needs of most individual sites within a category. The dissimilarity between samples within a category is usually a function of characteristics of the sample matrix.

The AOC, QATS, and the CRD-LV work with the

Regional site managers to provide PESs for various site categories in a variety of matrices. If a PES is not

available for a particular need, AOC, QATS, and the ORD will investigate the feasibility of designing a customized PES.

### Advantages

- Provides information about accuracy
- Legally defensible data
- Interlaboratory comparisons

### Limitations

- Difficulty matching matrices
- Visibility of PES
- Application to other situations must be explored

## FUTURE PLANS

The QATS is expanding its PES inventory. The Target Analyte Profiles (TAP) currently being developed by QATS describe sites by category. This system is based on the CLP Analytical Results Database (CARD) which contains a compilation of analyte/concentration information from Superfund sites in the Regions.

Meeting the existing needs for PESs and for technical support in their use and evaluation is a major goal, as is responding to growing Regional demands for quality PESs within the hazardous waste programs.

Another effort is the establishment of Regional repositories for PES. This inven-

tory will enable the Regions to evaluate the performance of contract laboratories by comparing results obtained for the same PES.

Working within AOC and ORD guidelines, QATS is ready to meet the needs of the Regions.

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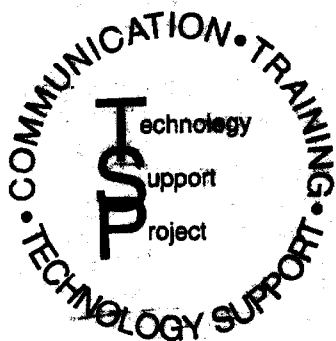
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TECHNOLOGY SUPPORT

# Monitoring Airborne Microorganisms



## INTRODUCTION

The Characterization Research Division in Las Vegas (CRD-LV) is evaluating methods for monitoring airborne microorganisms. Monitoring indoor air spans several research areas including radiochemistry (radon, low-level radiation), analytical chemistry (formaldehyde, cleaning solvents), and microbiology (fungi, bacteria, and other microorganisms). Through a cooperative research and development agreement (CRDA) with Dow-Corning, microbiologists at the CRD-LV are investigating the use of various monitoring techniques that assess the type and extent of microbiological contamination in indoor air.

It was necessary to create a laboratory setting which closely resembled a typical room but which could be controlled and monitored by scientists who wished to investigate various types of contamination, air movement patterns, and the efficacy of methods for their removal. This exposure chamber (known locally as "the plywood palace") is located in a research laboratory at the CRD-LV. The room is about 13'X13'X8' and is constructed of plywood sheets with a 6-inch insulation between the outer and inner walls.

Since its construction in 1990, the room has served as a test facility for various

research efforts. Principal among these, so far, are evaluations of methods for monitoring the quality of indoor air into which fungal spores have been introduced. Future efforts will include the evaluation of various mitigation agents and indoor air purification systems, the effects of human and mechanical movement on the dispersal of microorganisms in an enclosed area, and comparisons of testing and monitoring procedures for the accurate evaluation of indoor air quality.

## THE FACILITY AND EQUIPMENT

The indoor air facility is a custom-built room that has a well-sealed viewing window and an enclosed anteroom that serves as a suiting-up area for scientists donning respirators and protective clothing. The room has five sampling trees made of stainless steel and equipped with thermocouples and humidity sensors. Thus far, all testing has been done in an atmosphere at constant temperature and humidity. The air flow is 150 cfm, which is the standard recommended circulation for indoor air. The room is equipped with a HEPA (high efficiency particle air) filter that removes airborne particles greater than 1  $\mu$ m in diameter. The

room has a wood floor, that is presently covered with carpet to check the behavior of airborne microorganisms in the presence of absorbing materials. The simplicity of the room makes it a perfect mini-lab, able to adapt to various research requirements.

The equipment used to measure the extent and pathways of indoor air contamination varies from simple gravimetric methods to expensive mechanical samplers. The simplest method for retrieving fungal spores is the placement in the room of Petri dishes containing an agar medium. The drawback of this method

is that it relies on gravity and therefore preferentially samples larger species. Samplers that use a vacuum to draw indoor air onto an agar coated plate may err on the side of lighter species. A laser technique is being evaluated, too. So far, the most promising instrument for the detection of fungal spores is a six-stage sampler that is a tiered bank of sieve-like agar plates that filter out the larger species at the top and reduce gradually to the smallest species at the bottom. Several tests have been run that indicate this method is the most precise of the methods tested for monitoring studies of fungal spores.

## ADVANTAGES AND LIMITATIONS

The obvious advantage to conducting monitoring evaluations in a simulated but typical room is that results can be assumed to reflect the performance of testing equipment in a non-controlled environment. The room itself is easily changed to measure the effect of various parameters, such as fluctuating temperature and humidity,

the presence of carpeting, the use of biocides, and changes in the construction materials of the room.

A limitation of this facility is its inability to represent certain indoor environments, such as an open foyer, an older edifice constructed of materials that are no longer available, or an isolated situation

that may set the biological stage for a new or unnoticed microorganism.

The facility is a good working model that is flexible enough to provide an excellent testing ground for various monitoring devices and methods that target specific microorganisms in typical indoor air.

## FUTURE

Questions continue to arise about the quality of indoor air, the nature of microorganisms in an indoor environment, and the effective use of various biocides. The CRD-LV will continue to test

monitoring techniques designed to address these concerns. Future work in this facility will expand the species list to include bacteria as well as fungi. The ability to characterize and

enumerate indoor air contamination is the first step in solving an environmental problem of widespread concern.

## REFERENCES

Biological Contaminants in Indoor Environments, P. R. Morey, J. C. Feeley, Sr., J. A. Otten, eds., STP 1071, ASTM, Philadelphia, PA, 1990

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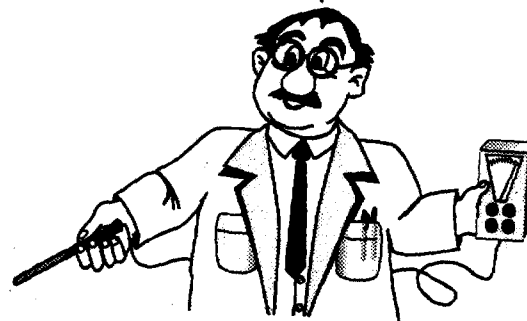


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TECHNOLOGY SUPPORT



# Biosensors For Environmental Monitoring



## INTRODUCTION

CRD-LV is conducting research on biosensors for environmental monitoring applications. This research is designed to address a critical and growing need for real-time and *in situ* monitoring devices which can be used at Superfund sites and RCRA facilities as well as for

ground water monitoring. Because biosensor technology lends itself to fast, economical and continuous monitoring capabilities, development of these systems to complement classical analytical measurements is expected to result in a substantial cost benefit, especially when sample

turnaround time and cost per analysis are important issues. Biosensors are currently being considered for development for detection of environmental pollutants such as polychlorinated biphenyls (PCBs), chlorinated hydrocarbons, benzene/toluene/xylene (BTX) and pesticides.

## BACKGROUND

A biosensor is an analytical device composed of a biological sensing element (enzyme, receptor or antibody) in intimate contact with a physical transducer (optical, mass or electrochemical) which together relate the

concentration of an analyte to a measurable electrical signal. In theory, and verified to a certain extent in the literature, any biological sensing element may be paired with any physical transducer. The majority of reported biosensor research

has been directed toward development of devices for clinical markets; however, driven by a need for better methods for environmental surveillance, research into this technology is also expanding to encompass environmental applications.

## POTENTIAL USES

The unique characteristics of biosensors will allow these devices to complement current field screening and monitoring methods such as immunoassay test kits as well as fiber-optic and chemical sensors. For example, enzyme-based biosensors show the potential for continuous monitoring of compounds such as phenolics in process

streams, effluents and groundwater. Further, since certain of these devices can operate in high concentrations of organics such as methanol and acetonitrile, these biosensors show promise for *in situ* monitoring of mixed organic wastes. Other potential applications include down-hole or perimeter groundwater surveillance as well as process stream monitoring for

remediation procedures. Antibody-based biosensors show the potential for coupling immunochemical specificity with recent advances in fiber-optics and microelectronics. These biosensors may yield instantaneous analysis of a wide variety of analytes without the need for multiple reagents and incubation steps required for immunoassay kits.

## FUTURE DEVELOPMENT

A variety of laboratory prototype biosensors have been reported which measure a fairly broad spectrum of

environmental pollutants. Although specific requirements must be met for each field monitoring scenario,

some general requirements for biosensors used in environmental applications are listed in the following table.

**FUTURE  
DEVELOPMENT  
(Continued)**

Requirement	Specification Range
Cost	\$1-15 per analysis.
Portability	Can be carried by one person; no external power
Assay time	1-60 minutes
Personnel training	Can be operated after 1-2 hour training period
Format	Reversible, continuous, <i>in situ</i>
Matrix	Minimal preparation for groundwater, soil extract, blood and urine
Sensitivity	Parts per million to parts per billion
Dynamic range	At least two orders of magnitude
Specificity	Enzymes/receptors: specific to one or more groups of related compounds  Antibodies: specific to one compound or closely related group of compounds

**FUTURE  
RESEARCH**

In addition to the basic and applied research conducted through CRD-LV, efforts

are currently underway for laboratory evaluation and field testing of commercial biosensors in preliminary

stages of development as well as those which are "in the queue" for introduction into the commercial market.

**REFERENCE**

Biosensors for Environmental Monitoring, K. R. Rogers & J. N. Lin, Biosensors & Bioelectronics 7, 317-321. 1992.

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TECHNOLOGY SUPPORT



# EPA Training Programs Available Through the CRD-Las Vegas



## INTRODUCTION

The EPA is committed to providing training for environmental scientists at federal, state, and local regulatory agencies. The EPA Characterization Research Division-Las Vegas (CRD-LV) of the National Exposure Research Laboratory (NERL), strives to "transfer its laboratory discoveries into products and applications that contribute measurably to environmental preservation and the National economy." The CRD-LV is part of the EPA Office of Research and Development which has considerable expertise and experience in various applications of analytical chemistry, quality assurance procedures, and other topics related to the monitoring and characterization of hazardous waste sites.

The CRD-LV has developed several training courses that are available to EPA employees and other federal, state,

and local government employees and contractors whose work would benefit from increased knowledge in the subject areas. Funding arrangements must be negotiated.

These courses are available to a suitable class size at the CRD-LV or can be presented at any EPA Regional Office upon request, if funding is available. No more than three courses or demonstrations can be given on a specific topic per fiscal year.

Target audiences include scientists and engineers who require specific training or continuing education in the latest methods, and environmental decision-makers whose responsibilities require knowledge of a broad range of technologies.

## LABORATORY

The CRD-LV has been a center of analytical chemistry applications - even before there was an EPA! The laboratory was established almost forty years ago as the Public Health Services Southwestern Radiological Health Laboratory (SWRHL). SWRHL work consisted of air monitoring for radionuclides and radioactivity whole body counting for Nevada citizens living downwind of the Nevada Test Site. In 1970, when EPA was created, SWRHL became an ORD research laboratory and was renamed the Western Environmental Research Laboratory. Since then effort has been expended on developing, evaluating, validating, and utilizing advanced monitoring methods for hazardous, radioactive, and mixed waste.

The Technology Support Center (TSC) at the CRD-LV bridges the gap that

sometimes exists between research and end users. Through the TSC, the EPA Regions are able to access the expertise of the CRD-LV for special analytical services and high-tech instrumental support during the monitoring and characterization of hazardous waste sites, including those regulated under Superfund and RCRA.

Analytical equipment at the CRD-LV includes a suite of chromatographic instruments, high-resolution mass spectrometers, capillary electrophoresis units, a fully equipped immunochemical laboratory, and geophysical measurement devices.

Training in the use of these instruments will be arranged if there is sufficient interest and if resources can be negotiated.

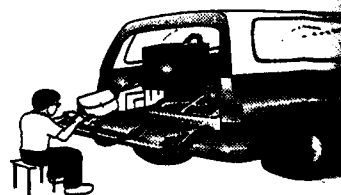
## FIELD

The CRD-LV provides the EPA Regions with access to a growing number of field analytical instruments and instruction in their use. When a Region makes a request for technical support from the TSC at the CRD-LV, a quality assurance project plan (QAPP) is written, a field crew is deployed, measurements are taken, data are analyzed, and the Region is supplied with a final report detailing the findings and results.

Each stage of this process is carefully researched and implemented according to the latest technological guidance available. A carefully written QAPP can spell the difference between the success or failure of a field analytical procedure. By establishing data quality objectives early in the process, expensive repeat analyses and extra site visits can be avoided. A field crew with experience in using and modifying portable analytical instruments can reduce the need for expensive and less immediate analytical procedures done at a remote laboratory. This experience is especially critical in the successful

application of innovative technologies. Data analysis is integral to the success of any field (or laboratory) effort. The use of geostatistics, for example, can provide much-needed information about the spatial distribution of contamination at a site. The TSC provides the Region with all pertinent documentation and includes significant results and conclusions in a final report. The technical support provided by CRD-LV is legally defensible.

Training in field quality assurance (QA) procedures is important in the overall education of those involved in sampling and analysis at hazardous waste sites and in a variety of ecological monitoring activities. The CRD-LV training in field QA shows sampling personnel and scientists how to extract the most information from field analytical results.



## SOFTWARE

Scientists involved in various programs at the CRD-LV have developed computer software packages that aid environmental decision-makers at all stages of site characterization.

The CRD-LV is able to provide training on the use of the following software programs:

See Software Continued on last page



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## HYDROGEOLOGICAL SITE CHARACTERIZATION

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## ICP-MS DATA AUDIT TRAINING

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## ON-SITE QA OF FIELD SAMPLING AND FIELD CHEMICAL ANALYSIS

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## USE OF PERFORMANCE EVALUATION MATERIALS

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## UNDERGROUND STORAGE TANK CHARACTERIZATION

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### COURSE GOAL:

The goal of the *Underground Storage Tank Characterization* course is to provide instruction to personnel engaged in the characterization and monitoring of leaking Underground Storage Tanks (USTs). The course will provide a background in the methods and procedures used, as well as the regulations that govern the areas surrounding these facilities.

### PREREQUISITES:

None.

### DESCRIPTION:

This 3-day course provides an overview of the UST regulations, methods for monitoring leakage from USTs, and a survey of the current sampling and analytical methods and instruments used to assess the level and extent of any leakage. Monitoring approaches include, but are not limited to, gas chromatography, fiber optic chemical sensors, immunoassays, and various "sniffer" instruments.



### COST:

To be negotiated.

### CONTACT:

For information about scheduling the *Leaking Underground Storage Tank Characterization* course, please contact:

Dr. Larry C. Butler, Training Program Director  
CRD-LV  
(702)798-2114

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## HYDROGEOLOGICAL SITE CHARACTERIZATION

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## ICP-MS DATA AUDIT TRAINING

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## ON-SITE QA OF FIELD SAMPLING AND FIELD CHEMICAL ANALYSIS

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## USE OF PERFORMANCE EVALUATION MATERIALS

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### COURSE GOAL:

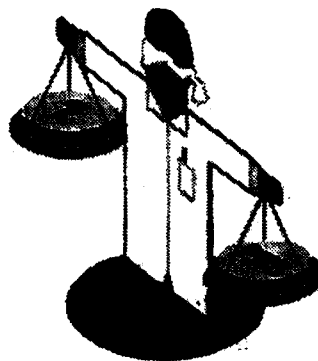
The goal of the *Use of Performance Evaluation Materials* course is to instruct personnel in the design, preparation, and use of performance evaluation materials as part of a comprehensive laboratory QA/QC program.

### PREREQUISITES:

None.

### DESCRIPTION:

This 3-day course will provide personnel with instruction to enable them to design, prepare, and use Performance Evaluation Materials (PEMs) for evaluating the performance of CLP and non-CLP laboratories. The course targets EPA Regional personnel who design PE programs, evaluate laboratories, review data packages, and prepare or use PEMs. The course encourages the use of PEMs and provides an avenue for support of Regional EPA efforts by CRD-LV. Specific topics covered include: selection of PEMs; requirements and suitability of PEMs for specific cases or sites; suitability of PE sample recipes for specific sites and problems; how to make PEMs; advantages and disadvantages of single-blind versus double-blind PEMs; PEM introduction into the case or sample delivery group; interpretation and use of results; and coordination of PE research results with CRD-LV.



### COST:

To be negotiated.

### CONTACT:

For information about scheduling the *Use of Performance Evaluation Materials* course, please contact:

Dr. Larry C. Butler, Training Program Director  
CRD-LV  
(702)798-2114

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## HYDROGEOLOGICAL SITE CHARACTERIZATION



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## ICP-MS DATA AUDIT TRAINING

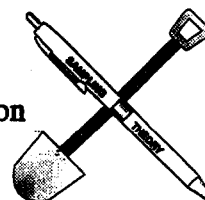


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## ON-SITE QA OF FIELD SAMPLING AND FIELD CHEMICAL ANALYSIS



**COURSE GOAL:** The goal of the *On-Site Quality Assurance of Field Sampling and Field Chemical Analysis* course is to provide training in the procedures involved in the preparation and implementation of on-site field audits, with an emphasis on proper field sampling and field chemical protocols and related documentation.



**PREREQUISITES:** None.

**DESCRIPTION:** The goal of the course is to provide instruction that enables the students to perform on-site field QA/QC audits. This 3-day course presents instruction on all aspects of the preparation necessary for an on-site visit to a field site. The course emphasizes proper methods of sample collection, chemical analytical procedures, and related documentation. The course consists of two sections: classroom discussion of the paperwork component of field on-site visits, and a classroom exercise that provides a walk through of a simulated field situation. While the course is specific to Superfund Quality Assurance guidelines, it is useful to anyone who conducts field on-site visits.

**COST:** To be negotiated.

**CONTACT:** For information about scheduling the *On-Site Quality Assurance of Field Sampling and Field Chemical Analysis* course, please contact:

Dr. Larry C. Butler, Training Program Director  
CRD-LV  
(702)798-2114

## HYDROGEOLOGICAL SITE CHARACTERIZATION

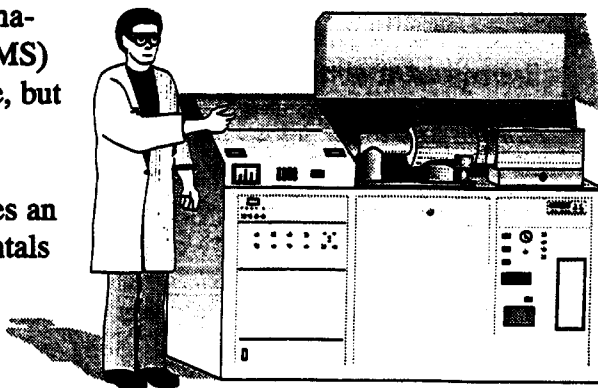
### ICP-MS DATA AUDIT TRAINING

**COURSE GOAL:** The goal of the *ICP-MS Data Audit Training* course is to train personnel in the interpretation and auditing of ICP-MS data.

**PREREQUISITES:** Prior experience in auditing inductively coupled plasma-mass spectrometry (ICP-MS) data packages is desirable, but not mandatory.

**DESCRIPTION:**

This 3-day course provides an overview of the fundamentals of ICP-MS Method 6020, including the QA/QC requirements specific to ICP-MS, and the differences between ICP-MS and ICP-OES. The course also addresses the use of the new QA/QC forms for ICP-MS. Since the potential for molecular interferences exists at many masses, much of the course is devoted to recognition and correction of these interferences with elemental and higher-level equations. Discussion will also focus on the use of internal standards for determining data usability near detection limits, recognition of matrix effects, and memory effect recognition.



**COST:** To be negotiated.

**CONTACT:** For information about scheduling the *ICP-MS Data Audit Training* course, please contact:

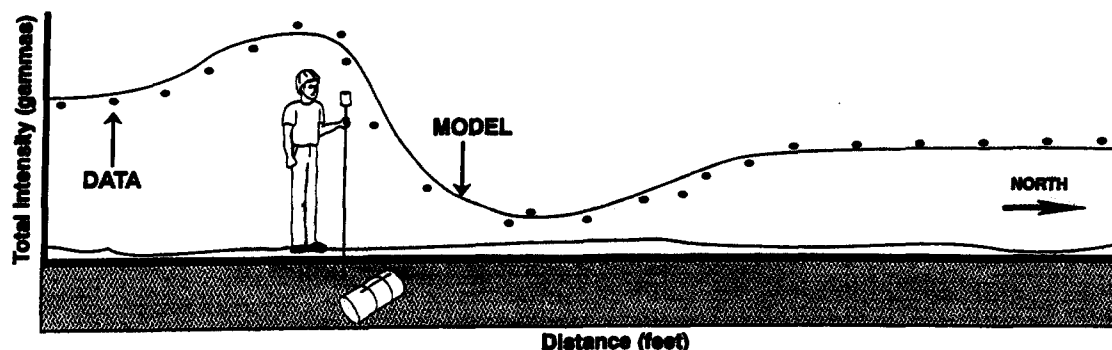
Dr. Larry C. Butler, Training Program Director  
CRD-LV  
(702)798-2114

## HYDROGEOLOGICAL SITE CHARACTERIZATION

**COURSE GOAL:** The goal of the *Hydrogeological Site Characterization* course is to provide a background in the various methods and approaches used by field personnel to assess the presence, type, and extent of subsurface hydrogeological contamination at hazardous waste sites.

**PREREQUISITES:** None.

**DESCRIPTION:** This 3-day course is based on the earlier Superfund University Training Institute course on the same topic. It outlines various instrumental, procedural, and statistical processes that are critical to successful monitoring of the subsurface environment. These methods include, but are not limited to, geophysical methods, use of the geoprobe, soil-gas measurement technologies, and the use of geostatistics to obtain information from spatially diverse data.



**COST:** To be negotiated.

**CONTACT:** For information about scheduling the *Hydrogeological Site Characterization* course, please contact:

Dr. Larry C. Butler, Training Program Director  
CRD-LV  
(702)798-2114

## SPECIALTIES



The CRD-LV specializes in the correct application of traditional and innovative monitoring methods, and the statistical and quality assurance protocols that support these methods. There are three branches at the CRD-LV: the Analytical Sciences Branch (ASB), the Monitoring Sciences Branch (MSB), and the Radiation Sciences Branch (RSB).

The ASB programs range from innovative monitoring methods, such as ion mobility spectrometry, immunochemistry, and capillary electrophoresis to refinements of established analytical procedures, such as gas chromatography/mass spectrometry and inductively coupled plasma-mass spectrometry.

The MSB features a remote sensing program, with expertise in aerial photointerpretation and geographical information systems. The EPA's ecological monitoring effort, the Environmental Monitoring and Assessment Program (EMAP), is also a part of MSB.

The RSB supports some of the research at the Nevada Test Site and is also an EPA center for radiation monitoring, such as ambient gamma radiation monitoring and internal dosimetry.

The training program at the CRD-LV can draw on the expertise of these programs. Courses can be tailored to meet the specific requirements of a given audience. Contact the director of the training program for further details.

## PROTOCOL

The courses described in this brochure were developed for environmental scientists and engineers whose work requires additional knowledge in the subject areas. Though the courses are primarily intended for EPA employees, they are open on an as-available basis to other federal agencies, state and local

regulators, and government contractors.

To discuss the details of these course offerings, contact the training program director, Dr. Larry Butler, CRD-LV, at (702) 798-2114 or Fax (702) 798-3146.

## GUIDE TO INSERTS

The inserts at the center of this document describe five courses already available through the training center at CRD-LV. These courses are:

- Underground Storage Tank Characterization
- Use of Performance Evaluation Materials
- On-Site Quality Assurance of Field Sampling and Field Chemical Analysis

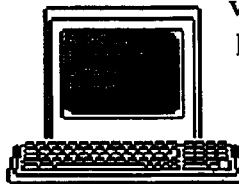
- ICP-MS Data Audit Training
- Hydrogeological Site Characterization

The locations and times for the CRD-LV training courses are flexible. The CRD-LV will try to meet the requirements of the student groups.

## SOFTWARE Continued

**Assess** is an interactive program designed to assist the user in statistically determining the quality of data from soil sample analyses done on-site.

**Scout** is a user-friendly program developed by statisticians to identify multivariate or univariate outliers, to check variables for lack of normality, to graph raw data, and to output the results of principal component analyses.



**Geo-EAS** is interactive software developed to meet the needs of environmental scientists who work with spatially distributed data, allowing them to benefit from geostatistical tools without becoming geostatisticians.

**CADRE** is a program used for data validation by the Regions that provides data analysts with quick and reliable data for use in decision-making at hazardous waste sites.

## THE FUTURE

The five courses described in the inserts are the flagships of the CRD-LV training program. New courses may be developed on tape audit interpretation, data validation (using the Regional functional guidelines) or statistics, health and safety issues in site work, or

hands-on courses in innovative immunoassay test kit methods.

The CRD-LV is committed to its mission of technology transfer, technical support, and high-quality training.

## FOR FURTHER INFORMATION

For information about the courses available through the CRD-LV training program, contact:

Dr. Larry Butler, Director  
Training Program  
U.S. Environmental Protection Agency  
National Exposure Research Laboratory  
Characterization Research Division  
P. O. Box 93478  
Las Vegas, NV 89193-3478

(702)798-2114  
(702)798-3146 (Fax)

For information about the Technical Support Center (TSC), contact:

Mr. Ken Brown, Director  
Technology Support Center  
U.S. Environmental Protection Agency  
National Exposure Research Laboratory  
Characterization Research Division  
P.O. Box 93478  
Las Vegas, NV 89193-3478

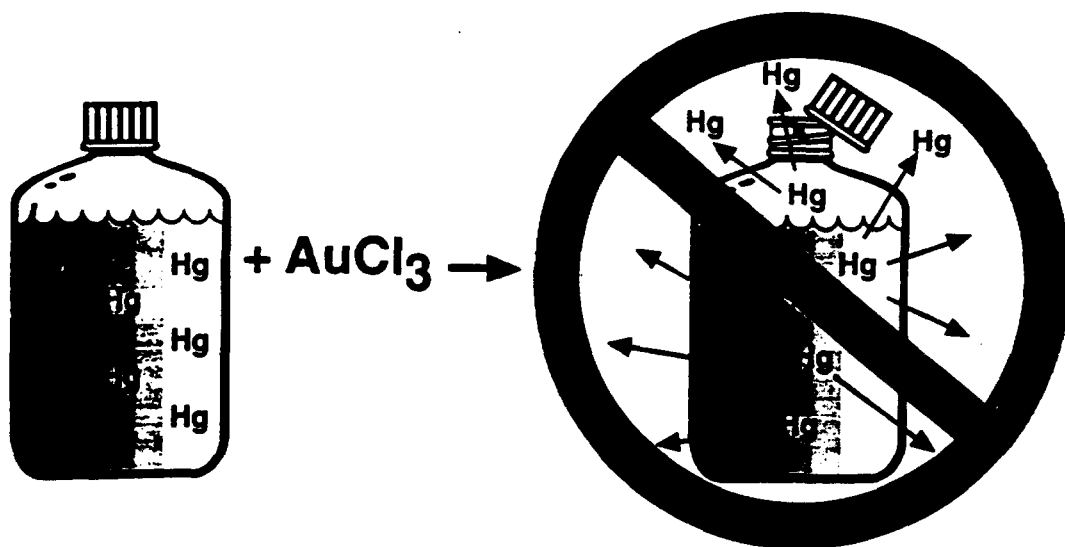
(702) 798-2270  
(702) 798-3146 (Fax)

This informational brochure was designed and developed by Clare L. Gerlach and Kit M. Peres, Lockheed Environmental Systems & Technologies Company, Las Vegas, Nevada.





# Mercury Preservation Techniques



## BACKGROUND

The analysis of environmental samples and the value of the observed data are dependent upon several factors:

- \* how representative the sample is,
- \* how stable the sample is, and
- \* how reliable the analytical procedures are.

Historically, interest has been focused on the stability of mercury compounds, especially in aqueous matrices. Factors that affect mercury stability include: the form of mercury, the container material, the matrix, and the preservation techniques.

The currently accepted method in the contract laboratory program (CLP) inorganic statement-of-work (SOW) for preservation of mercury samples requires a stabilization

with 2%  $\text{HNO}_3$ , with an allowed holding time of 26 days prior to instrumental analysis. Researchers at the Characterization Research Division in Las Vegas (CRD-LV) have investigated the reliability of 2%  $\text{HNO}_3$  as a preservative by studying the analytical data from synthetically prepared Performance Evaluation (PE) water samples.

Aqueous quarterly blind (QB) samples that were spiked with inorganic forms of mercury showed significantly low mercury recoveries when analyzed using 2%  $\text{HNO}_3$  preservative.

Some researchers believe that mercury ions bind to the reactive sites on the surface of the high-density polyethylene (HDPE) water sample containers. Mercury ions are thought to be reduced at these sites. Then elemental mercury is lost

on or through the walls of the plastic bottles. Mercury vapor may also be lost when the bottles are uncapped. Thus, mercury ions are lost to subsequent analyses and reenter the environment. Most low level (less than 100 ppb) mercury in synthetic environmental samples is lost within just a few days using 2%  $\text{HNO}_3$  preservation.

The research challenge was to find a method for stabilizing aqueous mercury samples that would be simple to use in the field, effective at retaining the true mercury concentration, and could be used with all major inorganic analytical instruments without presenting an interference. Though several potential preservatives were tested, only one was found that would meet requirements.



## THE CRD-LV SOLUTION

Researchers at the CRD-LV found that a trace amount of gold chloride ( $\text{AuCl}_3$ ) added to the  $\text{HNO}_3$  solution preserved all forms of mercury. The gold acts as a strong oxidizing agent that converts or maintains mercury as mercuric ion which remains in solution. Optimization of this technique revealed that a 1 ppm solution of  $\text{AuCl}_3$  in  $\text{HNO}_3$  was sufficient and did not affect any other analytes or analytical techniques. The  $\text{AuCl}_3$  adds no toxicity to the process or waste products.

The price of gold is not a major factor in the overall cost of sampling and analysis

because such low quantities of gold are needed. The cost for the  $\text{AuCl}_3$  is only about 10% of the cost of the  $\text{HNO}_3$  — or, about \$3 per 100 samples.

Inorganic samples preserved with  $\text{AuCl}_3$  can be analyzed by anodic stripping voltammetry (ASV), cold vapor atomic absorption spectrometry (CVAAS), and even by inductively coupled plasma mass spectrometry (ICP-MS), without interferences from the gold in solution. Previously, ICP-MS was not used for mercury analysis because the mercury would deposit in the ICP-MS sample introduction system and be released during subse-

quent analyses (carryover). The gold stabilization method directly prevents deposition by keeping all mercury in solution. The ability to use ICP-MS for mercury analysis adds a valuable multi-element instrument to the suite of mercury detection systems.

There are additional benefits using  $\text{AuCl}_3$ . Preservation with  $\text{AuCl}_3$  doubles the solubility of silver in 2%  $\text{HNO}_3$  and therefore helps stabilize silver. Silver is a relatively unstable element in water samples and this added preservation is a bonus.

## APPLICATION

When water samples are taken for mercury analysis, field personnel should add  $\text{HNO}_3$  with  $\text{AuCl}_3$  to a final concentration of 2%  $\text{HNO}_3$  and 1-ppm  $\text{AuCl}_3$ . The current procedure only calls for  $\text{HNO}_3$ . The samples can then be shipped to the analytical laboratory and analyzed without concern about mercury holding times. Early CRD-LV experiments indicat-

ed that mercury concentrations in samples preserved with  $\text{AuCl}_3$  did not decrease even after two years of storage. Using the  $\text{AuCl}_3$  preservative, NIST trace mercury in water standards (SRM 1641B) are stable for at least 10 years (the certificate value can still be met when analyzing 10 year old 1641B). By extending the length of time samples can be

held before analysis and by providing a simple method for ensuring sample integrity, the  $\text{AuCl}_3$  spiking procedure could save time, money, and enhance data reliability. Costs to monitor and enforce mercury holding times would no longer be an issue when  $\text{AuCl}_3$  preservation techniques are used.

## LIMITATIONS

Experiments show that adding concentrations of several ppm  $\text{AuCl}_3$  can precipitate Au and, therefore, may threaten to coprecipitate other analytes.

But even at 2 ppm (twice the recommended concentration), coprecipitation was not observed in synthetic samples. If field personnel inadvertently

add twice the amount of  $\text{AuCl}_3$  needed, there would be no negative effect on the analytical results.

## REFERENCES

Dobb, D. E., R. C. Metcalf, R. W. Gerlach, and L. C. Butler, "Optimizing Reactions for Preserving Mercury with Gold Chloride in Environmental Water Samples," Emerging Technologies in Hazardous Waste Management VI, Proceedings of the I & EC Special Symposium, American Chemical Society, Atlanta, GA, September 1994, pp. 1438-1441.

Dobb, D. E., G. A. Raab, J. T. Rowan, and L. C. Butler, "Preservation of Mercury in Environmental Aqueous Performance Evaluation Samples," Emerging Technologies in Hazardous Waste Management V, Proceedings of the I & EC Special Symposium, American Chemical Society, Atlanta, GA, September 1993, pp. 426-429.

## FOR FURTHER INFORMATION

Dr. Larry Butler  
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U.S. Environmental Protection Agency  
National Exposure Research Laboratory  
Characterization Research Division-Las Vegas  
P.O. Box 93478  
Las Vegas, NV 89193-3478  
(702) 798-2270



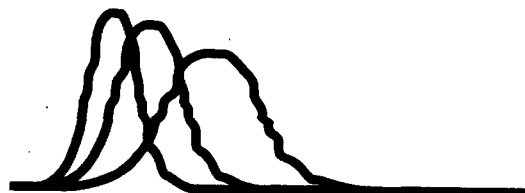
The Technology Support Center fact sheet series is developed by Clare L. Gerlach, Lockheed Environmental Systems & Technologies Company, Las Vegas.

TECHNOLOGY SUPPORT



# Field-Portable Scanning Spectrofluorometer

**CRD-LV  
Innovative  
Technology**



## The Need:

Field-portable instruments are available for the qualitative and quantitative evaluation of volatile organic compounds and non-volatile inorganic elements. Compounds that fall between these volatility extremes have received less attention in recent years. And yet these compounds comprise a surprising number of important contamination categories at Superfund and RCRA sites.

Polyaromatic hydrocarbons (PAHs) in complex mixtures such as oils, creosotes, and tars are found on numerous hazardous waste sites and, because of their high molecular weight, present special challenges to analytical chemists and instru-

ment developers. These compounds have relatively high luminescence yields and, therefore, can be readily measured by spectrofluorometry.

A recent technology that is in the production prototype stage is the Field-Portable Scanning Spectrofluorometer (FPSS). It is a light-weight battery-operated instrument that has shown early promise as a screening device for petroleum oils, PAHs and, especially, creosotes.

Creosote (wood preservation) and coal gasification sites are widespread, especially in the southeastern United States. These are complex sites that usually have various

PAHs in addition to the creosotes. These compounds are currently quantified by gas chromatography but their tarlike composition makes them difficult to detect and destructive to columns and detectors. The development of a field-portable instrument to rapidly identify and quantify PAH mixtures, such as creosotes, oils, asphalts, or coal tars is an important step in filling a field analytical niche.

The FPSS prototype is ready for field demonstration and comparative studies. It is anticipated that the FPSS will provide a more rugged and less expensive alternative to traditional methods for screening PAHs.

## The Use:

Scientists working at the Characterization Research Division in Las Vegas (CRD-LV) have performed laboratory evaluations of the battery-operated FPSS developed by T. Vo-Dinh and his co-workers at Oak Ridge National Laboratory.<sup>1,2,3</sup> Table 1 shows the physical characteristics of the instrument.

The FPSS can perform emission and synchronous wavelength scans. In the emission mode, relatively low detection limits are achieved (Table 2). The emission mode is useful for the determination of total PAHs or in identifying and classifying oils. In the synchronous mode both the excitation and emission monochromators are scanned simultaneously with a constant wavelength offset. The advantage to synchronous mode is that it separates spectra of compounds with a different number of fused rings, sharpens spectra, and allows the relative amount of various PAH classes to be quantified.

The FPSS consists of three parts: a small

**Table 1. Physical Characteristics of the Field-Portable Scanning Spectrofluorometer**

	SIZE	WEIGHT
Instrument	48 x 40 x 21 cm (18.5 x 11.5 x 8")	11.5 kg
Battery Pack	31 x 18 x 15 cm (12 x 7 x 6")	11.0 kg

suitcase-sized instrument that houses the optics and electronics, a battery pack, and a lap top computer used for instrument control, data storage and analysis. The spectral coverage of the instrument is 210-650 nm. The instrument parameters are chosen by the operator who uses the computer to control the instrument.

The FPSS can be operated two ways: using a

standard fluorescence cuvette cell or a bifurcated optical fiber. The optical fiber attachment is 2-meter long and allows direct screening of water samples. The cuvette can be used with liquid samples or extracts of soils. When the optical fiber attachment is used, care must be taken to avoid interference from light. This can be done by covering the sampling area with a black cloth.

**Table 2. Limit of Detection (S/N = 3)**

	SYNCHRONOUS (cuvette)	EMISSION (cuvette)	SYNCHRONOUS (fiber)
Perkin Elmer LS50 (laboratory instrument)	0.17*	0.02	24
FPSS prototype	3.5	0.55	1

\* All concentrations ng/mL of anthracene

## The Limits:

Some areas of concern exist relative to the successful operation of the FPSS in a field situation. The ruggedness of the optical components is crucial

to the in situ applicability of the system. The unit was shipped from Oak Ridge National Laboratory to the CRD-LV without affecting the optical alignment or

electronics. The instrument has been demonstrated to withstand normal handling in the laboratory. The instrument is ready to be

(continued on next page)

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**The Limits:  
(continued)**

demonstrated at a hazardous waste site.

The FPSS is particularly suited to the classification or identification of oils or PAH compounds. It can also be used with site-specific standards to quantify total oils or PAHs. It can be used to

determine relative amounts of the PAH classes present. In rare instances, like spills of solvents or PAHs with very high fluorescent yields and sharp structures such as benzo-(a)pyrene, it can be used to detect and quantify identified

PAHs. There is greater spectral separation capability when the instrument is operated in synchronous mode but lower detection limits can be achieved using the emission mode.

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**The Status:**

Laboratory evaluations and research efforts have resulted in a draft fluorescence method for the analysis of PAHs which is in the final stages of acceptance by the American Society for Testing and Materials. A comparison of the optical fiber mode and the standard cuvette mode was performed on samples of anthracene in methanol. This study showed the cuvette mode to be 2-3 times more sensitive than the optical fiber mode.

Synchronous luminescence has been demonstrated to be useful in characterizing crude and fuel oils.<sup>4</sup> The technique can be used to produce spectral fingerprints for the identification of oil contamination types and sources. The FPSS proved its ability in a study comparing samples from an oil spill with samples of the source oil which were provided by the U.S. Coast Guard.

The FPSS has shown considerable promise for the classification and quantitation of PAH compounds and oily mixtures. The next step is to take the portable instrument to a hazardous waste site where it can be evaluated against standard methods in a well-planned experimental design. The development of the FPSS was sponsored by the CRD-LV and commercialization is being planned.

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**References:**

<sup>1</sup> T.Vo-Dinh, "Synchronous Excitation Spectroscopy" in *Modern Fluorescence Spectroscopy*, Vol. 4, Edited E.L. Wehry, Plenum Press, New York, 1981, pp. 167-192.

<sup>2</sup> T. Vo-Dinh, "Synchronous Luminescence Spectroscopy: Methodology and Applicability", *Applied Spectroscopy*, Vol. 36, 576, 1982.

<sup>3</sup> J.P. Alarie, Vo-Dinh, T., Miller, G., M.N. Ericson, S.R. Maddox, W. Watts, D. Eastwood, R.L. Lidberg, and M. Dominguez, "Development of a Battery-Operated Portable Synchronous Luminescence Spectrofluorometer", in press, (Review of Scientific Instruments).

<sup>4</sup> K.J. Siddiqui, Lidberg, R.L., Eastwood, D., and Gibson, G., "Expert Systems for Classification and Identification of Waterborne Petroleum Oils", *Monitoring Water in the 1990s, Meeting New Challenges*, ASTM STP 1102, J.R. Hall and G.D. Glysson, Editors, American Society for Testing and Materials, Philadelphia, 1991.

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## The Contacts

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*For further information about synchronous luminescence spectroscopy, contact:*

Mr. William H. Engelmann, Manager  
Advanced in Situ Monitoring Program  
U.S. Environmental Protection Agency  
National Exposure Research Laboratory  
Characterization Research Division  
P.O. Box 93478

Las Vegas, NV 89193-3478  
(702) 798-2664

*For information about evaluating the FPSS at a hazardous waste site (Superfund or RCRA), contact:*

Mr. Ken Brown, Director  
Technology Support Center  
U.S. Environmental Protection Agency  
National Exposure Research Laboratory  
Characterization Research Division  
P.O. Box 93478  
Las Vegas, NV 89193-3478

(702) 798-2270  
(702) 798-3146 (Fax)

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*The Technology Support Center fact sheet series is developed by Clare L. Gerlach, Lockheed Environmental Systems & Technologies Company, Las Vegas*

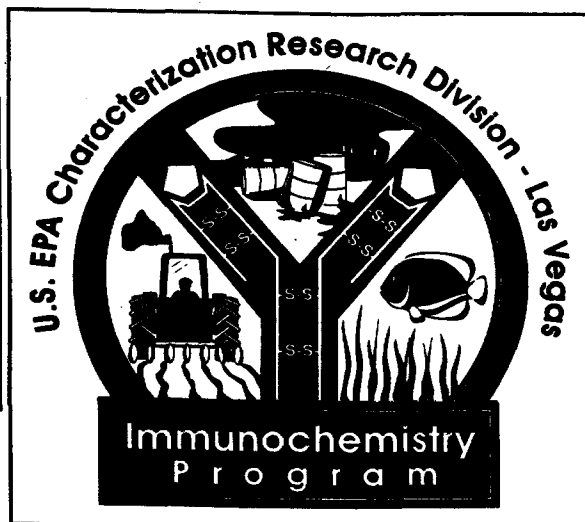


TECHNOLOGY SUPPORT



# Immunochemical Analysis Of Environmental Samples

**CRD-LV  
Innovative  
Technology**



## The Need

Field methods used for detecting compounds of environmental significance traditionally have been derived from standard laboratory methods. When laboratory methods are adapted to the field, they are often relatively slow, insensitive, expensive, and require bulky transportable equipment and skilled operators. There is a need for rapid, sensitive, low-cost, portable, and simple field methods for analysis of environmental samples. Immunochemistry offers those advantages. The only specialized equipment needed is a spectrophotometer, microtiter plates or test tubes, precision pipets, and immunologic reagents.

Commercial manufacturers sell kits for field screening, and new equipment and methods are being developed for rapid, accurate field analysis of a wide variety of analytes, such as heavy metals, dioxins, and PCBs, that are found at Superfund and RCRA sites. As a result the regulator and regulated communities view immunochemistry as a powerful technology for screening analysis of environmental contaminants.

Immunochemistry includes techniques such as immunoaffinity chromatography and immunoassay. Sample preparations based on immunoaffinity take advantage of the attraction between an

antibody and a specific analyte. The procedure has great potential for cleanup of complex samples like soils and sludges. By rinsing a sample over an antibody-treated surface, chemists can isolate particular compounds that adhere to the antibody. The isolated compound is then eluted from the immobilized antibody and is ready for analysis by chromatography or immunoassay. One common immunoassay is the enzyme-linked immunosorbent assay (ELISA). In this technique, the selectivity of the antibody for the analyte and the resultant antibody-analyte complex is the basis for the specificity of immunoassays.

## The Use

The Characterization Research Division in Las Vegas (CRD-LV) is pioneering an investigation into the usefulness of immunochemical techniques for monitoring the extent of contamination in environmental and biological matrices. CRD-LV has developed and demonstrated several of these techniques and believes that they hold great promise for the quantitative analysis of target analytes for use in ground-water surveillance, *in situ* hazardous waste site monitoring, and assessment of human exposure. Current work involves the analysis of chemicals like PCBs, nitroaromatics, and certain pesticides that are difficult to analyze by other analytical methods. CRD-LV has sponsored two national meetings that focused on regulatory issues and technological advances in environmental immunochemistry. These meetings brought together government, industry, and university scientists to discuss problems of mutual interest in the field.

A 1993 Technology Support Center project at a Superfund site in Region 5 demonstrated the usefulness of immunochemical methods for screening PCBs in soil and river sediment. This project was an example of

cooperation between EPA, DOE, the state of Michigan, and various contractors. Two immunoassays and a chloride-ion specific electrode were used on site and the real-time analytical results were compared with standard GC results from EPA method 8081. Preliminary results show good agreement between the immunoassays and GC and even stronger correlation could be achieved with tighter quality control measures.

In addition, other EPA offices have applied immunochemistry for screening and analysis in their programs. The Office of Water has used immunoassays to screen indirect discharges of specific analytes for permitting under the Clean Water Act (304h). Sample analysis data may soon be used for comparison and compliance monitoring within selected industries, such as commercial laundries. The Office of Pesticides is looking at ways to shorten the pesticide registration process by using immunochemistry as a cost-effective technology.

Other government agencies and universities are studying immunochemical methods. The Food and Drug Administration (FDA) may use immunoas-

says to obtain data for the calculation of safe concentrations of residues. A recent university project used immunoassays to track contamination during the 1993 Midwestern flood. In applications as diverse as organic geochemistry and military operations, immunochemical methods have been used for volatile organic compound measurement. The U.S. Department of Agriculture (USDA) is integrating immunoassays into rapid test procedures for detection of residues in meat and poultry. Results from these tests will be used in regulatory and compliance programs for veterinary drugs, sanitation, and pest control. The National Institute for Occupational Safety and Health (NIOSH) has applied immunoassays to herbicide research, clinical analysis, biomarkers, and immune biomonitoring. They use the methods to detect morphine factor, alachlor, atrazine, cyanazine, metalachlor, and 2,4-D. State laboratories have analyzed soil samples and water from private wells using immunochemical test systems for triazine (atrazine) samples.

The results of EPA's Superfund Innovative Technology Evaluation (SITE) studies indicate

## The Use (continued)

a strong correlation between field immunoassays, laboratory immunoassays, and gas chromatography-mass spectrometry.

Another field use of immunochemistry that is being explored at

CRD-LV, the personal exposure monitor (PEM), may revolutionize safety and exposure requirements for workers who deal with hazardous chemicals. Immunochemical dosimeter badges can be used to detect

pentachlorophenol and nitroaromatics, and are being developed for parathion and chlorpyrifos. These badges are lightweight, inexpensive, quick, and provide a real time indication of exposure.

## The Limits

The use of immunochemical techniques is gaining acceptance in the environmental sciences. One need that is being addressed is that of specificity. Frequently, immunoassays are available for a class of compounds, like PCBs. Specific quantitation for each component has been difficult.

The development of PEMs, for example,

must address the question of diffusion of chemicals through a semipermeable membrane, the optimum concentration of the antibody, detection limits of the PEM and quantitation by immunoassay, the efficiency of the antibody in capturing the analyte, and the capacity of the device.

Validation studies of reproducibility, matrix

effects, field trials, false negatives/positives, and correlation with other tests will assist acceptance of immunochemical methods at Superfund and RCRA sites. The legal defensibility of immunochemical results is yet to be determined.

Advantages and limitations are summarized below.

Advantages	Limitations
<ul style="list-style-type: none"> <li>• Field portable</li> <li>• User friendly</li> <li>• Quick and inexpensive</li> <li>• Potential for wide range of analytes</li> <li>• Useful for many matrices</li> <li>• Low detection limits</li> </ul>	<ul style="list-style-type: none"> <li>• Separate immunoassay needed for each analyte</li> <li>• More complex analysis required for quantitation of specific analytes</li> <li>• Long development time for new antibodies and methods</li> </ul>

## The Status

One new avenue of investigation is the use of antibody-coated, fiber-optic immuno-sensors. Another application is the integration of robotics capability for high

sample throughput and the development of a tiered analytical approach, i.e., biological and environmental samples, biomarkers, target analytes, and degradation products.

This system of analytical procedures will enable scientists to measure contamination at the source, follow the fate and transport of residual amounts, and assess

*(continued on next page)*



## The Status (Continued)

human exposure. Multianalyte immunoassays that can identify several analytes are expected to expand the desirability of immunoassay technology for environmental use. Work in this area is already underway at CRD-LV and elsewhere. Other applications of immunochemistry, such as multianalyte optical immunobiosensors and

biorefractometry, are being developed.

Industry recently formed the Analytical Environmental Immunochemistry Consortium (AEIC), which is focusing on performance-based method guidelines, method validation, and formation of consensus on regulatory and technological issues. The National Technology Transfer Center (NTTC) offers a

vehicle for collaborative studies. Cooperative Research and Development Agreements (CRADAs) between industry and the government can be used to promote technology development and licensing of immunochemical applications. The CRD-LV has a Technology Transfer Office that is able to coordinate CRADAs for the development of immunochemical methods.

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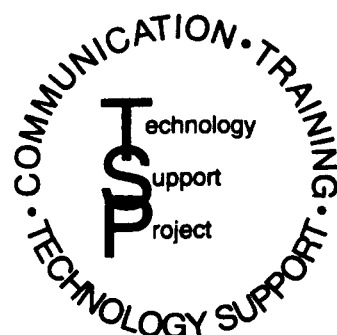
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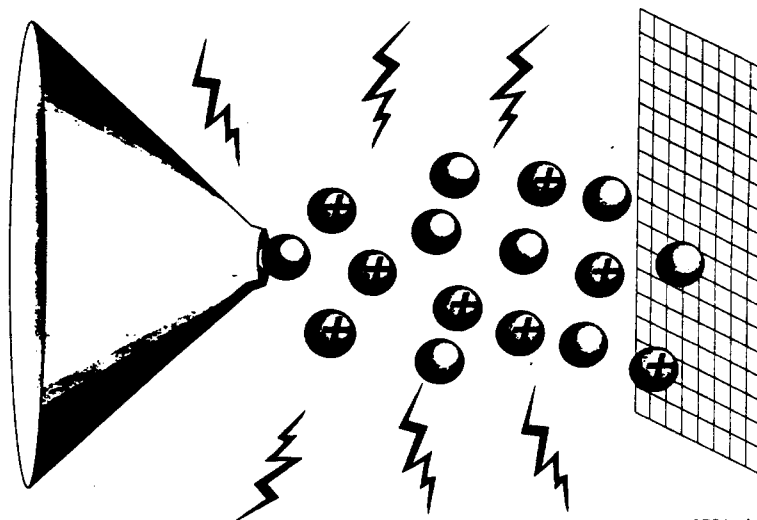
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Clare L. Gerlach, Lockheed Environmental Systems & Technologies Company, Las Vegas*

TECHNOLOGY SUPPORT



# Ion Mobility Spectrometry for the Analysis of Soil-Gas Samples

**CRD-LV  
Innovative  
Technology**



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## THE NEED

Environmental scientists recognize the need to quantify vinyl chloride and related compounds of environmental significance in soil gas at levels of 1 ppb or lower. Current field-portable methods, like gas chromatography - mass spectrometry (GC-MS) and GC equipped with a variety of traditional detectors, lack either the low cost, compound specificity, or ruggedness required for successful measurement techniques for

many of the analytes of interest.

Ion mobility spectrometry (IMS) has been used in various laboratory applications since the 1970s. It was adapted by the U.S. Army for use in hand-held chemical agent monitors (CAMs). The EPA is interested in the application of IMS to the area of environmental risk assessment analysis. Here, quick results at low cost are essential to the suc-

cessful characterization and remediation of hazardous waste sites.

Vinyl chloride, other chlorinated gases, and many chlorinated solvents are regulated at concentrations near the 1 ppb level in soils and water. These compounds are frequently trapped in the soil-gas spaces and are difficult to analyze because of the physical problems of obtaining and preserving the sample as well

## THE NEED (Cont.)

as the challenges inherent in the subsequent analysis.

The Characterization Research Division in Las Vegas (CRD-LV) and its cooperators at Washington State University (WSU) have conducted laboratory studies on a field-portable GC coupled with a Fourier transform ion mobility spectrometer (GC-FTIMS). Results are very encouraging and the next step is to test this method *in situ* at a hazardous waste site. The CRD-LV has

been investigating the use of IMS for environmental samples since a Superfund Innovative Technology Evaluation (SITE) study in 1990 indicated that IMS, with some refinements, could be useful for the characterization of environmentally significant organic compounds at hazardous waste sites.

Building on earlier work, scientists at WSU and the CRD-LV have developed this new hyphenated technique

that enhances the power and applicability of IMS. The GC-FTIMS merges the separation power of capillary gas chromatography with the sensitivity of ion mobility spectrometry and incorporates a Fourier transform to achieve ruggedness for *in situ* analysis. This instrumentation is in the prototype phase of development and is ready for field demonstration and evaluation.

## THE USE

Figure 1 is a schematic diagram of the IMS system. Reactive ions are formed from air or carrier gas molecules by using either a nickel-63 beta source or a photoionization source. These ions then react with analyte molecules, after having been separated by GC, to form ion clusters which are then measured by atmospheric-pressure time of flight (IMS). The ions enter a drift

region where they move through an applied field toward a collector electrode. The electrode current is monitored continuously, allowing a mobility spectrum to be measured. The specificity is imparted by the ionization preferences of analytes and the mobility differences of the ion clusters. Separations are a function of ion size.

Selectivity of IMS for various analytes is based on the atmospheric pressure ionization events themselves, which relate to the proton and electron affinities of the analytes, the polarity of the products (i.e., positive or negative ions) and the mobility of those ions. Analytes with higher proton or electron affinities than other constituents of the ambient environment are differentiated

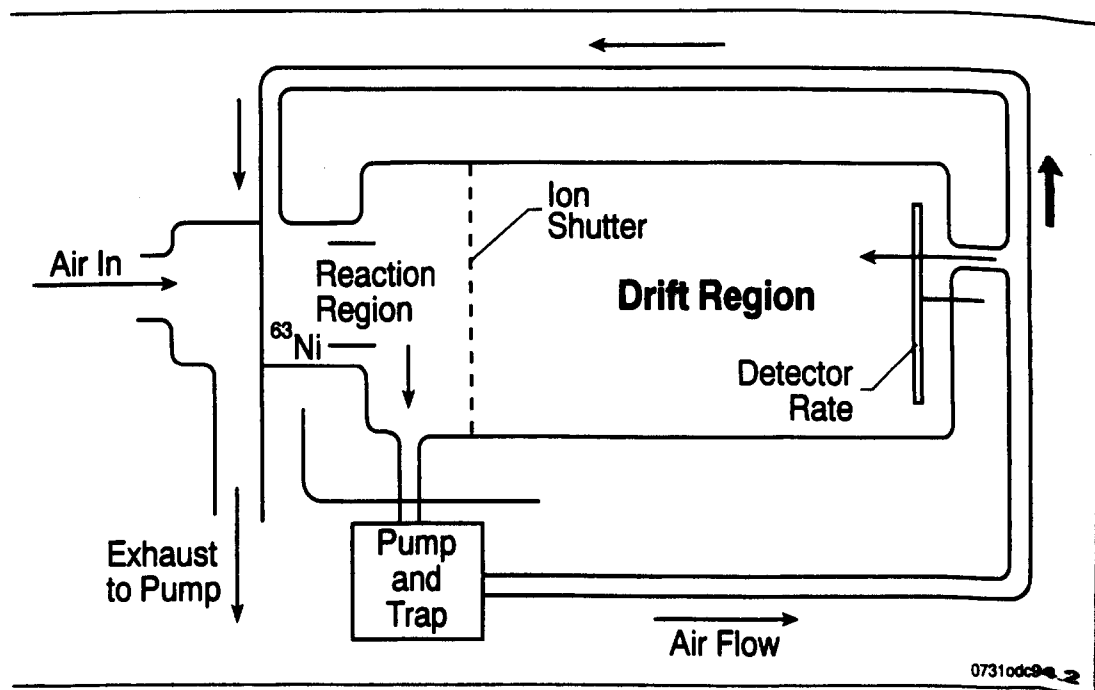


Figure 1. Schematic diagram of functional components in an Ion Mobility Spectrometer.

## THE USE (Cont.)

and detected easily. Analytes with low affinities can be measured when competing chemicals with higher affinities are not present. Thus, the compounds in Table 1 are better suited to analysis by IMS than are compounds like hexane and benzene. Varying humidity can result in the formation of ion-water clusters that cause errors in both the identification and the quantitation of the target analyte. This obstacle can be overcome by using GC prior to high-temperature IMS.

Scientists working at WSU and the CRD-LV have evaluated the GC-FTIMS system in the laboratory for various compounds, especially vinyl

chloride. Table 1 provides a partial list of analytes that can be detected by IMS with low limits of detection.

Experiments have been conducted on improving the sensitivity and selectivity of IMS.

These include experiments involving the ion source for IMS, and the refinement of an electrospray needle (Wittmer et al., 1994) to be used in electrospray-ion mobility spectrometry (ES-IMS).

**Table 1. Some common compounds that are detectable using GC-FTIMS.**

- |                                   |                          |
|-----------------------------------|--------------------------|
| • Benzyl chloride                 | • Phenols                |
| • Halogenated compounds (various) | • Phosphorus trichloride |
| • Hydrogen cyanide                | • Toluene diisocyanate   |
| • Nitro-compounds (explosives)    | • Vinyl chloride         |
| • Organophosphorus compounds      |                          |

## THE LIMITATIONS

IMS is sensitive to changes in humidity, which result in ion-water clusters that can cause erroneous identification and quantitation. This problem can be addressed by coupling GC to the IMS. Introduction by GC is imperative to eliminate interferences from the other organic compounds in the air. Though early laboratory work is encouraging, GC-FTIMS is still in the research stage. Its performance at a Superfund or other hazardous waste site remains to be seen.

Another complication occurs when analyte concentration is

too high. The ion chamber can be saturated easily — sometimes the instrument is too sensitive!

Some variability has been noted between various preconcentrator tubes that are sometimes used in IMS work.

The multipoint calibration curves used in some laboratory studies indicate that, for a Ni-63 ionization source, linearity decreases as the analyte concentration increases. The use of a photoionization source, in contrast, is linear over five orders of magnitude.

The use of Fourier transform provides some ruggedness to the analysis but may introduce a sense of black-box signal control. Though the prototype instrument is not set up for analyst intervention, that intervention may sometimes be warranted. The first few demonstrations of the GC-FTIMS system may benefit greatly from the technical input of an expert. The true value of the instrumentation will be seen when novice users can rely on the results obtained.

## THE STATUS

The period of extensive laboratory analysis is now at the stage where the instrument and methodology are ready for field demonstration and validation. Laboratory research

will continue on the models (notably, ES-IMS) that are not at the demonstration stage yet. Additional research may focus on the use of IMS to analyze soil samples, perhaps when

coupled with a headspace method that would free up trapped analytes prior to detection.

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## FOR FURTHER INFORMATION

For more information about GC-FTIMS, contact:

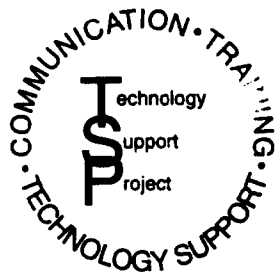
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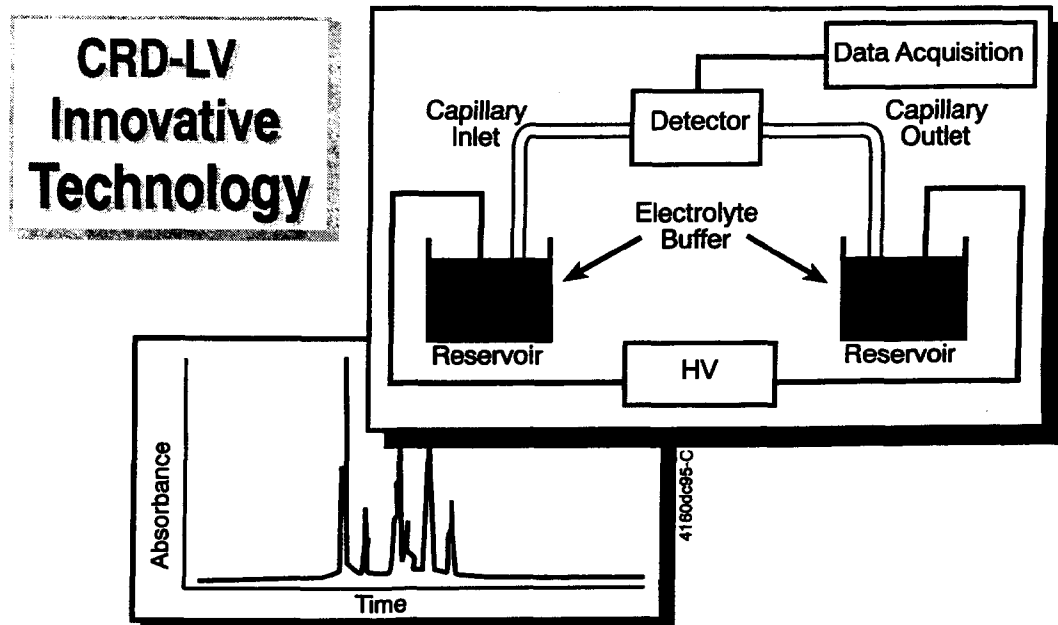
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TECHNOLOGY SUPPORT



# Capillary Electrophoresis for Environmental Monitoring



## THE NEED

The Analytical Chemistry Research Program of the National Exposure Research Laboratory's Characterization Research Division-Las Vegas (CRD-LV) is developing new methods for determining toxic and hazardous chemicals in samples from hazardous waste sites. This research is guided by several goals for analytical methods:

- Shorter analysis time to reduce costs and improve quality control procedures.
- Improved separations performance and applicability to

a wide spectrum of analytes, including nonvolatiles, as compared with current techniques based on capillary gas chromatography (GC).

- Field-screening capability to achieve faster results and better coordination between sampling and analytical workers.
- "Green" chemistry techniques that reduce the generation of laboratory waste (e.g., low solvent consumption) while simultaneously reducing personnel exposure to toxic chemicals.

- Simple technology, exportable to foreign countries and applicable to a broad range of analytes in a continuous monitoring format.

These goals are summed up by the phrase "cheaper, better, and faster," and are being met by an innovative separations technology called capillary electrophoresis (CE) that is new to environmental analysis.

Traditional methods for introducing a sample into an analytical device have various drawbacks. Liquid introduction of samples and liquid

## THE NEED (Cont.)

chromatographies and electrophoretic separations are the more universally applicable techniques since they do not depend on volatility of analytes or have molecular weight limitations. Thermally labile and polar compounds often deposit in the injector systems of gas chromatographs (even cold on-column retention gap systems) to degrade chromatography, precision, and quantitative accuracy. High performance liquid chromatography (HPLC) has attempted to fill the need for liquid state separations, but its application to ionic organics, neutral

hydrophobic compounds, and inorganic ions has not been universal. CE is a separations technique that can meet the goals stated above while filling a central, cross-cutting role in analytical chemistry for polar volatiles, most semivolatiles, nonvolatiles (e.g., herbicides), inorganic cations, inorganic anions, and biomarkers (i.e., indicators of exposure). Introduced in 1981, CE is now firmly established as the technique of choice for pharmaceutical and biomedical analysis.

CE is easily interfaced with optical detection methods

based on Uv-visible absorption, indirect detection (UV or fluorescence), and laser-induced fluorescence (LIF) detection.

CE methods that are applicable to routine problems are emerging, and EPA-approved CE methods are anticipated shortly. CE technology is widely developed commercially, and EPA staff at CRD-LV are confident that current CE methods are sufficiently robust to provide valuable contributions to environmental assessment at the present time

## THE USE

CE instrumentation is simple (see illustration in the brochure header). A fused silica capillary (typically 0.050 or 0.075 mm X 27 to 57 cm) connects two buffer (electrolyte) reservoirs. A high-voltage power supply (ca. 30 kV) connects the reservoirs via the buffer-filled capillary. The technique has been miniaturized as "CE on a chip", and it is capable of adaptation to continuous monitoring applications based on fast separations (see below).

CE analyte bands travel with flat profiles that produce extremely high resolutions (see Figure 1). Reported values usually range from 250,000 to 1,000,000 theoretical plates, with exceptional values up to 2.7 million.

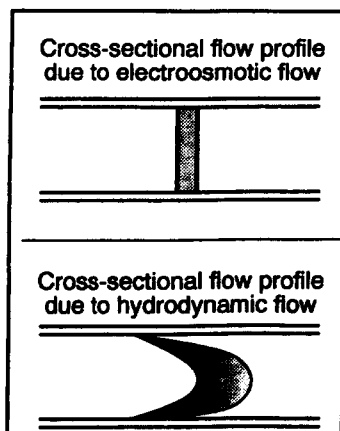


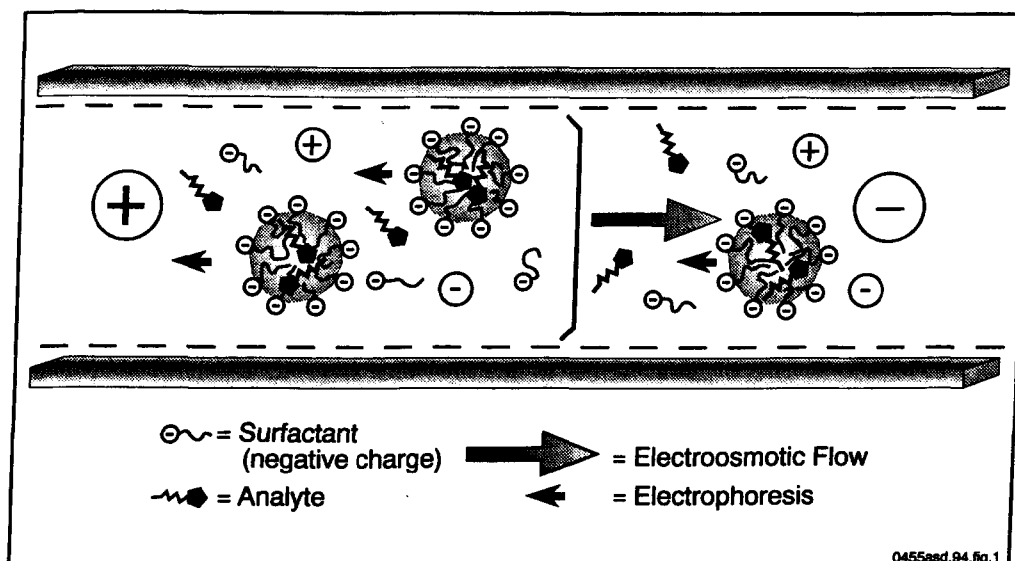
Figure 1. Flow Profiles

These values exceed those obtained with other liquid phase techniques such as HPLC, and equal or surpass the best capillary GC techniques. This extremely high resolution permits separation of many more analytes on a given column, eliminating chromatographic interferences.

Figure 2 illustrates some of the principles involved in CE and micellar electrokinetic chromatography (MEKC) which involves the addition of surfactant molecules to the buffer solutions. MEKC (also called MECC) was introduced by Terabe et al. in 1984. Terabe et al. also introduced applications of cyclodextrins and urea in MEKC for improving separations involving hydrophobic molecules. Electrophoresis (i.e., the migration or mobility of ions in an electric field) accounts for the movement of ions of the appropriate charge toward the cathode or anode in narrow bands. The electrophoretic flow is shown in Figure 2 by a smaller, dark arrow. In addition, an electroosmotic (EO) flow exists that transports bulk liquid with buffer from one reservoir to the other depending on conditions. Usually, for bare silica, an excess of mobile positive charge exists in solution

because of the ionization of silanol groups on the silica surface. The EO flow is illustrated by the large, white arrow. This flow is characterized by a flat, piston-like profile rather than the parabolic flow characteristic of pressure-driven systems. This flat-flow profile results in extremely narrow peaks and high efficiency in CE. The separation of neutral analytes under MEKC is based on their affinity for micelles (aggregates of surfactant molecules) that migrate under these conditions. These micelles are considered to form a pseudo-stationary phase. Another capillary format using EO flow, electrokinetic chromatography (EKC), involves the use of packed capillary columns with C18 derivatized silica particles forming the stationary phase.

The fact that CE is based on electromigration of ions means that the technique can be of great value in determining inorganic ion concentrations. The U.S. EPA Region VII has approved a method for determining hexavalent chromium (Cr(VI)). Ionic organic applications developed in the pharmaceutical and biomedical areas include separation of proteins and amino acids. Applications to



**Figure 2. Illustration of the components of MEKC**

environmental organic ions include determination of acids, phenols, and amines. Dr. William Brumley and co-workers at the EPA CRD-LV are actively pursuing research in CE and MEKC separations of such organic analytes as sulfonic acids, carboxylic acids, benzidines (substituted p,p'-diaminobiphenyls), phenols, anilines, and PNAs.

The combination of ion-based CE and MEKC CE provides a nearly universal analyte separation methodology. Two valuable characteristics of CE in developing routine methods are separation speed and sensitivity. Brumley and Brownrigg (1994) report high-speed CE separations of four substituted benzidines in a little over two minutes. For samples that do not require extensive preparation, replicate sample analyses can be performed to provide better confidence in analytical results. Because the detector is on-column, there is no band-broadening and signal loss due to "dead volume" mixing in the detector. This gives CE extremely low analyte mass detection limits.

Absolute mass sensitivity of detection by optical spectroscopy (no preconcentration or field amplification) is about  $10^{-6}$  M to  $10^{-7}$  M in a sample by UV or indirect UV or indirect fluorescence detection.

For a relative molecular mass of 100, this calculates to 1 pg to 100 fg on-column for a 10 nL injection. In the case of LIF, the detection limit may approach  $10^{-11}$  M to  $10^{-14}$  M in a sample resulting in 10 ag to 10 zg injected on-column. Reaching these mass sensitivities presents one of the greatest challenges in the development of CE/MS.

Lack of detection sensitivity under UV is one of the major factors that has limited the development of environmental applications of CE. Although detection in CE is very mass sensitive (i.e., the absolute amount of substance on-column), concentration limits of detection are substantially higher because of the small injection volume typically used (ca. 1 to 10 nL). This can be a serious limitation for environmental analysis, whereas for microenvironment studies (e.g., a single cell) it is an advantage. Various approaches for overcoming the limitations of nL injection volumes are discussed below. These include both sample handling and improving detector sensitivity (e.g., using LIF). One approach is to use preconcentration techniques such as solid-phase extraction before injecting samples. Additional approaches have coupled C18 columns with CE columns for preconcentration. An alternative approach is to use CE

techniques to concentrate analytes. These can involve coupled columns and a technique called isotachopheresis. Another approach is to use field amplification during sample injection to concentrate analyte ions. These techniques can lead to factors of 100 to 1000 improvement in detection limits.

CE is a highly leveraged analytical tool in terms of investment because of biomedical and pharmaceutical research. It is thus assured of continuous and rapid development. Current improvements in absorption detection, such as degenerate four-wave mixing, promise lowering detection limits to  $10^{-8}$  M.

Derivatization strategies to take advantage of LIF sensitivity (as low as 6 molecules on-column) are currently underway at CRD-LV.

Additional leveraging in environmental applications is being sought through interagency agreements. One of the tasks currently being considered is parallel processing of sample streams via bundled capillaries. Sample throughput could be increased 10-fold, for example, with 10 capillaries operating simultaneously with detection. Partners with EPA are also being sought for development of CE/MS.



## THE STATUS

Current developments in CE/MS at CRD-LV and elsewhere focus on electrospray ionization with quadrupoles, double focusing instruments, ion traps, and time-of-flight mass spectrometers. Currently, a cooperative agreement between CRD-LV and an external institution is awaiting implementation (Ms. Tammy Jones, Project Officer).

Laboratory evaluations and research efforts have resulted

in at least one EPA CE method for hexavalent chromium that was approved in Region VII in March 1994. Dr. W.C. Brumley, Dr. Wayne Garrison, ERL-Athens, as well as other EPA and independent researchers, have performed considerable research into the application of CE to environmentally important analytes. The results have been sufficiently successful that the next step is to apply the technology to real-world samples. Once

the methods have been demonstrated on these types of samples, EPA staff are interested in soliciting requests to perform CE analyses in a field setting. To submit environmental samples for CE analysis or to be considered for a CE field demonstration, contact Dr. Brumley or Mr. Ken Brown, listed at the end of this sheet.

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## FOR FURTHER INFORMATION

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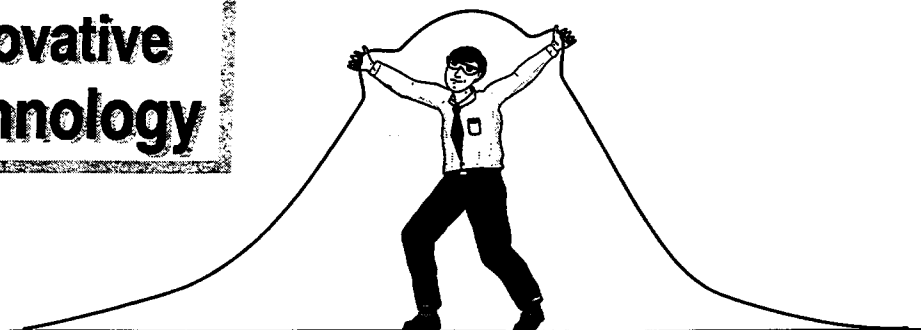


The Technology Support Center fact sheet series is developed by Clare L. Gerlach, with technical contributions in the CE sheet by Nelson R. Herron, Ph.D., Lockheed Environmental Systems & Technologies Company, Las Vegas.

TECHNOLOGY SUPPORT



# Robust Statistical Intervals for Performance Evaluations



## INTRODUCTION

Environmental samples collected at Superfund sites are routinely analyzed by the various commercial laboratories participating in quality assurance/quality control (QA/QC) programs such as the Contract Laboratory Program (CLP) of the U.S. EPA. The EPA Superfund CLP periodically evaluates, through the performance evaluation (PE) quarterly blind (QB) studies, the competence of participating laboratories in the quantitative analysis of prepared materials. Identically prepared PE samples are sent to participants. PE samples contain amounts of various organic or inorganic compounds known only to the evaluator. Laboratories are expected to report analytical results that are relatively close to the known amount. However, in practice, the recoveries reported by the participants may differ significantly from the "true" spiked amount.

In a PE study, the objective may be to obtain: (1) an interval estimate (LCL, UCL) for the overall mean recovery (where LCL and UCL represent the lower and upper confidence limits for mean,  $\mu$ , respectively), (2) an interval estimate (LSL, USL) within which the majority of the participants are expected to report their analytical results (where LSL and USL simultaneous limits, respectively), or (3) an interval estimate (LPL, UPL) for a delayed result,  $x_p$ , reported by a participant (where LPL and UPL represent the lower and upper prediction limits, respectively). These intervals are significantly different from each other and care must be exercised to use them

appropriately. For example, at a polluted site the objective may be to obtain a threshold value estimating the background level contamination prior to any activity that polluted the site. Here, the upper simultaneous limit, USL, and not the upper confidence limit, UCL, for the population mean may be used. It is inappropriate to compare an individual observation,  $x_p$ , with the UCL for the population mean,  $\mu$ , and expect an adequate coverage for all of the values of  $x_p$ , as is sometimes mistakenly done in practice.

There are two main issues that need to be considered. First, an adequate interval estimate should be used for a typical application. The use of the confidence interval (CI) for the mean,  $\mu$ , or a prediction interval for a single future observation is inappropriate when the objective is to obtain a statistical interval providing simultaneous coverage for the majority of the participants. The test-statistics and the associated critical values change from application to application. Secondly, appropriate statistical methods need to be used to obtain robust and resistant estimates of the population mean,  $\mu$ , and variance,  $\sigma^2$ . It is important that the degrees of freedom (df) be computed accurately by making the appropriate adjustment for the outliers. All of these measures, when considered collectively, result in more accurate and reliable interval estimates.

Scientists at the National Exposure Research Laboratory's Characterization Research Division in

## INTRODUCTION (Continued)

Las Vegas (CRD-LV) have studied the CLP database extensively and have developed improved methods for assessing some QA measurements. Chief among these improvements is a more robust

statistical method, based on simultaneous confidence intervals, for evaluating the performance of the participating laboratories in the QA/QC programs of the U.S. EPA.

## THE CURRENT PROCESS

Let  $x_1, x_2, \dots, x_n$  represent the recoveries of a certain compound reported by the  $n$  participants in a typical PE study. The classical maximum likelihood estimates (MLEs) of population mean,  $\mu$ , and standard deviation (sd),  $\sigma$ , are the sample mean,  $\bar{x}$ , and sample sd,  $s$ , respectively.

The U.S. EPA evaluates the analytical results reported by the participants using statistical quality control (SQC) techniques based on the classical MLEs,  $\bar{x}$  and  $s$ . The classical estimates,  $\bar{x}$  and  $s^2$ , get distorted in the presence of outliers and may result in unreliable and imprecise estimates of the above-mentioned intervals. Thus, the outlying observations inherent in most environmental applications can distort the entire estimation process, which in turn can result in incorrect decisions. The robust statistical intervals should be used when outliers are present.

Horn et al. (1988) used the Biweight influence function to obtain a robust prediction interval and recommended its use to assess the performance of a *future* (delayed) result reported by a *single* participant in a PE study of the U.S. EPA. However, in PE studies, one of the main objectives is to obtain adequate acceptance regions within which *most* of the participants are expected to report their analytical results simultaneously. The prediction interval currently used is not appropriate to provide simultaneous coverage for the majority of the participants. Moreover, the Biweight function does not perform well in samples of small sizes ( $n \leq 15$ ). In the current Biweight procedure, no adjustment for the outliers is made in the computation of the df used to obtain the critical values of the associated test-statistics and, consequently, inflated df are used to obtain these critical values.

## THE PROPOSED PROCESS

A more statistically rigorous approach to determine misquantified analytes in PE studies has been discussed by Singh and Nocerino (1993). Comparisons are made with the existing techniques. The "proposed" PROP acceptance interval is a *simultaneous confidence interval* with a built-in outlier detection criterion. The PROP simultaneous confidence intervals: (1) use the robust estimates of population mean,  $\mu$ , and variance,  $\sigma^2$ , which are not distorted by the presence of multiple outliers (Singh, 1993), (2) use more accurate estimates of df to obtain critical values of the associated test-statistics, and (3) by definition, are better suited for such PE studies and provide adequate simultaneous coverage for the majority of the participants. Some of these intervals are given as below. In the following equations,  $\bar{x}^*$ ,  $s^*$ , and wsum refer to the robust estimate of  $\mu$ , the robust estimate of  $\sigma$ , and the sum of the squared weights, respectively, and are given by:

$$\bar{x}^* = \sum w_i (d_i) x_i / \sum w_i (d_i) \quad (1)$$

and

$$s^{*2} = \sum w_i (d_i) (x_i - \bar{x}^*)^2 / df$$

where the weights are obtained using the PROP or the Huber (Singh, 1993) influence functions.

The distances,  $d_i^2$ , are given by  $d_i^2 = (x_i - \bar{x})^2 / s^2$  and are identically distributed as a beta distribution:

$$((n-1)^2/n) \text{ B } (1/2, (n-2)/2)$$

- The  $(1-\alpha)100\%$  *confidence interval* (LCL, UCL) for the population mean,  $\mu$ , is given by:

$$P\left(\bar{x}^* - \frac{t_{df, \alpha/2} s^*}{\sqrt{wsum}} \leq \mu \leq \bar{x}^* + \frac{t_{df, \alpha/2} s^*}{\sqrt{wsum}}\right) = 1 - \alpha \quad (2)$$

where  $t_{df, \alpha/2}$  represents the critical value from the Student's t-distribution.

- The  $(1-\alpha) 100\%$  *simultaneous confidence interval* (LSL, USL) for the majority of the participants is developed as follows. Let  $d_{m, \alpha}^2$  represent the  $\alpha$  (100%) critical values for the distribution of  $\max(d_i^2)$ . The simultaneous interval with a built-in outlier identification criterion is given by  $P(\max(d_i^2) \leq d_{m, \alpha}^2) = 1 - \alpha$ , or equivalently, given by the probability statement (Singh and Nocerino, 1993),

$$P(\bar{x}^* - s^* d_{m, \alpha} \leq x_i \leq \bar{x}^* + s^* d_{m, \alpha}; i=1, 2, \dots, n) = 1 - \alpha \quad (3)$$

- The  $(1-\alpha) 100\%$  *prediction interval*, (LPL, UPL), for a future observation,  $x_0$ , is given by:

$$P\left(\bar{x}^* - t_{df, \alpha/2} s^* \sqrt{\frac{1}{wsum} + 1} \leq x_0 \leq \bar{x}^* + t_{df, \alpha/2} s^* \sqrt{\frac{1}{wsum} + 1}\right) = 1 - \alpha \quad (4)$$

## AN EXAMPLE

The following data set from a QB study illustrates the differences among the above-mentioned interval estimates. Using the analytical results reported by 43 laboratories for the semivolatile chemical, 4-methylphenol, the computations for the various intervals with a confidence coefficient ( $CC=1-\alpha$ ) of 0.95 are summarized in Table 1. The estimated df obtained using the PROP procedure is  $df=34.39$ . This is expected because of the reduced weights assigned to the outlying observations. Using Iglewicz's (1983) recommendation, one might use a substantially smaller number of df,  $(0.7)(42) = 29$ . Notice that the PROP sd is also much smaller, again due to the negligible contribution of the outliers. Figures 1 and 2 show the classical and robust simultaneous intervals. The classical interval in Figure 1 is distorted by the outlying observations (e.g., number 28, circled in the figures). The robust interval estimate of Figure 2 is not influenced by the outliers and provides appropriate simultaneous coverage to the majority of the participants.

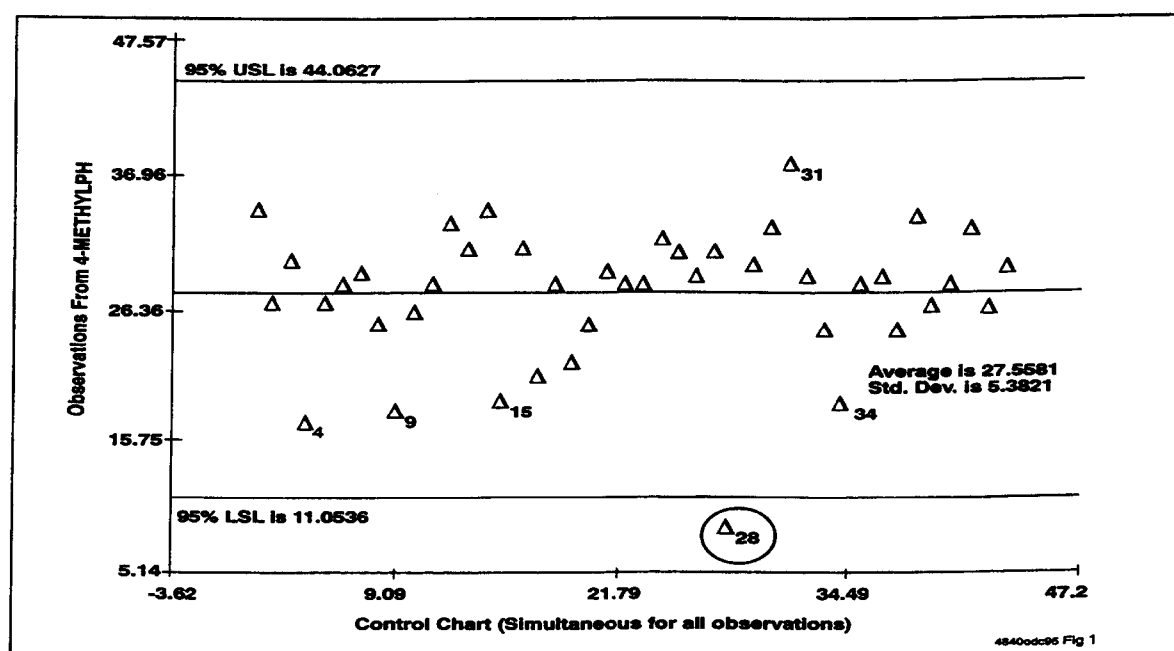
It should be emphasized here that the outliers do not necessarily represent poor performance laboratories (bad values). In a typical PE study, a high discordant recovery close to the true spiked amount may indicate extremely good performance by the associated participant. However, consistent occurrences of

such high values for the same participant in several PE studies may call for an examination regarding the appropriate use of the analytical method. In any case, all of the outliers, low or high, should be down-weighted appropriately so that the resulting estimates will correspond to the estimates of the parameters of the dominant population representing the majority of the participants.

The procedure described here: (1) identifies multiple outliers, (2) uses appropriate test-statistics, (3) computes the adjusted df associated with the test-statistics by assigning reduced weights to the outlying observations, and (4) provides more precise and accurate estimates of the underlying population parameters and the associated intervals. The acceptance intervals based upon the PROP method result in higher probabilities of correctly estimating the performance of a laboratory. Using the PROP method, EPA data analysts can appropriately assess the performance of a member laboratory in a PE study by considering all of the relevant factors that affect bottom line performance. The computations and graphs for these intervals were obtained using the Scout software package developed by Lockheed Environmental Systems & Technologies Company for the U.S. EPA.

**Table 1. Sampling Statistics and Intervals Obtained Using the Four Estimation Procedures for the PE Analytical Results Data Set Reported by 43 Laboratories Participating in the CLP ( $CC=0.95$ ).**

	df	mean	sd	LCL	UCL	LPL	UPL	LSL	USL
MLE	42.00	27.56	5.38	25.90	29.21	16.57	38.54	11.05	44.06
Huber	40.49	27.83	4.62	26.40	29.26	18.38	37.27	13.72	41.93
PROP	34.39	29.01	2.78	28.08	29.93	23.29	34.73	20.72	37.29
Biwt	42.00	28.38	4.56	26.98	29.78	19.07	37.69	14.40	42.36



**Figure 1. Classical simultaneous interval for 4-methylphenol.**

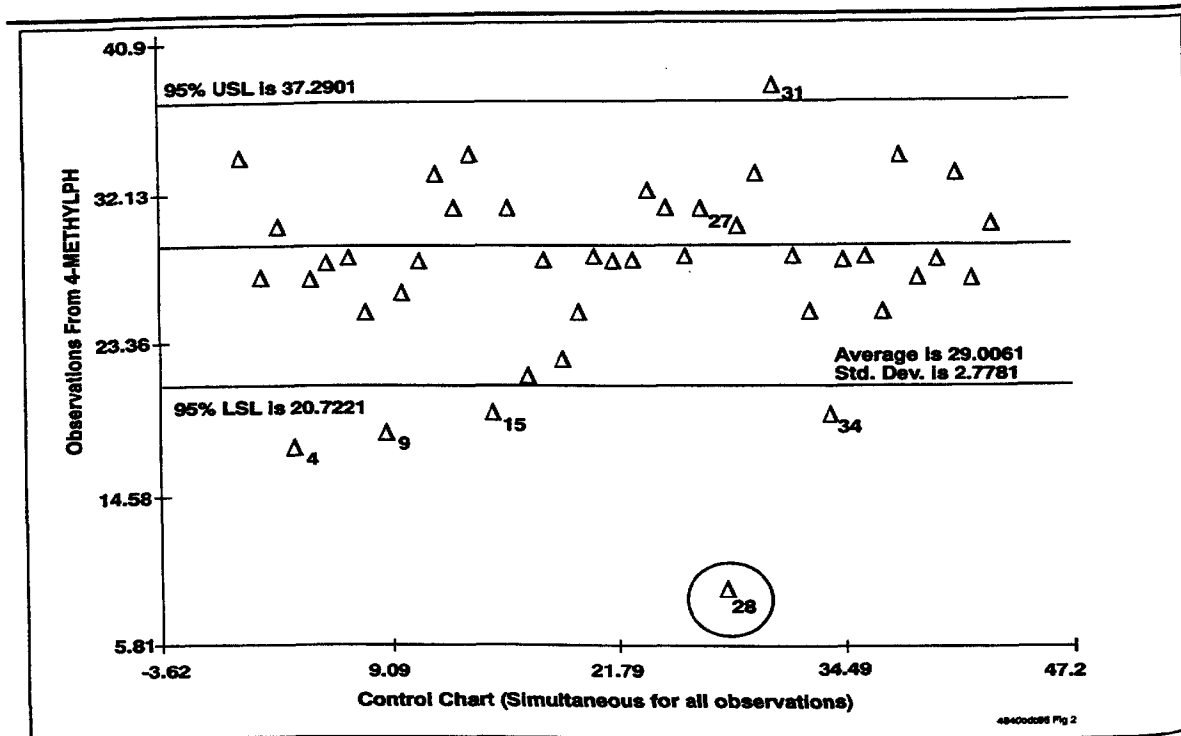


Figure 2. Robust simultaneous interval for 4-methylphenol.

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# Ground-Water Issue

## SURVEY OF LABORATORY STUDIES RELATING TO THE SORPTION/DESORPTION OF CONTAMINANTS ON SELECTED WELL CASING MATERIALS

José L. Llopis<sup>1</sup>

### INTRODUCTION

The Regional Superfund Ground Water Forum is a group of ground-water scientists representing U.S. Environmental Protection Agency's (U.S. EPA's) Regional Offices, organized to exchange up-to-date information related to ground-water remediation at hazardous waste sites. Well casing materials used at hazardous waste sites is an issue identified by the forum as a concern of CERCLA decision makers.

To address this issue, this paper was prepared through support from the Environmental Monitoring Systems Laboratory-Las Vegas (EMSL-LV), under the direction of J. Lary Jack, with the support of the Superfund Technical Support Project. For further information, contact Ken Brown, EMSL-LV Center Director, at FTS (702) 798-2270 or J. Lary Jack at FTS (702) 798-2270.

All aspects of a ground-water sampling program have the potential to affect the composition of a ground-water sample. The potential for the introduction of sample error exists from the time drilling commences and continues to the time water samples are analyzed in the laboratory. The high degree of accuracy (parts per billion (ppb) range) required of some chemical analysis dictates that all potential sources of error of a ground-water sampling program be identified and sources of error in such aspects be minimized. One potential

source of error is the interaction of the ground-water sample with material used in well casings for monitoring wells. Well casing materials may introduce error in a sample by interacting with water while it is still in the well and altering the water composition. Proper selection of casing materials used for ground-water monitoring wells is critical in minimizing errors introduced by this interaction. This paper is a survey of scientific studies related to a specific process which potentially affects materials used to produce monitoring well casings and screens. This paper should not be exclusively used to select the proper well casing/screen material for a site specific situation. Other factors must be considered into the selection process, including: site specific water chemistry, substrate physical bearing properties, formation conductivity, design life of monitoring well, presence of NAPL's, etc.

Selection of the proper casing material for monitoring wells has been a subject of much controversy since the publication of the U.S. EPA's Resource Conservation and Recovery Act (RCRA) Ground-Water Monitoring Technical Enforcement Guidance Document (TEGD) (U.S. EPA 1986). The TEGD suggests the use of polytetrafluoroethylene (PTFE, Teflon®) or stainless steel (SS) for sampling volatile organics in the saturated zone and further states "National Sanitation Foundation (NSF) or American Society for Testing and Materials (ASTM) approved polyvinylchloride (PVC) well casing and screens may be appropriate if only

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<sup>2</sup> For a list of abbreviations, see page 15.



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trace metals or nonvolatile organics are the contaminants anticipated".

## SOURCES OF ERROR

Error can be introduced into the ground-water sample by casing materials with several processes including:

- Chemical attack of the casing material.
- Sorption and desorption.
- Leaching of the casing material.
- Microbial colonization and attack (Barcelona et al., 1985)

Before proceeding further, it is necessary to define the terminology used in this report. The terms "sorbed" or "sorption" are used many times in the literature to refer to the processes of adsorption and absorption especially when the exact mechanism is not known. Adsorption is defined as the adherence of atoms, ions, or molecules of a gas or liquid called the adsorbate onto the surface of another substance, called the adsorbent; whereas, absorption is the penetration of one substance (adsorbate) into the inner structure of another called the absorbent. In this report, rather than distinguishing between the processes of adsorption and absorption, the term sorbed will be used synonymously with both processes, unless otherwise noted. Desorption refers to the process of removing a sorbed material from the solid on which it is sorbed. Leaching refers to the removal or extraction of soluble components of a material (i.e., casing material) by a solvent (Sax and Lewis, 1987).

Casing material in contact with a liquid has the potential to allow either leaching and/or sorption. Factors influencing sorption of organics and metals are discussed by Jones and Miller (1988) and Massee et al., (1981), respectively. These factors include:

- The surface area of the casing. The greater the ratio of casing material surface area to the volume of adsorbate the greater the sorption potential.
- Nature of the analyte (chemical form and concentration).
- Characteristics of the solution. This includes factors such as pH, dissolved material (e.g., salinity, hardness), complexing agents, dissolved gasses (especially oxygen, which may influence the oxidation state), suspended matter (competitor in the sorption process), and microorganisms (e.g., trace element take-up by algae).
- Nature of the casing material (adsorbent). This includes factors such as the chemical and physical properties of the casing material.
- External factors. These factors include temperature, contact time, access of light, and occurrence of agitation.

According to Barcelona et al., (1988) considerations for selecting casing material should also include the subsurface geochemistry and the nature and concentration of the contaminants of interest. They also state that strength, durability, and inertness of the casing material should be balanced with cost considerations. Ford (1979) summarized factors related to the analyte that can affect adsorption (Table 1).

TABLE 1. FACTORS AFFECTING ADSORPTION

- An increasing solubility of the solute in the liquid carrier decreases its adsorbability.
- Branched chains are usually more adsorbable than straight chains. An increasing length of the chain decreases solubility.
- Substituent groups affect adsorbability.

Substituent Group	Nature of Influence
Hydroxyl	Generally reduces adsorbability; extent of decrease depends on structure of host molecule.
Amino	Effect similar to that of hydroxyl but somewhat greater. Many amino acids are not adsorbed to any appreciable extent.
Carbonyl	Effect varies according to host molecule; glyoxylic are more adsorbable than acetic but similar increase does not occur when introduced into higher fatty acids.
Double Bonds	Variable effect as with carbonyl.
Halogens	Variable effect.
Sulfonic	Usually decreases adsorbability.
Nitro	Often increases adsorbability.
Aromatic Rings	Greatly increases adsorbability.

- Generally, strong ionized solutions are not as adsorbable as weakly ionized ones; i.e., undissociated molecules are in general preferentially adsorbed.
- The amount of hydrolytic adsorption depends on the ability of the hydrolysis to form an adsorbable acid or base.
- Unless the screening action of the adsorbent pores intervene, large molecules are more sorbable than small molecules of similar chemical nature. This is attributed to more solute-adsorbent chemical bonds being formed, making desorption more difficult.
- Molecules with low polarity are more sorbable than highly polar ones.

(Source: Ford, 1979)

Berens and Hopfenberg (1981) conducted an investigation to determine a correlation between diffusivity and size and shape of the penetrant molecules. Their study indicated that as the diameter of "spherical" penetrant molecules increased, the diffusivity decreased exponentially. Another finding of the study was that flattened or elongated penetrant molecules such as n-alkanes had greater diffusivities than spherical molecules of similar volume or molecular weight. This may indicate that elongated molecules can move along their long axis when diffusing through a polymer.

Reynolds and Gillham (1985) used a mathematical model to predict the absorption of organic compounds by the different

polymer materials. Curves based on their model were fit to experimental data and showed reasonable agreement. This agreement supports their concept that uptake is the result of absorption. They also determined that no relationship was found between the order of absorption and readily available parameters such as aqueous solubility or octanol/water partitioning coefficient. They concluded that predicting the amount of absorption for a particular organic compound was not possible at that time.

Gillham and O'Hannesin (1990) attempted to predict the rate of uptake of benzene, toluene, ethylbenzene, and p-, m-, and o-xylene onto samples SS316, PTFE, rigid PVC, flexible PVC, polyvinylidene fluoride (PVDF), flexible PE, and FRE employing the same model as that used by Reynolds and Gillham (1985). Their results showed the diffusion model data fitted their experimental data quite well, suggesting the sorption mechanism was absorption into the polymer materials agreeing with the results of Reynolds and Gillham (1985). They also determined, that for the organic compounds used in this study, the rate of uptake increased with increasing hydrophobicity of the organic compound and varied with the physical characteristics of the polymer casing material.

## TYPES OF CASING MATERIALS

A variety of materials may be used for casing and screening ground-water monitoring wells. These materials include glass and metallic and synthetic materials. Rigid glass has the least potential for affecting a sample and is the material of choice for sampling organics (Pettyjohn et al., 1981). However, because the use of glass as a casing material is impractical for field applications because of its brittleness, it will not be further considered in this report. Instead, this report will focus on the metallic and synthetic materials most commonly used for monitoring well construction.

### Metals

Metals are often chosen as casing materials because of their strength. Metals used for casing include SS, carbon steel, galvanized steel, cast iron, aluminum, and copper. The various metals used for well casings may react differently to different compounds. Reynolds et al., (1990) conducted a study using SS, aluminum, and galvanized steel to determine their potential to cause problems in samples collected for analysis for halogenated hydrocarbons. The metals were subjected to aqueous solutions of 1,1,1-trichloroethane (1,1,1-TCA), 1,1,2,2-tetrachloroethane (1,1,2,2-TET), hexachloroethane (HCE), bromoform (BRO), and tetrachloroethylene (PCE) for periods up to 5 weeks. The study indicated that, of the metals used, SS was the least reactive followed by aluminum and galvanized steel. Stainless steel caused a 70 percent reduction of BRO and HCE after 5 weeks. Aluminum caused over a 90 percent reduction for all but one of the compounds while galvanized steel showed over a 99 percent reduction for all of the compounds.

Many investigations have shown that errors may be introduced into the water sample as a result of using metal casings. For instance, Marsh and Lloyd (1980) determined steel-cased wells

modified the chemistry of the formation water. They state that trace element concentrations of the ground water collected from the wells were not representative of the aquifer conditions and did not recommend the use of steel casing for constructing monitoring wells. They suspected that reactions between the ground water and the steel casing raise the pH of the water which causes the release of metal ions into solution. Pettyjohn et al., (1981) found metals strongly adsorb organic compounds. For example, they claim that DDT is strongly adsorbed even by SS. Hunkin et al., (1984) maintain that steel-cased wells are known to add anomalously high iron and alloy levels as well as byproducts of bacterial growth and corrosion to a sample. Houghton and Berger (1984) discovered that samples from steel-cased wells were enriched in cadmium (Cd), chromium (Cr), copper (Cu), iron, manganese, and zinc (Zn) relative to samples obtained from plastic-cased wells.

Stainless steel is one type of metal used for casing and that appears to have a high resistance to corrosion. In fact, the U.S. EPA (1987) states that SS is the most chemically resistant of the ferrous materials. Two types of SS extensively used for ground-water monitoring are stainless steel 304 (SS304) and stainless steel 316 (SS316). These are classified as austenitic type SS and contain approximately 18 percent chromium and 8 percent nickel. The chemical composition of SS304 and SS316 is identical with the exception being SS316 which contains 2-3 percent molybdenum. Brainard-Kilman (1990) indicate SS316 has improved resistance to sulfuric and saline conditions and better resistance to stress-corrosion.

The corrosion resistance of SS is due to a passive oxide layer which forms on the surface in oxidizing environments. This protective layer is only a few molecules thick. It recovers quickly even if removed by abrasion (Fletcher 1990). However, several investigators note that SS is still susceptible to corrosion. Under corrosive conditions, SS may release iron, chromium, or nickel (Barcelona et al., 1988). Hewitt (1989a) found in a laboratory study that samples of SS316 and SS304 were susceptible to oxidation at locations near cuts and welds. When these cuts and welds are immersed in ground water, this surface oxidation provides active sites for sorption and also releases impurities and major constituents. SS may be sensitive to the chloride ion, which can cause pitting corrosion, especially over long term exposures under acidic conditions (U.S. EPA, 1987).

Parker et al., (1989) evaluated samples of SS304 and SS316 for their potential to affect aqueous solutions of 10 organic compounds. The 10 organics used in the study were RDX, trinitrobenzene (TNB), c-1,2-DCE, t-1,2-DCE, m-nitrotoluene (MNT), TCE, MCB, o-dichlorobenzene (ODCB), p-dichlorobenzene (PDCB), and m-dichlorobenzene (MDCB) at concentrations of 2 mg/L. Their study indicated the SS well casings did not affect the concentration of any of the analytes in solution.

### Synthetic Materials

Synthetic materials used for casing evaluation include PTFE, PVC, polypropylene (PP), polyethylene (PE), nylon, fiberglass reinforced epoxy (FRE), and acrylonitrile butadiene styrene (ABS). The two most commonly used synthetic casing materials are PVC and PTFE. Very little information regarding the suitability of FRE as a casing material is presently available in



the literature; however, a 3-week dwell-time study conducted by Cowgill (1988) indicated that FTFE revealed no detectable quantities of the substances used in its manufacture. Hewitt (1989a and 1989b) determined that PTFE was the material of choice for sampling inorganic compounds whereas, Barcelona (1985) recommends PTFE for most all monitoring applications.

PTFE is a man-made material composed of very long chains of linked fluorocarbon units. PTFE is considered as a thermoplastic with unique properties. It is very inert chemically and no substance has been found that will dissolve this polymer (The Merck Co. Inc. 1984). The Merck Co. Inc. (1984) reports that nothing sticks to this polymer. This antistick property may prevent grouts from adhering to PTFE casing and prevent the development of an effective seal around a PTFE casing. PTFE also has a very wide useful temperature range, -100° to +480° F; however, for most ground-water monitoring applications these extremes of temperature would rarely be encountered.

PTFE has a low modulus of elasticity making the screened portion PTFE casing prone to slot compression under the weight of the well casing above. PTFE is also very flexible and the casing sometimes has the tendency to become "crooked" or "snake" especially in deep boreholes. Special procedures are then required to install the casing. Morrison (1986) and Dablow et al., (1988) discuss different techniques used to overcome installation problems inherent to PTFE wells. PTFE also has the tendency to stretch thus, making PTFE cased wells susceptible to leaks around threaded joints.

PVC casing is an attractive alternative to PTFE and SS because it is inexpensive, durable, lightweight, has better modulus and strength properties than PTFE, and is easy to install. However, these characteristics alone do not justify its use as a monitoring well casing material. The casing material must not react significantly with the surrounding ground water, leach, sorb, or desorb any substances that might introduce error into the sample. Many studies have been conducted comparing PVC to other casing materials to determine its suitability for use in monitoring wells.

Various compounds are added to the basic PVC polymer during the manufacturing process of rigid PVC. These compounds include thermal stabilizers, lubricants, fungicides, fillers, and pigments (Boettner et al., 1981; Packham, 1971). It is presumed that the additional compounds have the potential to leach into the ground water. Tin, found in some thermal stabilizers, is one of the compounds suspected of leaching from PVC. Boettner et al., (1981) found that as much as 35 ppb dimethyltin could be leached from PVC in a 24-hour period. Other compounds used as thermal stabilizers, and potential sources of contaminants, are calcium, Zn, and antimony.

Another compound suspected of leaching from PVC casing is residual vinyl chloride monomer (RVCM). According to Jones and Miller (1988), 1-inch diameter Schedule 40 PVC pipe containing 10-ppm RVCM leaches undetectable quantities (at the 2.0-ppb sensitivity level) of vinyl chloride into stagnant water retained in the pipe. They also report that 98 percent of the PVC casing currently manufactured in North America contains less than 10-ppm RVCM and most casing contains less than 1 ppm RVCM. This implies that a 1-inch diameter pipe should leach 2.0-ppb or less RVCM. The amount of RVCM leached would

also decrease as the casing diameter increased because of the lower specific surface. Specific surface (R) is defined as the ratio of the surface area of the casing material in contact with the solution, to the volume of the solution. Thus, as casing diameter increases, the specific area decreases.

The NSF (1989) has established maximum permissible levels (MPL) for many chemical substances used in the manufacturing of PVC casing (Table 2). These levels are for substances found in low pH extractant water following extraction procedures described by the NSF (1989). Sara (1986) recommends the use of NSF-tested and approved PVC formulations to reduce the possibility of leaching RVCM, fillers, stabilizers, and plasticizers.

TABLE 2. MAXIMUM PERMISSIBLE LEVELS FOR CHEMICAL SUBSTANCES

Substances	MPL mg/L	Action levels mg/L
Antimony	0.05	
Arsenic	0.050	
Cadmium	0.005	
Copper	1.3	
Lead	0.020	
Mercury	0.002	
Phenolic Substances		0.05 <sup>1</sup>
Tin	0.05	
Total Organic Carbon		5.0 <sup>1</sup>
Total Trihalomethanes	0.10	
Residual Vinyl Chloride Monomer*	3.2	2.0 <sup>2</sup>

\* In the finished product ppm (mg/kg).

<sup>1</sup> This is an action level. If the level is exceeded, further review and/or testing shall be initiated to identify the specific substance(s), and acceptance or rejection shall be based on the level of specific substances in the water.

<sup>2</sup> Additional samples shall be selected from inventory and tested to monitor for conformance to the MPL.

(Source: NSF Standard Number 14)

Common practice was to use cleaner-primers and solvent cements to join PVC casing sections used in monitoring wells. Cements used for joining casing sections dissolve some of the polymer and "weld" the casing sections together. Past studies showed a correlation between certain organic compounds found in ground-water samples and the use of PVC solvent cement (Boettner et al., 1981; Pettyjohn et al., 1981; Sosebee et al., 1983; Curran and Tomson, 1983). Sosebee et al., (1983) found high levels of tetrahydrofuran, methylethylketone, methylisobutylketone, and cyclohexanone, the major constituents of PVC primer and adhesive, in water surrounding cemented casing joints months after installation. Sosebee et al., (1983) determined that besides contaminating the ground-water sample these contaminants have the potential to mask

other compounds found in the ground water during laboratory analysis. Boettner et al., (1981) found, in an experiment in which solvent cement was used for joining PVC casing, methylethylketone, tetrahydrofuran, and cyclohexanone leaching into water supplies after more than 2 weeks of testing.

Houghton and Berger (1984) conducted a study to determine the effects of well casing composition and sampling method on water-sample quality. Three wells were drilled on 20-ft centers to a depth of 60 feet and cased with PVC, ABS, and steel. Samples collected from the wells indicated ABS-cased wells were enriched in dissolved organic carbon by 67 percent and in total organic carbon (TOC) by 44 percent relative to samples from the steel-cased well. The PVC-cased well was enriched in dissolved organic carbon and TOC by approximately 10 percent relative to the steel-cased well. The high TOC concentrations found in the ABS and PVC casings are suspected to have been derived from the cement used to connect the casing sections.

Other compounds suspected of leaching from PVC and into ground water are chloroform ( $\text{CHCl}_3$ ) and carbon tetrachloride ( $\text{CCl}_4$ ). Desrosiers and Dunnigan (1983) determined that PVC pipe did not leach  $\text{CHCl}_3$  or  $\text{CCl}_4$  into deionized, demineralized, organic-free water, or tap water in the absence of solvent cement even after a 2-week dwell time.

PVC primers and adhesives should not be used for joining PVC monitoring well casing sections. The recommended means for joining PVC casing is to use flush-joint threaded pipe casing. Foster (1989) provides a review of ASTM guideline F480-88A which describes in detail the standard PVC flush-joint thread.

Junk et al., (1974) passed "organic free" water through PE, PP, latex, and PVC tubings, and a plastic garden hose. They found o-cresol, naphthalene, butyloctylfumarate, and butylchloroacetate leaching from the PVC tubing. These contaminants are related to plasticizers which are added to PVC during the manufacturing process to make it more flexible. Rigid PVC well casing contains a much smaller quantity of plasticizer and should be less prone to leaching contaminants (Jones and Miller, 1988).

## LEACHING AND SORPTION STUDIES

Many studies have been undertaken to determine the interaction of different casing materials with volatile organic compounds (VOCs) and trace metals. Much of the research has been aimed at determining whether PVC can be used as a substitute for more expensive materials such as PTFE, FRE, and SS. A review of the literature investigating the potential effects of assorted well casing materials on ground-water samples is presented below.

### Organic Studies

Lawrence and Tosine (1976) found that PVC was effective for adsorbing polychlorinated biphenyls (PCB) from aqueous sewage solutions. They reported that the low solubility and hydrophobic nature of the PCBs makes them relatively easy to adsorb from aqueous solution. Parker et al., (1989) suggest the PVC appears to be effective only in sorbing PCBs at concentrations close to their solubility limits.

Pettyjohn et al., (1981) discuss materials used for sampling organic compounds. They provide a list of preferred materials for use in sampling organic compounds in water. Their choice in order of preference is glass, PTFE, SS, PP, polyethylene, other plastics and metals, and rubber. They do not indicate whether the materials in the list were sections of rigid or flexible tubing or what testing procedures were followed. They note that experimental data on the sorption and desorption potential of casing materials using varied organic compounds were not available.

Miller (1982) conducted a laboratory study in which one of the objectives was to quantify adsorption of selected organic pollutants on Schedule 40 PVC 1120, low density PE, and PP well casing materials. These materials were exposed to six organic pollutants and monitored for adsorption over a 6-week period. The VOCs used, along with their initial concentrations, were BRO (4 ppb), PCE (2 ppb), trichloroethylene (TCE) (3 ppb), trichlorofluoromethane (2 ppb), 1,1,1-TCA (2 ppb), and 1,1,2-trichloroethane (14 ppb). The results showed that PVC adsorbed only PCE. The PVC adsorbed approximately 25 to 50 percent of the PCE present. The PP and PE samples adsorbed all six of the organics in amounts ranging from 25 to 100 percent of the amount present.

Curran and Tomson (1983) compared the sorption potential of PTFE, PE, PP, rigid PVC (glued and unglued), and Tygon (flexible PVC). The procedures used in this investigation consisted of pumping 20 L of organic-free water with a 0.5-ppb naphthalene spike through each tubing at a rate of 30 mL/min. The tests showed that 80 to 100 percent of the naphthalene was recovered from the water for all materials except Tygon tubing. Tygon tubing sorbed over 50 percent of the naphthalene. PTFE showed the least contaminant leaching of the synthetic materials tested. They concluded that PVC can be used as a substitute for PTFE in monitoring wells if the casing is properly washed and rinsed with room temperature water before installation. They also conclude that PE and PP could suitably be used as well casings.

Barcelona et al., (1985) presented a ranking of the preferred rigid materials based on a review of manufacturers' literature and a poll of the scientific community. The list presented by Barcelona et al., (1985) recommended the following casing materials in order of decreasing preference: PTFE, SS316, SS304, PVC, galvanized steel, and low carbon steel. Table 3 presents recommended casing materials tabulated in Barcelona et al., (1985) along with specific monitoring situations.

Reynolds and Gillham (1985) conducted a laboratory study to determine the effects of five halogenated compounds on six polymer materials. The five compounds used in this study were 1,1,1-TCA, 1,1,2,2-TET, HCE, BRO, and PCE. The polymer materials studied were PVC rod, PTFE tubing, nylon plate, low density PP tubing, low density PE tubing, and latex rubber tubing. The authors evaluated nylon plate because nylon mesh is often used as a filter material around screened portions of wells. Latex rubber tubing was evaluated as a material that represented maximum absorption. The materials were tested under static conditions to simulate water standing in the borehole. Measurements were made over contact times that ran from 5 minutes to 5 weeks.

**TABLE 3. RECOMMENDATIONS FOR RIGID MATERIALS IN SAMPLING APPLICATIONS**  
(In decreasing order of preference)

Material	Recommendations
PTFE (Teflon®)	Recommended for most monitoring situations with detailed organic analytical needs, particularly for aggressive, organic leachate impacted hydrogeologic conditions. Virtually an ideal material for corrosive situations where inorganic contaminants are of interest.
Stainless Steel 316 (flush threaded)	Recommended for most monitoring (flush threaded) situations with detailed organic analytical needs, particularly for aggressive, organic leachate impacted by hydrogeologic conditions.
Stainless Steel 304 (flush threaded)	May be prone to slow pitting corrosion in contact with acidic high total dissolved solids aqueous solutions. Corrosion products limited mainly to Fe and possibly Cr and Ni.
PVC (flush threaded) other noncemented connections, only NSF-approved materials for casing or potable water applications.	Recommended for limited monitoring situations where inorganic contaminants are of interest and it is known that aggressive organic leachate mixtures will not be contacted. Cemented installations have caused documented interferences. The potential for interaction and interferences from PVC well casing in contact with aggressive aqueous organic mixtures is difficult to predict. PVC is not recommended for detailed organic analytical schemes.
	Recommended for monitoring inorganic contaminants in corrosive, acidic inorganic situations. May release Sn or Sb compounds from the original heat stabilizers in the formulation after long exposure.
Low Carbon Steel Galvanized Steel Carbon Steel	May be superior to PVC for exposures to aggressive aqueous organic mixtures. These materials must be very carefully cleaned to remove oily manufacturing residues. Corrosion is likely in high dissolved solids acidic environment, particularly when sulfides are present. Products of corrosion are mainly Fe and Mn, except for galvanized steel which may release Zn and Cd. Weathered steel surfaces present very active sites for trace organic and inorganic chemical species.

(Source: Barcelona et al., 1985)

Results of the study are presented in Table 4. The results show that PVC absorbed four of the five compounds; however, the rate of absorption was relatively slow (periods of days to weeks). Given this slow absorption rate, they do not consider there would be significant absorption by PVC if wells were purged and sampled the same day. The one organic compound that was not absorbed significantly by the PVC during the 5-week test period was 1,1,1-TCA. The loss of BRO to PVC in this study was approximately 43 percent after 6 weeks; whereas, Miller (1982), in a similar experiment, indicated no losses from solution over the same time period.

**TABLE 4. TIME AT WHICH ABSORPTION REDUCED THE RELATIVE CONCENTRATION IN SOLUTION TO 0.9**

PVC	1,1,1-TCA >5 weeks	1,1,2,2-TET -2 weeks	BRO -3 days	HCE -1 day	PCE -1 day
PTFE	BRO >5 weeks	1,1,2,2-TET -2 weeks	1,1,1-TCA -1 day	HCE -1 day	PCE <5 minutes
Nylon	1,1,1-TCA -6 hours	1,1,2,2-TET -1 hour	BRO -30 minutes	PCE -30 minutes	HCE <5 minutes
PP	1,1,2,2-TET -4 hours	BRO -1 hour	1,1,1-TCA -1 hour	HCE <5 minutes	PCE <5 minutes
PE	1,1,2,2-TET -15 minutes	BRO <5 minutes	1,1,1-TCA <5 minutes	HCE <5 minutes	PCE <5 minutes
Latex Rubber	1,1,2,2-TET <5 minutes	1,1,1-TCA <5 minutes	BRO <5 minutes	PCE <5 minutes	HCE <5 minutes

(Source: Reynolds and Gillham, 1985)

PTFE showed absorption of four of the five compounds tested. There was no significant absorption of BRO over the 5-week test period. It is noted that approximately 50 percent of the original concentration of PCE was absorbed within an 8-hour period. The concentration of this compound may be affected even when the time between purging and sampling is short.

The other casing materials demonstrated significant absorption losses within minutes to a few hours after exposure to the organic compounds. The use of nylon, latex rubber, PP, and PE as a well casing material will cause a significant reduction in the concentration of the organic compounds even when the time between purging and sampling is short. They state that agreement between the model study and experimental results support the concept that absorption of the organic compounds by the polymers occur by sorption/dissolution of the compounds into the polymer surface followed by diffusion into the polymer matrix.

Parker and Jenkins (1986) conducted a laboratory study to determine if PVC casing was a suitable material for monitoring low levels of the explosives 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro 1,3,5,7-tetrazocine (HMX), and 2,4-dinitrotoluene (DNT). Samples of PVC casing were placed in glass jars containing an aqueous solution of TNT, RDX, HMX, and DNT. After 80 days, the solution was tested to determine the concentration of TNT, RDX, HMX, and DNT left in solution. After the 80 days, the solutions containing RDX, HMX, and DNT showed little loss, whereas TNT showed a significant loss. PVC casing was tested under sterile and nonsterile conditions in a 25-day experiment to determine whether microbial degradation or sorption by PVC was the cause for losses of TNT, RDX, HMX, and DNT. Results indicated that the loss of TNT in the test was caused by microbial activity rather than to adsorption. The increased microbial activity may be caused by bacteria initially present on the unsterilized PVC casing, increased surface area for colonization provided by the PVC surface, leaching of nutrients from the casing increasing the growth of bacteria, and the rate of biodegradation.

Parker and Jenkins (1986) do not consider PVC casing to significantly affect ground-water samples when monitoring for TNT, RDX, DNT, and HMX if the time between purging of the well and sampling is short. They concluded PVC is an acceptable casing material for ground-water monitoring of TNT, RDX, DNT, and HMX.

Sykes et al., (1986) performed a laboratory study to determine if there was a significant difference in the sorption potential between PVC, PTFE, and SS316 when exposed to methylene chloride (dichloromethane or DCM), 1,2-dichloroethane (1,2-DCE), trans-1,2-dichloroethylene (t-1,2-DCE), toluene, and chlorobenzene (MCB). Samples of the various well casing materials were placed in jars containing aqueous solutions of the solvents at concentrations of approximately 100 ppb. The concentration of each solvent was determined after 24 hours and again after 7 days. The study concluded that there were no statistically different chemical changes in the solutions exposed to PVC, PTFE, and SS316 casing. Thus, it could be presumed that PVC, PTFE, or SS316 are suitable casing materials for monitoring DCM, 1,2-DCE, t-1,2-DCE, toluene, and MCB when the period between well purging and sampling is less than 24 hours.

Barcelona and Helfrich (1986) conducted a field study at two landfills to determine the effects of different casing materials on sample quality. Wells were constructed upgradient and downgradient of each of the two landfill sites. The wells at Landfill 1 were constructed of PTFE, PVC, and SS304; whereas, the wells at Landfill 2 were constructed of PVC and SS.

They observed that the downgradient SS and PTFE wells at Landfill 1 showed higher levels of TOC than did the PVC wells. The upgradient wells at Landfill 1 showed no significant difference among casing material type. TOC sampling at Landfill 2 showed similar results; however, no significant differences among material types were determined either upgradient or downgradient of the landfill.

Levels of 1,1-dichloroethane (1,1-DCE) and cis-1,2-dichloroethylene (c-1,2-DCE) were significantly higher for the

downgradient SS wells than for PTFE and PVC cased wells at Landfill 1. They suspect that PTFE and PVC tend to have a greater affinity for these organic compounds than does SS.

At Landfill 2 they noted greater levels of 1,1-DCE and total volatile halocarbons in the PVC wells than in the SS wells. They hypothesize that the higher levels of the organic compounds found in the water samples from the PVC cased well may be caused by the sorptive and leaching properties of PVC which tend to maintain a higher background level of organic compounds in the ground water relative to SS. They did not suspect the SS and PVC wells at Landfill 2 are intercepting ground water of different quality since the wells are approximately 4 feet apart. The authors conclude that well casing materials exert significant, though unpredictable effects on TOC and specific VOC determinations. Parker et al., (1989) suspect that a larger statistical base is needed before such conclusions can be drawn. Parker et al., (1989) also suggest the possibility that differences in well construction methods may have had an effect on the quality of these water samples.

Gossett and Hegg (1987) conducted a laboratory test to determine the effects of using a PVC bailer, a PTFE bailer, and an ISCO Model 2600 portable pump on the recovery of  $\text{CHCl}_3$ , benzene, and 1,2-DCE. The effect on recovery of VOCs was studied by varying the lift height and the casing material. The casing materials consisted of either PVC or SS. In their conclusion they state that either PVC or SS would be suitable for collecting VOC samples.

Parker et al., (1989) performed a laboratory study to compare the performance of PVC, SS304, SS316, and PTFE subjected to aqueous solutions of RDX, trinitrobenzene (TNB), c-1,2-DCE, t-1,2-DCE, m-nitrotoluene (MNT), TCE, MCB, o-dichlorobenzene (ODCB), p-dichlorobenzene (PDCB), and m-dichlorobenzene (MDCB) at concentrations of 2 mg/L. A biocide was added to the samples to eliminate possible losses due to biodegradation.

Prior to the experiment, they conducted a test to determine if the casing materials were capable of leaching any compounds into water. Samples of casing material were placed in vials containing well water and allowed to stand for 1 week. No evidence of materials leaching from any of the casing materials was noted.

Casing samples were placed in sample jars containing an aqueous solution of the organic compounds and sampled initially and at intervals between 1 hour and 6 weeks. Table 5 presents results after a 1-hour, 24-hour, and 6-week dwell time. The test results indicated that after 6 weeks PTFE had sorbed significant amounts of all the compounds with the exception of RDX and TNB. In the same time period, PVC showed significant sorption of TCE, MCB, ODCB, PDCB and MDCB. In each one of the cases where the PVC and PTFE both sorbed significant amounts of analytes, PTFE always had the greatest sorption rate. After 6 weeks, the SS samples exhibited no significant sorption of the tested compounds.

At the 24-hour mark, PTFE and PVC had experienced significant sorption of all the compounds with the exception of RDX, TNB, and MNT. For the compounds sorbed by PTFE and PVC, PTFE had the higher rate of uptake with the exception of c-1,2-DCE. SS showed no significant sorption of any of the com-

**TABLE 5. NORMALIZED\* CONCENTRATION OF ANALYTES FOR FOUR WELL CASINGS WITH TIME**

Analyte	Treatment	1 hour	24 hours	6 weeks
RDX	PTFE	1.03	1.00	0.99
	PVC	1.01	0.98	1.00
	SS304	0.99	1.01	0.98
	SS316	1.01	1.01	1.00
TNB	PTFE	1.01	1.00	1.01
	PVC	1.01	0.98	1.02
	SS304	0.99	1.00	1.00
	SS316	1.02	1.01	1.02
c-1,2-DCE	PTFE	1.01	0.96†	0.79†
	PVC	1.00	0.95†	0.90
	SS304	0.97	1.00	0.98
	SS316	0.95	1.00	0.99
t-1,2-DCE	PTFE	1.00	0.88†	0.56†
	PVC	1.00	0.93†	0.83
	SS304	0.95†	1.00	1.00
	SS316	1.00	1.00	1.00
MNT	PTFE	1.03	0.99	0.90†
	PVC	1.02	0.98	0.94
	SS304	1.00	1.01	1.07
	SS316	1.02	1.02	0.99
TCE	PTFE	1.00	0.85†	0.40†
	PVC	1.01	0.94†	0.88†
	SS304	0.96	1.01	0.99
	SS316	1.00	1.00	1.00
MCB	PTFE	1.01	0.90†	0.51†
	PVC	1.01	0.95†	0.86†
	SS304	0.98	1.00	0.99
	SS316	0.99	1.01	0.99
ODCB	PTFE	1.01	0.88†	0.43†
	PVC	1.02	0.94†	0.86†
	SS304	0.98	1.00	1.00
	SS316	1.01	1.01	1.00
PDCB	PTFE	0.92†	0.77†	0.26†
	PVC	0.95	0.92†	0.80†
	SS304	0.91†	1.00	1.02
	SS316	0.94	1.00	1.02
MDCB	PTFE	1.00	0.78†	0.26†
	PVC	1.02	0.92†	0.80†
	SS304	0.99	1.00	1.02
	SS316	1.03	1.00	1.01

\* The values given here are determined by dividing the mean concentration of a given analyte at a given time and for a particular well casing by the mean concentration (for the same analyte) of the control samples taken at the same time.

† Values significantly different from control values.

(Source: Parker et al., 1989)

pounds tested. It appears that PTFE cased wells will introduce a greater bias into ground-water samples than those cased with PVC if the time between sampling and purging is 24 hours.

They also conducted a desorption experiment on the samples that had sorbed organics for 6 weeks. After 3 days of testing, the PVC and PTFE samples showed desorption of analytes sorbed in the previous experiment. The desorption study showed that PTFE, in general, showed a greater loss of analytes than PVC.

Jones and Miller (1988) conducted laboratory experiments to evaluate the adsorption and leaching potential of Schedule 40 PVC (PVC-40), Schedule 80 PVC (PVC-80), ABS, SS, Teflon-PFA, Teflon-FEP, PTFE, and Kynar-PVDF. Organic compounds used in this experiment were 2,4,6-trichlorophenol (2,4,6-TCP), 4-nitrophenol, diethyl phthalate, acenaphthene, naphthalene, MDCB, 1,2,4-trichlorobenzene, and hexachlorobenzene. Samples of casing material were placed into glass vials each containing an organic compound having an approximate initial concentration of 250 ppb.

In their first experiment, the organic compounds were mixed with neutral pH ground water. The batches were sampled immediately and then at intervals of 1-, 3-, and 6-weeks. The results showed that there was no appreciable change in adsorption of the compounds after 1 week except for 2,4,6-TCP, which totally adsorbed after 3 weeks. The results also indicate that PTFE might be less likely to adsorb these compounds. Jones and Miller (1988) also point out that at the concentrations used in this study, PTFE, PVC-40, and PVC-80 exhibited very little difference in the amounts of adsorption.

In their second experiment, Jones and Miller (1988) attempted to determine the amount of the adsorbed compounds that would be released back into uncontaminated ground water after a 6-week exposure time. After a 2-week period, very little release of organic contaminants was observed. They state that only zero to trace amounts of the sorbed contaminants were desorbed into the noncontaminated ground water. Only PVC-80 and Teflon-PFA desorbed naphthalene.

They repeated their adsorption and leaching experiments using polluted ground water with a pH of 3.0. The adsorption experiment showed that, with the exception of ABS casing, the casing materials showed less adsorption at the contaminated low pH level than at the noncontaminated neutral pH level. One possible explanation is there could be stronger binding and more preferential complexing of the experimental pollutants with other pollutants in the contaminated ground water. Another, more likely explanation, is that there is a relationship between the extent of adsorption, pH, and pK, with a maximum adsorption occurring when the pH is approximately equal to pK. They explain that as the pH decreases, the hydrogen ion concentration increases and the adsorption tends to decrease, suggesting a replacement of the adsorbed compound by the more preferentially adsorbed hydrogen ions.

Jones and Miller (1988) concluded there is no clear advantage to the use of one particular well casing material over the others for the organics used in the study. Well purging procedures, sampling device selection and composition, and sample storage are probably of greater influence to sample integrity and representativeness than well casing material selection. They found

the amount of adsorption generally correlates with the solubility of the chemical independent of the well casing material.

Gillham and O'Hannesin (1990) conducted a laboratory study to investigate the sorption of six monoaromatic hydrocarbons onto/into seven casing materials. The six organic compounds used were benzene, toluene, ethylbenzene, and p-, m-, and o-xylene. The seven casing materials used in the evaluation were SS316, PTFE, rigid PVC, flexible PVC, polyvinylidene fluoride (PVDF), flexible PE, and FRE. The materials were placed in vials containing an aqueous solution of all six organic materials. Concentrations of the organics in the solution ranged between 1.0 and 1.4 mg/L. Sodium azide (0.05 percent), a biocide, was added to the solution to prevent biodegradation of the organics. The solutions were sampled 14 times from 5 minutes to 8 weeks.

Results of the study are presented in Table 6 and indicate that SS is the most favorable casing material for sampling organics. Stainless steel showed no significant uptake after an 8-week exposure period; whereas, all the polymer materials adsorbed all the organic compounds to some degree. The order of magnitude of adsorption for the various polymer materials tested was flexible PVC > PE > PTFE > PVDF > FRE > rigid PVC (from greatest to least sorption). Flexible tubing materials showed substantial uptake after 5 minutes of exposure. Rigid PVC showed the lowest rate of uptake of the polymer materials.

**TABLE 6. TIME INTERVAL WITHIN WHICH THE CONCENTRATION PHASE FOR THE COMPOUND AND CASING MATERIAL BECAME SIGNIFICANTLY DIFFERENT FROM 1.0**

Material	Time, hours					
	Benzene	Toluene	Ethylbenzene	m-Xylene	o-Xylene	p-Xylene
SS316	>1344					
PVC (rigid)	48 - 96	24 - 48	12 - 24	12 - 24	12 - 24	12 - 24
FRE	24 - 48	3 - 6	0.1 - 1.0	3 - 6	3 - 6	3 - 6
PVDF	24 - 48	3 - 6	1 - 3	1 - 3	0.1 - 1.0	1 - 3
PTFE	24 - 48	3 - 6	1 - 3	3 - 6	6 - 12	1 - 3
PE	0 - 0.1	0 - 0.1	0 - 0.1	0 - 0.1	0 - 0.1	0 - 0.1
PVC (flexible)	0 - 0.1	0 - 0.1	0 - 0.1	0 - 0.1	0 - 0.1	0 - 0.1

(Source: Gillham and O'Hannesin, 1990)

Gillham and O'Hannesin (1990) conclude all of the polymer materials tested, except flexible PVC and PE, are suitable casing materials in monitoring wells. This is based on selection of an appropriate casing diameter and an appropriate interval between purging and sampling. They state rigid PVC is the most favorable polymer material for casing in monitoring wells.

Reynolds et al., (1990) conducted laboratory tests to evaluate the effects of five halogenated hydrocarbons on several casing materials. The halogenated hydrocarbons and casing materials used in the experiment were identical to those used by Reynolds and Gillham (1985) with the addition of glass, SS316, aluminum, and galvanized sheet metal to the casing materials.

The results indicated borosilicate glass was the least likely of the 10 materials to affect the samples. The results also showed that all of the metals had the potential to sort compounds from solution. The order of the compound sorption rate for the metals was galvanized steel > aluminum > SS (greatest to least sorption).

Results of the sorption experiments indicated rigid PVC was preferable to PTFE for sampling low concentrations of halogenated hydrocarbons. The compound sorption rates, from greatest to least sorption, are latex > low density PE > PP > nylon > PTFE > rigid PVC. The rates of compound loss, from greatest to least loss, are PCE > HCE > 1,1,1-TCA > BRO > 1,1,2,2-TET. It should be noted the inequalities shown above are not necessarily significant. For example, the rates between PTFE and rigid PVC are not significant and the same is true for nylon and PP. Their study showed flexible polymer tubing is likely to have greater sorption rates than rigid polymers which is in agreement with Barcelona et al., (1985). They also found evidence that there is a correlation between compound solubility and sorption, substantiating earlier studies. Reynolds et al., (1990) found diffusivity decreased as mean molecular diameter increased which agrees with a study performed by Berens and Hopfenberg (1982), based on polymeric diffusivity tests.

They suggest the use of PTFE in monitoring wells in areas where higher concentrations might be encountered, for instance near a solvent spill. Their study showed a polymer exposed to high concentrations of an organic compound that is a good solvent for the polymer, that the polymer will absorb large quantities of the solvent and swell. However, it is difficult to predict the swelling power of various solvents. As an example, rigid PVC can absorb over 800 percent of its weight in DCM but only 1 percent of CCL<sub>4</sub>. Schmidt (1987), however, found no swelling or distortion of rigid PVC casing or screen when exposed to various gasolines for 6.5 months.

Taylor and Parker (1990) visually examined PVC, PTFE, SS304, and SS316 with a scanning electron microscope (SEM) to determine how they were affected by long-term exposures (1 week to 6 months) to organic compounds. Organics used in this test were PDCB, ODCB, toluene, and PCE at concentrations of 17.3, 33.5, 138, and 35.0 mg/L, respectively (approximately 25 percent of their solubilities in water).

SEM examinations showed no obvious surface structure changes for any of the materials exposed to the different concentrated organic aqueous solutions. They caution, however, that this study cannot be extended to instances where casing materials are exposed to pure organic solvents. They did not report the amount of compound sorbed by the different casing materials.

### Inorganic Studies

Massee et al., (1981) studied the sorption of silver (Ag), arsenic (As), Cd, selenium (Se), and Zn from distilled water and artificial sea water by borosilicate glass, high-pressure PE, and PTFE containers. The effect of specific surface (R in cm<sup>-1</sup>), i.e., the ratio of the surface area of the material in contact with the solution, to the volume of the solution, was also studied. Metals were added to the distilled and artificial sea water. The pH levels of the aqueous solutions used were 1, 2, 4, and 8.5. Water

samples were tested at intervals ranging between 1 minute and 28 days. Losses of As and Se were insignificant for all the treatments. At pH levels of 1 and 2, no significant sorption from either distilled water or artificial sea water was observed for any of the containers or metals used in this study. Test results of the sorption of Ag, Cd, and Zn from distilled water and sea water are presented in Tables 7 and 8, respectively.

The results showed PTFE sorbed substantial amounts of Ag, Cd, Zn, and the amounts sorbed were dependent on the pH and salinity of the solutions. Specific surface was found to have a significant effect on the sorption of metals by PTFE. For example, at the end of 28 days the loss of Ag to PTFE with  $R = 5.5 \text{ cm}^{-1}$  was almost 4 times higher than for  $R = 1.0 \text{ cm}^{-1}$ .

Massee et al., (1981) concluded that sorption losses are difficult to predict because the behavior of trace elements depends on a variety of factors such as trace element concentration, material, pH, and salinity. They noted that a reduction in contact time, specific surface, and acidification may reduce sorption losses.

Miller (1982) conducted a study to determine the potential of PVC, PE, and PP to sorb and release Cr(VI) and lead (Pb) when in a Cr(VI)-Pb solution and in a solution of these two metals along with the following organics; BRO, PCE, TCE, trichlorofluoromethane, 1,1,1-TCA, and 1,1,2-trichloroethane. Tables 9 and 10, respectively, present the results for the Cr(VI) and Pb adsorption and leaching studies. The results showed that none of the materials tested adsorbed Cr(VI) to any significant extent when in a solution with Pb. When in a solution with Pb and 6 other organics, 25 percent of Cr(VI) was adsorbed by the 3 casing materials. No leaching of Cr(VI) was observed from any of the materials either in the metals only or metals and organics solutions. Seventy-five percent of the Pb was adsorbed by PVC when in a solution with Cr(VI) and also when in a solution of Cr(VI) and the six organics. PE and PP showed about 50 percent adsorption of Pb when in a solution with Cr(VI). The casing materials did not leach any Pb when in a solution with Cr(VI); however, when in a solution with Cr(VI) and 6 organics, the 3 casing materials leached approximately 50 percent of the Pb initially adsorbed. In his study, Miller found that PVC

TABLE 7. SORPTION BEHAVIOR OF SILVER, CADMIUM, AND ZINC IN DISTILLED WATER

Metal	Contract Time	PE				Borosilicate Glass		PTFE			
		pH		Sorption (%)		pH		Sorption (%)		pH	
		4	8.5	4	8.5	4	8.5	4	8.5	4	8.5
		1.4	3.4	1.0	3.4	1.0	4.2	1.0	4.2	1.4	5.5
Ag	1 hour	10	15	25	36	*	4	9	21	*	10
	1 day	25	66	72	49	32	18	26	48	4	25
	28 days	96	100	59	100	82	80	72	63	15	28
Cd	1 hour	*	*	7	69	*	*	6	26	*	38
	1 day	*	*	*	47	*	*	10	32	*	48
	28 days	*	*	*	31	*	*	*	*	15	46
Zn	1 hour	*	*	*	65	*	*	23	22	*	18
	1 day	*	*	8	56	*	*	26	22	*	27
	28 days	*	*	12	56	*	*	*	*	6	29

\*Denotes a loss smaller than 3 percent.

(Source: Massee et al., 1981)

TABLE 8. SORPTION BEHAVIOR OF SILVER, CADMIUM, AND ZINC IN ARTIFICIAL SEA WATER

Metal	Contract Time	PE				Borosilicate Glass		PTFE			
		pH		Sorption (%)		pH		Sorption (%)		pH	
		4	8.5	4	8.5	4	8.5	4	8.5	4	8.5
		1.4	3.4	1.0	3.4	1.0	4.2	1.0	4.2	1.4	5.5
Ag	1 hour	*	*	6	5	*	*	3	3	*	*
	1 day	*	*	24	29	4	4	6	9	*	12
	28 days	*	*	48	78	82	71	40	67	*	37
Cd	1 hour	*	*	*	*	*	*	*	*	*	*
	1 day	*	*	*	*	*	*	*	*	*	*
	28 days	*	*	*	*	14	36	*	*	*	*
Zn	1 hour	*	*	*	*	*	*	9	31	*	*
	1 day	*	*	*	*	*	*	5	26	4	*
	28 days	*	*	*	*	20	19	4	9	5	*

\*Denotes a loss smaller than 3 percent.

(Source: Massee et al., 1981)



**TABLE 9. TRENDS OF CHROMIUM (VI) EXPOSED TO SYNTHETIC WELL CASING (COMPARED TO CONTROLS)**

Casing Material	Adsorption		Adsorption/Leaching	
	Metals Only	Metals and Organics	Metals Only	Metals and Organics
PVC	No adsorption	Slight (25%) adsorption	No leaching	No leaching
PE	No adsorption	Slight (25%) adsorption	No leaching	No leaching
PP	No adsorption	Slight (25%) adsorption	No leaching	No leaching

(Source: Miller, 1982)

**TABLE 10. TRENDS OF LEAD EXPOSED TO SYNTHETIC WELL CASING (COMPARED TO CONTROL)**

Casing Material	Adsorption		Adsorption/Leaching	
	Metals Only	Metals and Organics	Metals Only	Metals and Organics
PVC	Mostly (75%) adsorbed	Mostly (75%) adsorbed	No leaching	Mostly (75%) adsorbed
PE	Moderate (50%) adsorption (delayed)	Moderate (50%) adsorption	No leaching	Mostly (75%) adsorbed
PP	Moderate (50%) adsorption (delayed)	Slight (25%) adsorption	No leaching	Mostly (75%) adsorbed

(Source: Miller, 1982)

generally causes fewer monitoring interferences with VOCs than PE and PP and that PVC adsorbed and released organic pollutants at a slower rate relative to PE and PP.

Hewitt (1989a) examined the potential of PVC, PTFE, SS304, and SS316 to sorb and leach As, Cd, Cr, and Pb when exposed to ground water. The pH, TOC, and metal concentrations of the solution were varied and samples taken between 0.5 and 72 hours. The study showed that PTFE had the least-active surface and showed an affinity only to Pb (10 percent sorption after 72 hours). PVC and SS leached and sorbed some of the metals tested. PVC was a source for Cd and sorbed Pb (26 percent sorption after 72 hours). The SSs were the most active of the materials tested. SS304 was a source of Cd and sorbed As and Pb. SS316 was also a source of Cd and sorbed As, Cd, and Pb. The study showed results were affected by the solution

variables (i.e., pH, TOC, and concentration). SS304 and SS316 showed evidence of corrosion near cuts and welds which may provide active sites for sorption and release of contaminants. Hewitt (1989a) concludes PTFE is the best material for monitoring the metals used in this study whereas, SSs are not suitable. He states that although PVC was affected by Cd and Pb it should still be considered as a useful casing material based on economics, and that when the time between purging and sampling is less than 24 hours, the effects of Cd and Pb on PVC may be of less concern.

Hewitt (1989b) conducted a study to determine the amounts of barium, Cd, Cr, Pb, Cu, As, Hg, Se, and Ag leached from PTFE, PVC, SS304, and SS316 in ground water. Table 11 summarizes the results of the investigation. Results indicate that PTFE was the only material tested not to leach any metals into the ground-water solution. PTFE, however, did show a trend to sorb Cu with time. PVC and SS316 showed a tendency to leach Cd; in addition, these two materials, along with SS304, sorbed Pb. PVC was also shown to leach Cr and provide sorption sites for Cu. SS316 significantly increased the concentration of Ba and Cu in the ground-water solution. SS304 consistently contributed Cr with time to the ground-water solution. None of the well casing materials contributed significant levels of As, Hg, Ag, or Se to the ground water.

**TABLE 11. SUMMARY OF RESULTS**

	Ba	Cd	Cr	Pb	Cu
Materials that leached >1% of the EPA drinking water quality level in ground-water solutions	SS316 PVC	SS316 PVC	SS304 SS316 PVC	SS304 PVC SS316	NA*
Materials that showed the highest average overall amount of analyte leached	SS316	SS316	SS304	SS304	SS316

\*Does not apply

(Source: Hewitt, 1989b)

Hewitt (1989b) concludes PTFE is the best casing material when testing for trace metals while SS should be avoided. He also states PVC is an appropriate second choice because its influence on metal analytes appears to be predictable and small.

### Casing Material Cost Comparison

A consideration when installing monitoring wells is cost. Costs to be considered in the installation of monitoring wells are cost of construction materials, drilling costs, and expected life (replacement costs) of the casing material. Table 12 presents a cost comparison among five casing materials: PVC, SS304, SS316, PTFE, and FRE. The prices shown were obtained from Brainard-Kilman (1990) with the exception of the FRE casing,



**TABLE 12. CASING MATERIAL COST COMPARISON**

Prices reflect the cost of ten 10-ft long by 2-in. diameter casing sections, a 5-ft long 0.010-in slotted screen, and a bottom plug.

Casing Material	Price
PVC*	\$ 179.50
FRE**	966.00
SS304	1,205.00
SS316	1,896.00
PTFE	3,293.50

\* Schedule 40 PVC

\*\* Low flow screen

whose price was provided by ENCO (1989). The cost estimates are for ten 10-foot sections (100 feet) of 2-inch threaded casing, 5 feet of 0.010-inch slotted screen, and a bottom plug.

The cost of materials for 1 PTFE well is approximately 18 times greater than 1 constructed on PVC (Table 12). At first glance, PVC, by far, is the most economical material for constructing monitoring wells. However, if drilling and material (bentonite, cement, sand, etc.) costs are considered, the percent difference in cost between PVC wells and wells constructed of SS, FRE, or PTFE is reduced.

For example, assume that the cost of installing, materials, and completing a 100-foot deep monitoring well (exclusive of casing material costs) in unconsolidated material is \$5,000. When the cost of casing material is added to the drilling and materials costs, a PVC-cased well costs \$5,179.50 and an SS316-cased well \$6,896.00. When drilling and materials costs are considered, a PVC-cased well costs approximately 25 percent less than a SS316-cased well. However, when drilling and materials costs are not taken into account, PVC casing looks especially attractive since it is approximately 90 percent less expensive than SS316 casing. In this case, a SS316-cased well may be considered to be cost effective especially if organics are expected to be sampled. Thus, the significance of the "cost of casing materials versus ground water-casing interaction" issue is reduced.

## CONCLUSIONS

All aspects of a ground-water sampling program have the potential to introduce error to a ground-water sample. Interaction between monitoring well casing materials and ground water is only one of the ways in which error may be introduced in a sampling program. Presently, there are a variety of materials available for fabricating monitoring wells. The potential for these casing materials to interact with ground water has

found to be affected by many factors, including pH and composition of the ground water and the casing-ground water contact time. The complex and varied nature of ground water makes it very difficult to predict the sorption and leaching potential of the various casing materials. Consequently, the selection of the proper casing material for a particular monitoring application is difficult. This is evidenced by the lack of agreement among researchers on which is the "best" material. The problem is compounded by the inconclusive and incomplete results of laboratory studies on the effects of rigid well casing materials with inorganic or organic dissolved species.

Many of the experiments examined the effects of time on the sorption and leaching potential of the various casing materials. The experiments were usually run under laboratory conditions in which distilled or "organic free" water was used and casing materials were subject to contaminants for periods ranging from minutes to months. These experiments, in general, indicate a trend for the materials to be more reactive with the aqueous solutions with time. Experiments showed if the time between well purging and sampling is relatively short, some of the more sorptive materials could be used without significantly affecting sample quality.

The selection of appropriate materials for monitoring well casing at a particular site must take into account the site hydrogeology and several general requirements. These general requirements for the screens and casing of wells that are used for ground-water monitoring are the following:

1. Depth to zones being monitored and total depth of well must be considered.
2. The geochemistry of the geologic materials over the entire interval in which the well is to be cased and screened must be taken into account.
3. The wells must be chemically resistant to naturally occurring waters.
4. The well materials must be chemically resistant to any contaminants that are present in any and all contaminated zones of the aquifer or aquifers being monitored.
5. The strength of the materials must be physically strong enough to withstand all compressive and tensile stresses that are expected during the construction and operation of the monitoring well over the expected lifetime.
6. Installation and completion into the borehole during construction of the monitoring well must be relatively easy.
7. The well materials must be chemically resistant to any anticipated treatments which are strongly corrosive or oxidizing.

It may be necessary to conduct site-specific, comparative performance studies to justify preference for a particular well casing or screening material over another.

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## ABBREVIATIONS

1,1-DCA	1,1-Dichloroethane	ODCB	o-Dichlorobenzene
1,1,1-TCA	1,1,1-Trichloroethane	p-	Para
1,1,2,2-TET	1,2,2,2-Tetrachloroethane	Pb	Lead
1,2-DCA	1,2-Dichloroethane	PCB	Polychlorinated biphenyl
2,4,6-TCP	2,4,6-Trichlorophenol	PCE	Tetrachloroethylene
ALS	Acrylonitrile butadiene styrene	PDCB	p-Dichlorobenzene
Ag	Silver	PE	Polyethylene
As	Arsenic	pH	Hydrogen ion concentration of the solution
ASTM	American Society for Testing and Materials	pK	Log dissociation constant
BRO	Bromoform	PP	Polypropylene
c-1,2-DCE	cis-1,2-Dichloroethylene	ppb	Parts per billion (by weight)
CCl <sub>4</sub>	Carbon tetrachloride	ppm	Parts per million (by weight)
Cd	Cadmium	PTFE	Polytetrafluoroethylene (Teflon®)
CHCl <sub>3</sub>	Chloroform	PVC	Polyvinylchloride
Cr	Chromium	RCRA	Resource Conservation and Recovery Act
Cu	Copper	RDX	Hexahydro-1,3,5,7-trinitro-1,3,5-triazine
DCM	Methylene chloride (dichloromethane)	RVCM	Residual vinyl chloride monomer
DNT	2,4-Dinitrotoluene	Se	Selenium
EMSL-LV	Environmental Monitoring Systems Laboratory- Las Vegas	SEM	Scanning electron microscope
FRF	Fiberglass reinforced epoxy	SS	Stainless steel
HCE	Hexachloroethane	SS304	Stainless steel 304
Hg	Mercury	SS316	Stainless steel 316
HMX	Octahydro-1,2,5,7-tetranitro 1,3,5,7-tetrazocine	t-1,2-DCE	trans-1,2-Dichloroethylene
m-	Meta	TCE	Trichloroethylene
MCB	Chlorobenzene	TEGD	Technical Enforcement Guidance Document
MDCB	m-Dichlorobenzene	TNB	Trinitrobenzene
MNT	m-Nitrotoluene	TNT	2,4,6-Trinitrotoluene
MPL	Maximum permissible levels	TOC	Total organic carbon
NSF	National Sanitation Foundation	U.S. EPA	U.S. Environmental Protection Agency
o-	Ortho	VOC	Volatile organic compound
		Zn	Zinc

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# Ground-Water Issue

## POTENTIAL SOURCES OF ERROR IN GROUND-WATER SAMPLING AT HAZARDOUS WASTE SITES

K. F. Pohlmann and A. J. Alduino

### INTRODUCTION

The Regional Superfund Ground Water Forum is a group of ground-water scientists representing the U.S. EPA's Regional Superfund Offices that was organized to exchange up-to-date information related to ground-water remediation at Superfund sites. The introduction of error during ground-water sampling is an issue identified by the Forum as a concern of Superfund decision makers.

To address this issue, this paper was prepared under the direction of K. F. Pohlmann of the Desert Research Institute/Water Resources Center, with the support of the Environmental Monitoring Systems Laboratory - Las Vegas (EMSL-LV) and the Superfund Technical Support Project. For further information contact Ken Brown, EMSL-LV Technology Support Center Director, at 702/798-2270 or K. F. Pohlmann at 702/895-0485.

Acquisition of ground-water samples that accurately represent in situ physical, chemical, and biological conditions is critical to all phases of Superfund site investigations. Nonrepresentative data collected during the remedial investigation (RI) may interfere with the characterization of site hydrogeology, contaminant distribution, and the determination of whether ground water is providing a pathway for migration of waste constituents away from the site. The feasibility study (FS) phase of the investigation depends on representative data to adequately define the optimal remediation technologies for the site. Finally, accurate data are required during the remediation phase to determine whether remedial actions are functioning effectively.

Sample error is defined here as the deviation from in situ values of hydrochemical parameters and constituents caused by the conduct of ground-water sampling investigations. Errors in ground-water quality data reduce the ability of samples to accurately represent in situ ground-water conditions resulting in increased variability of analytical results and weakened confidence in ground-water data. As a consequence, the objectives of the site investigation may be jeopardized. To ensure representative data, it is necessary to identify, evaluate, and reduce potential sources of error for every aspect of the sampling program. Errors that are most difficult to identify may be the most critical to sampling programs because important conclusions may be unknowingly based on erroneous or inadequate data.

### PURPOSE AND SCOPE

This paper is intended to familiarize RPMs, OSCs, and field personnel with the sources of error inherent to ground-water sampling, and the relative impact of these errors on sample representativeness. Elements of typical sampling protocol will be discussed in relation to how these sources of error can be identified and minimized. Where possible, the error associated with a particular method or material will be quantified and the elements ranked as to their potential for adversely impacting sample representativeness. Some of the elements of sampling protocol to be addressed include monitoring well drilling, design, construction, and purging, sample collection methods and devices, sample filtration, equipment decontamination, sample transport and storage, and analytical methods.



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Each Superfund site has unique geologic, hydrologic, biologic and chemical conditions that may influence the type and magnitude of potential sample errors. This paper provides an overview of sample error; types of error potentially important at each site must be evaluated on an individual basis. Furthermore, while this paper will remain static, the conduct of site investigations will be in a constant state of flux as new technology is developed and as the understanding of contaminant transport and fate and the sampling process is improved. As a result, sources of sampling error described herein may be resolved through the application of new technology and methods while new sources of error are likely to be identified.

## MONITORING WELL DESIGN

The design of ground-water monitoring installations must be consistent with geologic, hydrologic, and hydrochemical conditions to obtain representative ground-water samples. Important aspects of monitoring well design include length of well intake interval, design of the filter pack and screen, design and installation of borehole seals, and well location.

### *Intake Length*

The length and location of well intakes have important effects on the degree with which samples represent ground-water conditions. Long well intakes (long screens) are open to a large vertical interval and therefore are more likely to provide samples that are a composite of the ground water adjacent to the entire intake. Conversely, short intakes (short screens) may be open to a single strata or zone of contamination and are more likely to provide samples that represent specific depth intervals. Wells that are screened over more than one depth interval (multi-screened wells), regardless of their screen lengths, may impact ground-water conditions and samples in much the same way as long-screened wells.

Long-screened wells have been suggested as being more cost effective in detection monitoring than several short-screened wells because they sample greater vertical sections of aquifers (Giddings, 1986). However, pumping-induced vertical flow in wells with long screens can impact ground-water flow and contaminant concentrations near the well (Kaleris, 1989). In addition, when ground-water contamination is vertically stratified, composite samples collected from a long-screened well represent some sort of average of concentrations adjacent to the screen, and provide little information about the concentrations in individual strata. In particular, in cases where contaminants may be of low concentration and restricted to thin zones, long-screened wells may lead to dilution of the contaminants to the point where they may be difficult to detect (Cohen and Rabold, 1987). Likewise, long-screen wells intersecting contaminants of differing densities may allow density-driven mixing within the well bore and subsequent dilution of contaminant concentrations (Robin and Gillham, 1987). The use of inflatable packers to isolate specific zones within a long screen may not be an effective solution because ground water may flow vertically through the filter pack from other zones in response to the reduced hydraulic head in the packed-off zone during sampling.

Vertical head gradients in aquifers near long-screened wells may lead to error in two ways: (1) if contaminants are moving through a zone with low hydraulic head, cleaner water moving

from zones of higher head may dilute the contaminants, leading to detection of artificially low concentrations, and, (2) if higher concentrations of contaminants are moving through a zone of high hydraulic head, cross-contamination between water-bearing zones may occur via the well bore (McIlvride and Rector, 1988). These workers describe a case history in which two aquifer zones were identified at a site, with only the top zone contaminated with VOCs. Wells screened only in the contaminated zone resulted in detection of VOCs in the few hundred  $\mu\text{g/L}$  range while samples collected from long-screened wells open to both intervals showed no VOC contamination. A numerical flow model of a long-screened well developed by Reilly et al. (1989) demonstrated that very low head gradients can lead to substantial cross-flow within long-screened wells. At sites where delineation of vertical hydraulic and concentration gradients is important, errors can be reduced by utilizing a system of nested short-screened wells that can more accurately characterize the contaminant distribution.

Multilevel sampling devices provide an alternative monitoring technique in situations where vertical head gradients are important or where contamination is vertically stratified. These devices can be installed in such a way that individual zones can be sampled separately without vertical movement of ground water or contaminants between zones. Using a multilevel device, Smith et al. (1987) detected a zone containing nitrate concentrations over 10 mg/L that had been previously undetected by observation wells with two-foot screens. The samples from the multilevel sampler also detected large vertical gradients in electrical conductivity (EC) and chloride that were not detected with the monitoring wells.

Residential and municipal water-supply wells that are often used during early phases of RI programs are generally constructed with long screens, therefore concentrations of contaminants in samples collected from these wells may not represent ambient ground-water concentrations. When defining human receptors this may not be an issue because the overall quality of ground-water extracted from water-supply wells may not reflect the quality of water in individual strata. In these cases, dilution may reduce concentrations of contaminants to within health-based standards. However, gross errors may be introduced into the analysis if these concentrations are used for detailed delineation of the geometry and concentrations of contaminant plumes or detection of contaminants at very low concentrations.

To mitigate hazards, waste management options at Superfund sites may include remediation of contaminated ground water by pumping and treatment. Long-screen wells are often the most effective for extraction of ground water because they are hydraulically more efficient than wells with short screens. However, because accurate ground-water contaminant concentrations cannot be determined from these wells it may be necessary to install separate wells for monitoring the progress of ground-water extraction and treatment.

### *Filter Pack and Well Intake*

Suspended solids that originate from drilling activities or are mobilized from the formation during development, purging, or sampling may disrupt hydrochemical equilibrium during sample collection and shipment. A properly designed combination of

filter pack and well intake provides an efficient hydraulic connection to a water-bearing zone and minimizes the suspended solids content of sampled water. However, to be most effective, filter pack and well intake design must be based on the sediments encountered in each borehole. Inadequate well performance resulting from application of a generic well design may lead to incomplete well development and high suspended solids content in samples. Descriptions of the methods of filter pack and intake design can be found in Driscoll (1986) and Aller et al. (1989).

Artificial filter packs should be composed of a chemically-inert material so as to reduce the potential for chemical alteration of ground water near the well. Clean silica (quartz) sand is generally recommended and widely used because it is nonreactive under most ground-water conditions. Other types of materials may induce chemical changes. For example, filter pack materials containing calcium carbonate, either as a primary component or as a contaminant, may raise the pH of water that it contacts and lead to precipitation of dissolved constituents (Aller et al., 1989).

The use of a tremie pipe to install filter pack materials minimizes the potential for introducing sample error to this phase of well construction. Dropping filter pack materials directly into an uncased borehole may lead to cross-contamination by mobilizing sediments or ground water between depth intervals. Furthermore, installation of filter pack materials by methods which introduce water to the borehole may modify hydrochemistry to an unknown extent or add contaminants to the sampling zone. Water-based methods may also lead to cross-contamination within the borehole.

### **Borehole Seals**

Borehole seals, generally composed of expandable bentonite or cement grout, are well-known as potential sources of sampling error. The expandable bentonite clay used in many seals has high ion exchange capacity which may alter major ion composition of water (Gillham et al., 1983) or concentrations of contaminants that form complexes with these ions (Herzog et al., 1991). The effects of these reactions are seldom revealed by measurement of field parameters and normally-conducted analyses, but in cases of extreme sodium bentonite contamination may be seen as abnormally high sodium concentrations.

Cement grout can also significantly influence ground water chemistry, particularly if the grout doesn't set properly. Contamination by grout seals, which generally results from its calcium carbonate content and high alkalinity, may be identified by elevated calcium concentrations, pH (generally over 10 pH units), EC, and alkalinity (Barcelona and Helfrich, 1986). These workers found that cement contamination of several wells persisted for over 18 months after well completion and was not reduced by ten redevelopment efforts. Barcelona et al. (1988a) indicate that solution chemistry and the distribution of chemical species can be impacted by cement contamination although these impacts have not been quantified to date. In low-permeability sediments, the impacts of grout materials may be much greater due to insufficient flushing of the installation by moving ground water.

Contamination from borehole seals can be minimized by separating the seals from sampling zones by fine-grained transition

sand, estimating the volume of seal material required before installation to more easily detect bridging problems during emplacement, and by allowing sufficient time for the seals to set. In addition, cement grout can be isolated from sampling zones by installation of a bentonite seal. Error can also be reduced by installing borehole seals with a tremie pipe. Dropping seal materials directly into an uncased borehole may lead to cross-contamination by mobilizing sediments or ground water between depth intervals, or may contaminate sampling zones if the seal materials are dropped past the sampling zone depth. Furthermore, installation of seal materials by methods which introduce water to the borehole may modify hydrochemistry to an unknown extent or introduce contaminants to the sampling zone. Water-based methods may also lead to cross-contamination within the borehole.

### **Well Location**

The location of monitoring wells with respect to ground-water contaminant plumes is important to the accurate depiction of contaminant movement and concentration distribution, especially in areas where concentration gradients are large. A discussion of optimum well placement is beyond the scope of this document, but aspects of this topic can be found in the works of Keith et al. (1983), Meyer and Brill (1988), Scheibe and Lettenmaier (1989), Spruill and Candela (1990), and Andricevic and Fouloula-Georgiou (1991). These investigators discuss various aspects of monitoring well network design and how monitoring well coverage of the area under investigation relates to accurate quantification of spatial variation in hydrochemical parameters. Generally implied within network design is the reduction in error associated with delineating spatial variation. Sampling from wells whose locations were determined without adequate consideration of network design and geologic, hydrologic, and hydrochemical conditions may lead to significant errors in data interpretation and conclusions. For example, resolution of concentration distribution may be reduced in areas where wells spacing intervals are too large for the scale of the investigation.

To summarize the topic of monitoring well design, collection of accurate ground-water quality data in three dimensions is strongly dependent on the design of the ground-water monitoring system, including both individual wells and well networks. Significant errors can be introduced into sampling data, and the resultant conclusions, if well intakes and filter packs are not designed for ambient conditions, or are placed at inappropriate depths or over excessive vertical intervals, or if borehole seals are improperly installed. Furthermore, the design of monitoring well networks may introduce error by inadequately representing spatial variation through inadequate coverage of the site. Although the magnitude of these errors is heavily dependent on the geologic, hydrologic, and hydrochemical conditions present at a particular site, order of magnitude effects are easily within the realm of possibility.

### **DRILLING METHODS**

Long-term or permanent disturbance of hydrogeologic and hydrochemical conditions may result from the drilling method used for monitoring well installation, possibly leading to significant error during subsequent ground-water sampling. Drilling methods may disturb sediments, allow vertical movement of ground water and/or contaminants, introduce materials foreign



to the subsurface, and clog void spaces. The extent to which conditions are altered depends on the drilling method utilized and the nature of the geologic materials (Gillham, et al., 1983). In addition, the properties of the contaminants at the site will influence their sensitivity to the impacts of drilling.

Monitoring wells are commonly constructed by auger, rotary, drill-through casing, and cable-tool methods. Auger drilling methods utilize hollow- or solid-stem auger flights and are generally restricted to use in unconsolidated materials. Rotary techniques are classified based on the composition of the drilling fluid (water, air, and various additives), the mode of circulation (direct or reverse), and the type of bit (e.g. roller cone, drag, or button) and are adaptable to most geologic conditions. The drill-through casing method utilizes rotary or percussion drilling techniques but uses a casing driver to advance temporary casing in conjunction with the advancing borehole. In cable-tool drilling, the borehole is advanced by alternately raising and lowering a heavy string of drilling tools suspended from a cable. Temporary casing can also be advanced as drilling progresses.

Some drilling methods may alter the hydrogeologic environment by smearing cuttings (particularly fine sediments) vertically along the borehole wall. This action may form a mudcake that can reduce the hydraulic efficiency of the borehole wall and modify ground-water flow into the completed well (McIlvride and Weiss, 1988). Smearing may also transport sediments between zones and alter the vertical distribution of contaminants adsorbed onto these sediments. In addition, methods that mix sediments horizontally near the well bore may affect the transport of contaminants near the completed well (Morin, et al., 1988).

Vertical movement of ground water may occur during drilling, primarily in situations where the borehole remains uncased during drilling operations. Ground water can be transported vertically by circulating drilling fluid or by hydraulic head differences between zones. In situations where contaminated ground water is vertically stratified, vertical ground-water movement may cause cross-contamination within the well-bore and adjacent formation (Gillham et al., 1983). Movement of ground water and contaminants between zones may also disrupt hydrochemical equilibrium near the well.

Drilling activities can alter hydrochemistry as a result of contact with introduced materials foreign to the subsurface environment. For example, lubricants or hydraulic fluids may enter the borehole directly by falling from the drilling rig or may enter indirectly via drilling fluids. In the latter case, contaminants may originate in mud pumps, air compressors, or down-hole drilling equipment. Soils or other material from the drilling site may also enter the open borehole or may adhere to drilling equipment as it is prepared for use. However, the material most commonly introduced to boreholes is drilling fluid, which is used to remove cuttings, stabilize the borehole wall, and provide cooling, lubrication, and cleaning of the bit and drill pipe (Driecoll, 1986). Drilling fluids commonly are composed of water or air alone or in combination with clay (usually bentonite) and/or polymeric additives.

Water from water-based drilling fluids that migrates away from the borehole and mixes with ambient ground water may alter hydrochemical conditions (Aller et al., 1989). For example,

introduction of a different water type may add contaminants or disrupt hydrochemical equilibrium and cause precipitation of dissolved constituents. During sampling, some of these precipitates may be redissolved by ground water flowing toward the well causing non-representative samples.

The bentonite additives used in many drilling fluids have a high capacity for ion exchange and may alter hydrochemistry of ground-water samples if not completely removed from the borehole and surrounding formation (Gillham et al., 1983). Ion exchange reactions that alter major ion composition may also affect the concentrations of contaminants that form complexes with these ions (Herzog et al., 1991). Organic polymeric additives can introduce organic carbon into ground water and provide a substrate for microbial activity leading to errors in water quality observations for long periods. Barcelona (1984) reported that total organic carbon (TOC) levels in wells drilled with fluids containing organic additives remained over three times higher than background levels for two years. In that study, TOC levels could not be reduced to less than two times background levels, even after substantial pumping.

The presence of drilling fluids in the formation surrounding well installations, even after well development, was shown by Brobet and Buszka (1986). That study, which used chemical oxygen demand (COD) as an indicator of the presence of drilling fluid, tested three additives of water-based drilling fluids: guar fluid, guar fluid with a breakdown additive, and bentonite. Brobet and Buszka (1986) reported that, using standard well purging and sampling methods, COD levels were elevated for 50 days in a well drilled with the guar-and-additive fluid, 140 days in a well drilled with bentonite, and 320 days in a well drilled with the guar fluid alone. More intense well-purging reduced the COD levels, but not to background values.

Contaminants present in drilling fluid may also mix with ground water and bias sampling results. Mud pumps used with water-based drilling fluids can add trace quantities of lubricants to the fluid and deposit them in the wellbore and surrounding formation. Air compressors used to develop and maintain pressure of air-based drilling fluids may have similar impacts. Filtration units in air-based systems are designed to prevent this occurrence, however, if feasible, the air stream should be sampled during drilling to determine the effectiveness of the filter. Filtration is generally not possible for water-based systems so if ground water samples are to be collected for compounds related to these lubricants it may be necessary to sample the drilling fluid before it enters the borehole.

An outline of potential impacts of drilling methods on ground-water sample quality is shown in Table 1, which was compiled from the work of Scall et al. (1981), Gillham et al. (1983), Keely and Bosteng (1987), Aller et al. (1989), and Herzog et al. (1991).

## WELL DEVELOPMENT

Ground-water monitoring wells are developed to restore the sampling zone to conditions present prior to drilling so that sampled ground water can flow unimpeded and unaltered into the well. Materials associated with the drilling process, including borehole wall mudcake, smeared and compacted sediments, and drilling and other fluids, all must be removed from the sampling zone to the extent possible. This can be accomplished

**TABLE 1. POTENTIAL IMPACTS OF DRILLING METHODS ON GROUND-WATER SAMPLE QUALITY**

Method	Potential Impacts
Auger	<p>Drilling fluids generally not used but water or other materials added if heaving sands are encountered may alter hydrochemistry</p> <p>Smearing of fine sediments along borehole wall</p> <p>Vertical movement of ground water and/or contaminants within borehole</p> <p>Lateral mixing of sediments near well bore</p>
Rotary	<p>Drilling fluids are required and may cause cross-contamination, vertical smearing of sediments, alteration of hydrochemistry, and introduction of contaminants</p> <p>Smearing of fine sediments along borehole wall</p> <p>Vertical movement of ground water and/or contaminants within borehole</p>
Drive-Through-Casing	<p>Drilling fluids required but advancing casing reduces potential for drilling fluid loss, cross-contamination, and vertical smearing of sediments, ground water, and contaminants.</p>
Cable Tool	<p>Advancing casing reduces potential for cross-contamination, and vertical smearing of sediments, ground water, and contaminants.</p>

in monitoring wells by several methods including surging with a surge block mechanism, surging and pumping with compressed air, pumping and overpumping with a pump, jetting with air or water, backwashing with water, and bailing. All of these methods have the potential (to varying degrees) to influence the quality of ground water samples; the extent depends on the nature of their action and the condition of the sampling zone after drilling.

Development should be considered complete when representative samples can be collected and can continue to be collected indefinitely. Unfortunately, under most ground-water sampling circumstances determining when samples are representative of in situ conditions is not possible, so some related criteria are often chosen. Ideally, these criteria should include (1) the production of clear water during development, and (2) the removal of a volume of water at least equal to the amount lost to the formation during drilling and well installation (Kraemer et al., 1991). In addition, certain conditions may require that development be continued after the well has been allowed to recover

from the first round of development efforts. This condition may exist if the first round of samples exhibit turbidity.

Incomplete or ineffective well development may allow drilling and other introduced fluids to remain in the sampling zone or may not remove all mudcake or smeared sediments from the borehole wall. The presence of these materials may introduce error by disrupting hydrochemical equilibrium or by introducing contaminants to the well or sampling zone. In addition, these materials can reduce the hydraulic conductivity of the filter pack and formation and modify ground water flow near the well before and during sampling.

Development methods that utilize air pressure can entrap air in the filter pack and formation, disrupt hydrochemical equilibrium through oxidation, or introduce contaminants from the air stream to the formation and filter pack. These effects may be reduced if precautions are taken to eliminate air contact with the well intake. The addition of water during development may modify hydrochemistry to an unknown extent or may introduce contaminants to the sampling zone, even if all the water is removed during development. In light of these potential problems, jetting methods that inject air or water directly above the well intake are not recommended (Keely and Boateng, 1987). Likewise, other methods that introduce air or water to the well (surging and pumping with compressed air, and backwashing, for example) also may not be suitable for monitoring well development (Aller et al., 1989).

Development of wells at very high rates may displace filter pack and formation materials and reduce the effectiveness of the filter pack, particularly if the method involves excessive surging (Keely and Boateng, 1987). On the other hand, development at low rates (as is generally attained with sampling pumps) may not provide enough agitation to meet development objectives (Kraemer et al., 1991). In many monitoring well situations, using surge-block methods to loosen material and either pumping or bailing to remove the material has been found to be an effective development technique (Aller et al., 1989).

In low-yield wells, surging methods may result in excessive mobilization of fine-grained materials. For example, in a study conducted in fine-grained glacial tills, Paul et al. (1988) found that auger-drilled wells developed by surge-block methods produced samples with up to 100 times greater turbidity than samples from similar wells developed by bailer. In addition, the turbidity of samples from the surged wells did not significantly decrease after a second round of sampling while samples from the bailed wells showed a four-fold decrease (Paul et al., 1988). Because these wells were drilled in low permeability sediments without added fluids, the action of drawing down the water level within the well by bailing may have been sufficient to provide adequate development. On the other hand, bailing or pumping techniques alone may not be effective in wells constructed by drilling methods that introduce fluids or cause significant disturbance of sediments because the development force is dissipated by the filter pack.

The potential impacts of monitoring well development on ground-water sample quality are outlined in Table 2 which is

**TABLE 2. POTENTIAL IMPACTS OF DEVELOPMENT METHODS ON GROUND-WATER SAMPLE QUALITY**

Method	Potential Impacts
Surging with surge block	Displacement of filter pack and formation materials or damage to the well intake (primarily a problem in poorly designed and constructed wells when surging is conducted improperly)  Excessive mobilization of fine-grained materials from low-permeability formations
Surging and pumping with compressed air	Entrapment of air in filter pack and formation  Disruption of hydrochemical equilibrium  Introduction of contaminants
Pumping and over-pumping with pump	Low-volume pumps may be incapable of sufficient surging action (primarily in high-yield wells with little or no drawdown)
Jetting with air or water	Entrapment of air in filter pack and formation  Disruption of hydrochemical equilibrium  Introduction of contaminants  Excessive mobilization of fine-grained materials from low-permeability formations
Backwashing with water	Disruption of hydrochemical equilibrium  Introduction of contaminants
Bailing	May be incapable of sufficient development action

based on the work of Keely and Boeteng (1987), Paul et al. (1988), Aller et al. (1989), and Kraemer et al. (1991).

## MATERIALS

Transfer of ground water from the subsurface sampling zone to a sample container at ground surface often involves contact of the sample with a variety of materials comprising the well, sampling device, tubing, and container. Some of these materials have the potential to bias chemical concentrations in samples as a result of sorption, leaching, and chemical attack, and biological activity (Barcelona et al., 1983). As a result, the materials selected for ground-water sampling must be appropriate for the hydrochemical conditions at the site and the constituents being sampled. Other factors that may influence the choice of materials, including costs versus benefits, availability, strength, and ease of handling, can be found in Aller et al. (1989).

Materials commonly used in the ground-water sampling train can be divided into five general categories (modified from Nielsen and Schalla, 1991):

1. fluoropolymers, which include polytetrafluoroethylene (PTFE), tetrafluoroethylene (TFE), and fluorinated ethylene propylene (FEP);
2. thermoplastics, which include polyvinyl chloride (PVC), acrylonitrile butadiene styrene (ABS), polypropylene (PP), and polyethylene (PE);
3. metals, which include stainless steel (SS), carbon steel, and galvanized steel;
4. silicones; and
5. fiberglass-reinforced, which include fiberglass-reinforced epoxy (FRE) and fiberglass-reinforced plastic (FRP);

This document will focus on the most commonly used materials including the rigid materials PTFE, PVC, and metals (particularly SS) and the flexible materials PE, PP, PTFE, PVC, and silicone.

## Chemical and Biological Impacts

Sorption, which includes the processes of adsorption and absorption, may remove chemical constituents from samples thereby reducing the concentrations of these constituents from levels present in the ambient ground water. If compounds present in the ground water are removed entirely, false negative analytical results will be produced. Additionally, desorption of compounds previously sorbed can occur if water moving past the material contains lower concentrations of the sorbent than exists in the material. In this case, contaminants may be detected in samples that do not exist in the ground water, causing false positive analytical results. Sorption/desorption processes may be particularly important in situations where contaminant concentrations are at trace levels and change with time or where samples contact potentially sorbing materials for long periods (for example, during water level recovery in low-yield wells or in inadequately purged wells).

Leaching of chemical constituents from some types of materials may occur under the conditions present at many hazardous waste sites. Constituents of the materials' matrix, or compounds added during fabrication, storage, and shipment, may have solubilities in water high enough to be leached under natural ground-water conditions (Gillham et al., 1983). Ground water contaminated by high concentrations of organic solvents may cause significant degradation of the matrix of some polymeric materials, resulting in leaching of various compounds (Barcelona et al., 1983). As a result, false positive analytical results can be produced if the source of target constituents in ground-water samples is leaching from casing materials rather than the ambient ground water. In addition, corrosion of metal casing may introduce dissolved metals to ground-water samples and reduce the integrity of the well.

Under certain ground-water conditions, well-casing materials may impact biologic activity, and vice versa, in the vicinity of the well (Barcelona et al., 1988b) and lead to errors that are difficult to predict. For example, the presence of dissolved iron in ground-water may favor the growth of iron bacteria near metallic wells and degrade the casing and screen (Driscoll, 1986). In addition, permeation of contaminants or gases through materi-

als may be a potential source of sample bias with flexible tubing (Barker et al., 1987; Holm, 1988) but is unlikely with rigid materials, as demonstrated by Berens (1985) for organic compounds and rigid PVC pipe over time periods less than 100 years.

### **Rigid Materials**

Rigid materials that contact ground-water samples are generally used in well casings and screens, sampler components, and filtration equipment.

#### **PTFE**

PTFE has been widely considered the best choice for monitoring well materials because of its apparent resistance to chemical attack and low sorption and leaching potential. However, several recent laboratory studies have shown that rigid PTFE materials actually demonstrate a significant ability to sorb hydrocarbons from solution. Sykes et al. (1986) found that PTFE materials sorbed several hydrocarbons from a solution containing concentrations of approximately 100 µg/L, but did not report quantities. Parker et al. (1990) found that rigid PTFE materials sorbed significant quantities of all tested chlorinated organics and a nitroaromatic; higher, in fact, than PVC materials. These workers found that losses of some of these compounds from test solutions (initial concentrations of each compound were approximately 2 mg/L) exceeded 10% within eight hours. Likewise, rigid PTFE materials showed significant sorption of aromatic hydrocarbons in 24 hours of exposure for benzene, and six hours for several other hydrocarbons (Gillham and O'Hannesin, 1990). After eight weeks of PTFE exposure to benzene, 75% losses from the test solution were observed.

In contrast, PTFE materials tend to show lower potential for interaction with trace metals than PVC or SS (Barcelona and Helfrich, 1986). For example, lead was the only metal of four tested (arsenic, chromium, cadmium, and lead) in a laboratory study to be actively sorbed onto PTFE materials although only 5% of the lead concentration in the test solution was removed after 24 hours of exposure (Parker et al., 1990).

#### **PVC**

Early studies of PVC materials found substantial potential for sample error from sorption and leaching effects. Many of the conclusions about sorption were based on flexible PVC, which has a much higher sorption potential than rigid PVC. Leaching of high VOC concentrations was found to be a particular problem from PVC solvents and cements used for casing joints and bailer construction. Boettner et al. (1981) found cyclohexanone, methylethylketone, and tetrahydrofuran leached into water at concentrations ranging from 10 µg/L to 10 mg/L for more than 14 days after the glue was applied to PVC pipe. In addition to these compounds, methylisobutylketone was detected in ground-water samples several months after the installation of cemented PVC casing (Sosebee et al. 1982). The results of these studies indicate that alternative methods of joining PVC casing, such as threaded joints, should be utilized to reduce sample error.

Laboratory investigations show that threaded PVC well materials sorb hydrocarbon compounds, but often at lower rates than other polymers, including PTFE. Miller (1982) found little

absorption of six VOCs over a six-week period, with the exception of tetrachlorethylene which showed a 50% decline in concentration in solution. These sorption results were significantly lower than those from PE and PP casing materials. Subsequent leaching from PVC was found to be at insignificant levels for all six VOCs. Gillham and O'Hannesin (1990) found that significant sorption onto rigid PVC from a solution containing six hydrocarbons did not occur until 12 hours after exposure. The PVC results were in contrast to three other rigid polymers (PTFE, FEP, and polyvinylfluoride) that showed significant uptake of at least one of the six compounds within three hours of exposure. After eight weeks of PVC exposure to benzene, 25% losses were observed from the original solution concentration of approximately 1.2 mg/L. Similar results were reported by Parker et al. (1990) who found that PVC sorption of 10% of initial organic compound concentrations didn't occur until over 72 hours of exposure, while PTFE sorption of 10% of three of the 10 tested organics occurred within eight hours of exposure. Two dichlorobenzene isomers showed the highest sorption rates on PVC: significant losses were observed within eight hours. Sykes et al. (1986) found no significant differences between PVC, PTFE, and SS materials in their tendency to sorb six organics at concentrations of approximately 100 µg/L each.

The results of these research studies indicate that rigid PVC materials have relatively low potential for sorption and leaching of organic compounds relative to other polymers when exposed to dissolved concentrations generally found at hazardous waste sites. However, Berens (1985) demonstrated that PVC may soften and allow permeation of organic compounds if exposed to nearly undiluted solvents or swelling agents for PVC. For this reason, PVC well casing should be avoided under these conditions.

PVC materials may also react with some trace metals. Miller (1982) concluded that in a six-week exposure to test solution, PVC materials did not affect chromium concentrations but that lead concentrations declined over 75%. A subsequent experiment showed that over 75% of the initial lead concentrations were desorbed from the PVC material. Parker et al. (1990) found that rigid PVC showed no measurable sorption or leaching of arsenic or chromium but that cadmium was leached and lead sorbed. For example, sorption of lead resulted in a 10% decline in lead concentration in their test solution in four hours, while subsequent desorption resulted in a 10% increase in lead concentration after four hours.

#### **Stainless Steel**

SS casing materials are often used when conditions warrant a strong, durable, corrosion-resistant material. Of the two types available, Type 316 is somewhat less likely than type 304 to be affected by pitting and corrosion caused by organic acids, sulfuric acid, and sulfur-containing species (Barcelona et al., 1983). However, long exposure to very corrosive conditions may result in chromium and nickel contamination (Barcelona et al., 1983), or iron, manganese, and chromium contamination (U.S. EPA, 1987) of samples. A field study by Barcelona and Helfrich (1986) found that stagnant water samples from SS installations showed higher levels of ferrous iron and lower levels of dissolved sulfide than nearby PTFE and PVC wells, suggesting leaching from the SS and precipitation of sulfide by the excess iron. However, these workers demonstrated that

proper well-purging techniques eliminated this stagnant water from ground-water samples, providing representative ground-water samples.

Laboratory experiments conducted by Parker et al. (1990) examined the potential for sorption on type 304 and 316 SS casing materials. These workers conducted experiments with aqueous solutions of arsenic, cadmium, chromium, and lead at concentrations of 50 µg/L and 100 µg/L and found that after 10 hours, sorption on both type 304 and type 316 caused a 10% decline in arsenic concentration in the test solution. Cadmium concentrations increased 10% in five hours due to leaching from type 304, before returning to initial concentrations after 72 hours. Cadmium leaching from type 316 caused a maximum 30% increase after 20 hours, with concentrations still 20% above initial values after 72 hours. No measurable sorption of chromium occurred for type 304, but 13% losses in 13 hours were observed for type 316. Sorption of lead on type 304 materials led to 20% losses after only four hours of exposure, and approximately 10% for type 316. Parker et al. (1990) concluded from this work that determinations of the concentrations of cadmium, chromium, and lead may be impacted by long-term contact with stainless steel materials. Unfortunately, these workers did not address whether well purging would eliminate these impacts and provide representative ground-water samples.

In a study with five halogenated hydrocarbons, Reynolds et al. (1990) found type 316 SS caused losses of bromoform and hexachloroethane over a five-week period. Losses of these compounds from the test solution were insignificant until one week, after which concentrations dropped up to 70% from initial concentrations of 20 to 45 µg/L. The losses were attributed to reactions involving the metal surfaces or metal ions released from the surfaces and not to sorption (Reynolds et al., 1990). A study by Parker et al. (1990) with ten organic compounds at concentrations of approximately 2 mg/L, found that type 304 and type 316 SS casing resulted in no detectable sorption or leaching effects after six weeks.

### Other Metallic Materials

Steel materials other than stainless steel may be more resistant to attack from organic solutions than polymers, but corrosion is a significant problem, particularly in high dissolved-solids, acidic environments (Barcelona et al., 1985a). Ferrous materials may adsorb dissolved chemical constituents or leach ions or corrosion products such as oxides of iron and manganese (Barcelona et al., 1988a). In addition, galvanized steel may contribute zinc and cadmium species to ground-water samples. The weathered steel surfaces, as well as the solid corrosion products themselves, increase the surface area for sorption processes and may therefore act as a source of bias for both organic and inorganic constituents (Barcelona et al., 1985a; Barcelona et al., 1983). Reynolds et al. (1990) determined that galvanized steel showed a 99% reduction in concentrations of five halogenated hydrocarbons in a five-week sampling period. Aluminum casing caused concentration reductions of 90% for four of the compounds. Although many of these aspects of steel materials have not been quantified for typical ground-water environments, they may be a significant source of sample error.

### Alternate Materials

Although not as widely tested or used, FRE may represent a rigid well material with relatively low potential for sample bias. In a 72-hour laboratory study, none of the 129 priority pollutants were detected to be leached from a powdered sample of the material (Cowgill, 1988). A three-week dwell-time study of casing materials by the same investigator resulted in detection of no base/neutral or acid compounds. Gillham and O'Hannesin (1990) concluded that sorption of benzene and other aromatic hydrocarbons onto FRE was slightly greater than onto rigid PVC but less than onto PTFE.

Borosilicate glass, another little-used well material, revealed no sorption effects after a 34-day exposure to five halogenated hydrocarbons (Reynolds et al., 1990). Of the ten well materials tested in that study, only the borosilicate glass showed no sorption characteristics. The low potential for sample error indicated by that study suggests that further investigation of borosilicate glass may be warranted to determine its suitability for ground-water sampling.

### Flexible Materials

Semi-rigid and flexible materials are used for transfer tubing and other flexible components of the sampling/analysis train. In general, these materials contain plasticizers for flexibility that give them a higher potential than rigid materials to sorb or leach compounds. Latex rubber tubing, flexible PVC, and low density PE were all found to sorb greater quantities than more rigid materials (Reynolds et al., 1990).

In a study of five tubing materials in solutions of four chlorinated hydrocarbons, Barcelona et al. (1985b) found that most sorption occurred in the first 20 minutes of exposure. With the exception of tetrachloroethylene, the materials ranked in order of increasing sorption PTFE, PP, PE, PVC, and silicone. PE showed the highest sorption of tetrachloroethylene. Desorption from all materials occurred rapidly with the same ranking: PTFE desorbed a maximum of 13% of the sorbed concentrations after one hour while silicone desorbed 2%. From the results of this work, Barcelona et al. (1985b) estimated sorptive losses of chlorinated hydrocarbons from sampling tubing under typical flow rates. As an example, using 15 m of 1/2-inch tubing, initial concentrations of 400 µg/L for the four halocarbons, and a sample delivery rate of 100 mL/min, these workers predicted 21, 29, 48, 67, and 74% sorptive losses for PTFE, PP, PE, PVC, and silicone tubing, respectively.

Sorption tests conducted by Barker et al. (1987) found that flexible PTFE led to 17% sorptive losses of benzene and 58% losses of p-xylene after two weeks. For PE, 49% losses of benzene and 91% losses of p-xylene were observed in two weeks. As found in other studies, initial rapid losses were followed by gradual concentration declines in all compounds. Desorption of these compounds followed a similar pattern, approximately 40% of the initial benzene mass and 20% of the initial p-xylene masses desorbed. Laboratory tests conducted by Gillham and O'Hannesin (1990) showed PVC and PE tubing caused sorptive losses of over 10% within five minutes of exposure to six hydrocarbons in solution. After 24 hours, 90% losses for the PVC and 80% losses for the PE had occurred.

These studies suggest that flexible PTFE tubing has lower potential for sorption and leaching than other materials, particularly PVC and silicone. However, even PTFE tubing may have significant impacts on concentrations of organic compounds in ground-water samples, depending on duration of contact. It is clear that the sorption and leaching effects of all materials used as tubing or other flexible portions of the sampling/analysis train should be considered when designing the sampling program. Those materials that demonstrate high potential for sorption and/or leaching should be avoided if those processes could impact concentrations of the compounds of interest to the investigation.

A further source of sample bias with respect to tubing is transmission of compounds or gases through the tubing materials. In a study of PE and PTFE, Barker et al. (1987) detected 2 µg/L benzene and 15 µg/L toluene passing through PE tubing within three days and 15 µg/L and 100 µg/L, respectively, after six days. Subsequent flushing of the tubing with three tubing volumes of clean water reduced the concentrations of both compounds detectable inside the tubing but they were still detectable after twenty volumes were flushed. Under the same conditions, the compounds did not pass through the PTFE tubing in detectable concentrations. These workers suggest that this mechanism may lead to sample bias in other polymeric materials, although perhaps at rates somewhat less than those exhibited by the flexible PE tubing, and could influence conclusions about when well purging procedures or remediation activities are complete. Holm et al. (1988) studied the diffusion of gases through FEP tubing, and found that the amount of gas transferred is proportional to the tubing length and inversely proportional to the flow rate through the tube. Calculations by the authors suggest that, given initially anoxic ground water, oxygen diffusion through sampling tubing could lead to detection of DO and changes in iron speciation within tens of feet. The results of these studies clearly indicate the potential errors that transmission through flexible tubing might introduce when sampling for both organic and inorganic compounds. This source of error can be reduced by using appropriate tubing materials for the sampling conditions and by minimizing tubing lengths.

### **Selection of Materials**

It is clear from laboratory studies of casing materials that concentrations of trace metals and hydrocarbons can be impacted by sorption and leaching from PTFE, PVC, and metallic casing materials. However, laboratory studies do not attempt to duplicate the complicated, interrelated physical, chemical, and biologic conditions present in the field that may cause materials to behave very differently in the hydrogeologic environment. It is also important to keep in mind that most of these experiments were conducted under static conditions and may not adequately represent field conditions where stagnant water is generally replaced with fresh ground water during well purging. In the field, sorption of compounds onto casing materials between sampling events may not affect subsequent ground-water samples, as long as adequate purging and sampling procedures are conducted. Desorption of previously sorbed compounds after long-term exposure may be of somewhat greater importance because continuous desorption may impact trace-level concentrations, which might have important implications to remedial investigations where concentrations are expected to eventually reach non-detectable levels. But again, proper

selection and implementation of materials and purging and sampling methods will reduce the impact of these processes.

Given the above discussion and current state of research, some generalizations may be made about the applicability of casing materials to various ground-water contamination scenarios, assuming that reducing sample error is the primary criterion for selection. When monitoring for low hydrocarbon concentrations in non-corrosive ground water, SS and PVC casing may be appropriate choices. Because PTFE has been shown to introduce error into hydrocarbon determinations, it may be most applicable under conditions where SS and PVC are not. As examples, SS would not be appropriate in corrosive ground water or where determination of trace metal concentrations is of primary concern and PVC wells would be inappropriate in situations where solvents in moderate to high concentrations could dissolve the PVC material. A summary of the properties of rigid PVC, PTFE, and SS materials that may introduce sample error is shown in Table 3.

Laboratory studies indicate that the potential for error from flexible tubing is much greater than from rigid materials. For this reason, efforts should be made to use tubing with low potential for sorption and leaching and to minimize tubing length and time of contact. It appears that sample error can be significantly reduced by substituting flexible PTFE for PVC and silicone where possible.

### **MONITORING WELL PURGING**

Purging stagnant water from monitoring wells prior to sampling is considered essential to collection of samples representative of ambient ground water. Stagnant water may result from biological, chemical and physical processes occurring between sampling events. These processes may include biological activity, sorption/desorption reactions with materials of the well, leaching from the materials of the well, degassing and volatilization, atmospheric contamination, and foreign material entering the well from ground surface.

An effective purging method must allow for flushing of the well and sampling device of stagnant water without causing undesirable physical and chemical changes in the adjacent water-bearing zone that may bias subsequent samples. Important aspects of purging include purge volume, pumping rate, depth of the purging device, and purging methods for low-yield wells. Field experiments have shown that purging has important impacts on sample chemistry, perhaps greater than other aspects of sampling protocol such as sampling device and materials (Barcelona and Helrich, 1986).

#### **Purge Volume**

To ensure complete purging of a ground-water monitoring well, there must be established criteria to determine when the water in the well is representative of ambient ground water. Three criteria commonly advocated to determine appropriate purge volume have been described by Gibb and Imbrigiotta (1990) as: (1) a specific, predetermined number of well-bore volumes, (2) stabilization of the values of field chemical indicator parameters (such as temperature, pH, and EC), and (3) hydraulic equilibrium between water stored in the casing and water entering the casing.

**TABLE 3. PROPERTIES OF COMMONLY-USED WELL CASING MATERIALS THAT MAY IMPACT GROUND-WATER SAMPLE QUALITY**

Material	Properties
Polytetrafluoroethylene (PTFE)	<p>Moderate potential for sorption of hydrocarbons.</p> <p>Low potential for leaching of organic constituents.</p> <p>Some potential for sorption and leaching of metals, but less than with thermoplastic and metallic materials.</p> <p>Particularly resistant to chemical attack, including aggressive acids and organic solvents.</p> <p>Not subject to corrosion.</p> <p>Resistant to biological attack.</p>
Stainless Steel (SS)	<p>Very low potential for sorption of hydrocarbons.</p> <p>Not subject to leaching of organic constituents.</p> <p>Significant potential for sorption and leaching of metals.</p> <p>Subject to chemical attack by organic acids and sulfur-containing species.</p> <p>Subject to corrosion.</p> <p>Subject to biological attack.</p>
Polyvinylchloride (PVC)	<p>Potential for sorption of hydrocarbons, but may be less than with fluoropolymers.</p> <p>Leaching of organic constituents may occur through chemical degradation by organic solvents.</p> <p>Sorption and leaching of some metals.</p> <p>Subject to chemical attack by organic solvents.</p> <p>Not subject to corrosion.</p> <p>Resistant to biological attack.</p>

The use of a specific number of well-bore volumes as the sole criterion for purge volume has been applied extensively in ground-water sampling with recommendations in regulations and the literature ranging from less than one to over 20 (Herzog et al., 1991). In addition, definitions of well-bore volume have included the volume contained within the casing, that volume plus the pore volume of the filter pack, and the volume of the entire borehole. Despite its widespread use, the well-bore volume approach does not directly address the issue of obtaining representative ground water because there is no proven

relation between the number of well volumes removed and the completion of purging. The combination of details of well construction, contaminant distribution, and geologic and hydrochemical conditions result in unique conditions at every well such that the volume of water required for purging cannot be determined a priori. It is impossible to predict the magnitude of error that might be introduced by arbitrarily choosing a number of well volumes that results in incomplete purging.

Determining purge volume by measuring field parameters is also widely used. The assumptions implied in this approach are that: (1) as these parameters stabilize, stagnant water in the well has been replaced by ambient ground water, and (2) this water contains representative concentrations of the compounds of interest. However, field experiments conducted by Gibb and Imbrigiotta (1990) showed that field parameters often stabilized before the concentrations of VOCs. In almost 90% of their experiments, field parameter measurements stabilized when three well casing volumes had been purged while VOC concentrations stabilized after three well volumes in only about half of the cases. Likewise, Pearsall and Eckhardt (1987) observed in a series of field experiments that trichloroethylene concentrations continued to change after three hours of pumping at 1.2 L/min while field parameters stabilized within 30 minutes. Furthermore, measurements of individual field parameters may not reach stable values at the same purge volume suggesting that some parameters are more sensitive to purging than others. For example, Pionke and Urban (1987) found that temperature, pH, and EC values of purge water from 14 wells studied generally stabilized before dissolved oxygen and nitrate concentrations. Puls et al. (1990) found that while temperature, pH, and EC values generally stabilized in less than a single well-bore volume, other indicators such as dissolved oxygen and turbidity required up to three well-bore volumes before stabilization. Puls et al. (1990) considered reduction of turbidity to stable values using low pumping rates as critical to the collection of representative metals samples. It should be pointed out that in all of the cases mentioned above, reliance on commonly measured parameters (temperature, pH, and EC) alone would apparently have underestimated the proper purge volume. These results suggest that the choice of purge indicator parameters should be made such that the indicators are sensitive to the purging process and relate to the hydrochemical constituents of interest. This can be accomplished by evaluating the patterns of indicator parameters and ground-water constituents during well purging (a purge-volume test) to determine the appropriate purge volume.

Another implied assumption of the field parameter approach is that purging will result in the stabilization of all constituent concentrations at approximately the same purge volume. In many hydrogeologic systems this assumption may not be valid. For example, in aquifers contaminated by several VOCs, concentration trends during pumping may be very different. In an evaluation of a purge-volume test, Smith et al. (1988) found that concentrations of two compounds started relatively high and decreased with purging to below detectable levels. Two other compounds that were undetected at three casing volumes were detected at four casing volumes and their concentrations increased until stabilizing at ten casing volumes. A fifth compound remained at a constant concentration throughout the purge-volume test. The authors did not report the concentrations observed or the volumes pumped, but it is clear that under these



conditions the choice of purging volume could significantly impact interpretations of contaminant concentrations.

It is important to keep in mind that the distribution of contaminants in limited plumes within a ground-water system is generally in contrast to the more homogeneous distribution of natural hydrochemical conditions in space and time. Consequently, attaining stable concentrations of field parameters, or even gross chemistry, may not indicate a representative sample of the targeted aquifer volume around a monitoring well (Keely and Boateng, 1987). As a result, these workers suggest that the 'inherent variability of the concentration of contaminants in many plumes far outstrip the additional variability potentially induced by incomplete purging,' and recommend that spatial and temporal variations in contaminant concentrations be studied to determine optimum purge volumes.

Methods of determining purge volume by estimating when hydraulic equilibrium occurs between water stored in the casing and water entering the casing may be useful where conservative, non-varying constituents are being monitored. However, determining hydraulic equilibrium by estimating the time at which water levels in the well are no longer affected by casing storage (the method of Papadopoulos and Cooper, 1967) may lead to erroneous results (Gibs and Imbrigiotta, 1990). These workers compared the calculated hydraulic equilibrium volume to measurements of field parameters and VOC concentrations during several well purging experiments and found that the calculated volume consistently underestimated the volumes required to reach both stable field measurements and stable VOC concentrations. The casing storage method might provide an approximation of purge volume under conditions where conservative, non-varying constituents are being monitored but the available evidence suggests that only sampling for the constituents of interest will provide a direct indication of when their concentrations stabilize.

Recent research reviewed by Puls et al. (1990) demonstrates that contaminants may be transported in ground water by association with colloidal-sized particles which are generally described as particles less than 10  $\mu\text{m}$  in diameter. Where contaminant transport by association with colloids is an important mechanism, obtaining representative concentrations of mobile colloids becomes critical to sample representativeness. However, the acts of purging, sampling, and even placing the sampling device in the well have been demonstrated to significantly impact colloidal suspension in the sampling zones of monitoring wells (Puls et al., 1991; Kearle et al., 1992). If a significant portion of contaminants are transported in association with colloids, the results of these investigations and others suggest minimizing or eliminating purging, minimizing sampling flow rates (100 to 500 mL/min), and using dedicated sampling devices placed within the well intake may all be necessary to collect representative ground water samples. This low-volume approach to purging and sampling was earlier proposed by Robin and Gillham (1987) when sampling for conservative, non-varying parameters in high-yield wells. Using non-reactive tracers, these workers demonstrated that natural ground water movement through the well intake was sufficient to prevent the formation of stagnant water with respect to conservative, non-varying parameters, making purging large volumes unnecessary. Robin and Gillham (1987) pointed out that, under these hydraulic and hydrochemical conditions, representative

samples can be collected with little or no purging using dedicated devices positioned within the well intake. In order to resolve the issue of low-volume purging, however, it appears that more research is necessary to better understand colloid movement in ground-water environments, their importance to contaminant transport, and their implications to purging and sampling techniques.

### *Purge Rate and Depth*

It was suggested previously that the pumping rate at which purging is conducted may impact sampling results. Although few detailed studies have been conducted to directly address this issue, the results of a few specific field studies suggest the types of impacts that purging rates might have on sampling results. For example, Imbrigiotta et al. (1988) reported that purging rates of 40 L/min were found to produce VOC concentrations up to 40% higher than concentrations obtained at purging rates of 1 L/min. Likewise, purging with a high-speed submersible pump at a rate of 30 L/min was found to generally produce higher colloid concentrations and larger particle sizes than a low-speed pump at rates lower than 4 L/min (Puls et al., 1990). Despite these colloid differences, however, metals and cation concentrations did not necessarily correlate to pumping rate. Both investigators attributed the variability to the effects that different pumping rates had on the distribution of hydrochemical conditions near the well. Imbrigiotta et al. (1988) further concluded that the variability in VOC concentrations caused by purging rate was of the same magnitude as that observed in a comparison of seven types of sampling devices, suggesting that purging rate may be at least as important to the collection of representative samples as the type of device utilized. Puls et al. (1990) suggested that the colloid differences might also have resulted from entrainment of normally non-mobile suspended particulates in the wells.

Although the issue remains unresolved, it appears that employing pumping rates that allow sample collection with minimal disturbance of the sample and the hydrochemical environment in and near the well may aid in minimizing sampling error. To this end, it has been suggested that the purging rate be chosen such that the rate of ground water entering the well intake is not significantly higher than the ambient ground-water flow rate (Puls and Barcelona, 1989). Under typical hydraulic conditions, this may be possible with pumping rates between 100 and 500 mL/min.

The depth at which purging is conducted may also affect sample representativeness. At high pumping rates or in low- and medium-yield wells, purging at depths far below the air-water interface may introduce error because stagnant water from the well above the pump may be drawn into the pump inlet. Under these conditions, pumping near the air-water interface significantly reduces the time required to remove stagnant water by reducing mixing from above the pump intake (Unwin and Huis, 1983; Robin and Gillham, 1987). Keely and Boateng (1987) suggest lowering the pump during purging so as to further reduce the possibility of migration of stagnant water into the intake during sample collection. On the other hand, under high-yield conditions, placing the pump at the well intake and utilizing low pumping rates may serve to isolate the stagnant water in the well bore above the pump thereby providing representative samples with minimal purging (Barcelona et al.,



1985; Robin and Gillham, 1987). Unwin and Maltby (1988) reported that pumping at virtually any depth within a well, including the intake, may lead to contamination of samples by stagnant water from above the pump inlet although their laboratory investigation demonstrated that at a pumping rate of 1 L/min, samples collected within the well intake contained less stagnant water than samples collected above the well intake. Regardless of the depth of the pumping device, if a stagnant water zone develops near the water surface subsequent movement of the pump or placement of a sampling device through this zone may cause contamination of the device by stagnant water.

As suggested above in the discussion of purge volume, certain hydrogeologic conditions and chemical constituents may require that samples be collected with little or no purging using dedicated devices positioned within the well intake. Under these circumstances, it would also be necessary to utilize low purging and sampling rates so as to minimize disturbance of the sample and sampling environment and to prevent migration of stagnant water from the well bore down into the sampler intake.

### **Purging in Low-Yield Wells**

Purging low-yield wells introduces conditions that by definition don't occur in medium- to high-yield wells. These conditions, which tend to have their greatest impact on constituents that are sensitive to pressure changes and/or exposure to construction materials or the atmosphere, often result from dewatering the filter pack and well intake. Dewatering may produce a large hydraulic gradient between the adjacent water-bearing zone and the filter pack as a result of the large drawdown in the well and the low hydraulic conductivity of the formation. One consequence of this condition may be the formation of a seepage face at the borehole wall causing ground water entering the borehole to flow down the borehole wall and fill the dewatered filter pack from the bottom up. Formation of a seepage face increases the surface area of the interface between the liquid phase (ground water) and vapor phase (headspace in the well) available for transfer of solutes. Another consequence of the large hydraulic gradient is the sudden pressure decline from the pressure head in the water-bearing zone to atmospheric pressure in the pumped well. The sudden release of this pressure may cause losses from solution (by degassing or volatilization) of solutes that have combined partial pressures, with that of water, greater than atmospheric. Finally, because water levels recover slowly in low-yield wells, significant changes in the chemical composition of the ground water may occur through sorption, leaching, or volatilization before sufficient volume is available for sample collection.

In a field study of purging and sampling in low-yield wells, Herzog et al. (1988) found that some VOC concentrations increased significantly from pre-purging conditions during the first two hours of water level recovery. For example, chlorobenzene concentrations increased from 25 µg/L before purging to over 125 µg/L at two hours after purging. Concentrations generally did not change significantly after two hours, although some concentrations declined. Although Herzog (1988) provided no explanation for the observed concentration trends, they were likely caused by more representative ground water entering the well and replacing the purged stagnant water. Smith et al. (1988) reported very different results in their field study of a trichloroethylene plume. Concentrations of trichloro-

ethylene declined from 100 µg/L directly after purging to 10 µg/L 24 hours after purging. In a laboratory study, McAlary and Barker (1987) found that if the water level in a simulated well was drawn down below the intake, VOC concentrations during recovery declined 10% in five minutes and 70% in one hour. These changes were attributed to volatilization from the water as it entered and filled the well.

In summary, aspects of well purging important to collection of representative samples include purging volume, pumping rate, depth of the purging device, and time of sampling in low-yield wells. Although error is strictly dependent on individual well and site conditions, the available evidence suggests that order-of-magnitude errors may easily result from improper purging techniques. In low-yield wells, time of sampling is clearly an important source of error although there are too few data available to completely understand concentration trends in these situations.

Contamination concentrations during purging vary in ways that are often difficult to predict, and various compounds may even exhibit opposite trends. To estimate the appropriate purge volume, it may be necessary to conduct preliminary purge-volume tests with sampling at regular intervals during purging. These tests may be useful for determining how indicator parameters and constituent concentrations respond to purging rates, purging volumes, and the distribution of contaminants around the well. In addition, for certain sensitive constituents such as trace metals under certain hydrogeologic and hydrochemical conditions, low-volume purging and sampling should be considered with dedicated sampling devices installed at the well intake.

### **SAMPLE COLLECTION**

Sample collection involves physical removal and transport of ground water from depth (generally from a monitoring well) to ground surface and into a sample container. As such, collection methods may have great potential for alteration of the sample's chemical state. Sampling devices must be chosen and used carefully to ensure that error is minimized. Important aspects of sample collection include sampling device, collection time after purging, and sampling depth.

#### **Chemical Impacts**

Sampling devices can cause chemical changes in the sample by contact with materials of the device (sorption, desorption, or leaching) or by the physical action of the device. Although the materials of the device are a potentially significant source of sample error, that topic was discussed previously and the following discussion will address chemical changes produced only by the operation of the sampling device.

Because fluid pressure in the saturated zone is greater than atmospheric, ground-water samples brought to the surface will tend to be under higher pressure conditions than the ambient atmosphere. Exposure of these samples to the lower atmospheric pressure will cause degassing and/or loss of volatile constituents until the partial pressures of the contained volatile components reaches equilibrium with atmospheric pressure. Degassing may cause losses of oxygen (O<sub>2</sub>), methane (CH<sub>4</sub>), nitrogen (N<sub>2</sub>), or carbon dioxide (CO<sub>2</sub>), while volatilization might affect any solute that exists as a liquid, solid, or gas under in situ

ground-water temperature and pressure conditions (Gillham et al., 1983). Furthermore, loss of CO<sub>2</sub> may raise the pH which can lead to precipitation of dissolved constituents, particularly iron (Gibb et al., 1981). Constrictions in the flow path within a device may also raise the sample pH by changing the partial pressure of CO<sub>2</sub> (Herzog et al., 1991).

Exposure of samples to the atmosphere, or the driving gas used in some devices, may introduce oxygen causing oxidation of iron, manganese, cadmium, or other species. Oxidation of ferrous iron to ferric iron has important implications to the speciation and concentrations of many constituents in ground water samples (Herzog et al., 1991). Contaminants may also be added to the sample by exposing it to the atmosphere or driving gas.

### **Sampling Devices**

Sampling devices designed for use in conventional monitoring wells can be divided into four general types: grab, positive displacement (no gas contact), suction lift, and gas contact (Pohlmann and Hess, 1988). Grab samplers include open bailers, point-source bailers, and syringe samplers. Positive displacement samplers are usually submersible pumps such as bladder pumps, gear-drive pumps, helical-rotor pumps, and piston pumps. Suction lift devices include peristaltic pumps and surface centrifugal pumps while gas contact pumps include those devices that lift water to the surface by direct gas pressure. Submersible centrifugal pumps, which operate on the principle of positive displacement at low flow rates, develop a partial vacuum at the pump impellers at higher flow rates. For this reason, high-speed submersible centrifugal pumps without variable motor speed capability should be considered as distinct from positive displacement pumps. On the other hand, submersible centrifugal pumps are now available that can be used in 5.1-cm (2-inch) diameter wells and that allow adjustment of the motor speed to produce very low flow rates. If used at low flow rates, these low-speed pumps could conceivably eliminate the application of a partial vacuum to the sample and thereby can be considered as positive displacement pumps. Discussion of the operating principles of many of ground-water sampling devices, and their potential for sample bias, can be found in Gillham et al. (1983).

Sampling devices for conventional monitoring wells can be used either portably or in a dedicated mode. Portable devices are used to collect samples in more than one well and so may cause cross-contamination between installations or sampling events if not properly decontaminated. Dedicated devices are permanently installed in a single well and are generally not removed for cleaning between sampling events. Dedicated samplers, when also used for well purging, may not have adequate flow control for effective purging in large wells (high discharge rate) and sampling (low discharge rate). Furthermore, parts of dedicated samplers may sorb contaminants during periods of contact with ground water between sampling events and then release them during sample collection. Alternatively, if inappropriate materials are used in the construction of dedicated samplers, contaminants may leach from these materials between sampling events.

To study the effects of sampling devices on sample quality, investigations have been conducted both in the laboratory and

in the field. Laboratory studies can provide values of absolute sample error by testing under controlled conditions, particularly constituent concentration. However, by their very nature, laboratory experiments represent ideal conditions that can never be duplicated in the field and therefore may not include important field-related errors. On the other hand, field studies include all the physical, chemical, biological, and operating conditions present in field sampling efforts, but the true concentration of the constituents of interest are unknown. As a result, field comparison studies cannot provide values of absolute sample error, only the relative ability of individual devices to recover the constituent of interest.

Values of field chemical indicator parameters can often be the first indication of sample errors due to sampling device. Laboratory investigations of a wide range of sampling devices by Barcelona et al. (1984) revealed that pH and redox potential (Eh) were the most sensitive to sampling device. The largest errors were produced by a peristaltic pump (an increase of 0.05 pH units and a 20 mV decline in Eh). All tested devices had O<sub>2</sub> and CH<sub>4</sub> losses of 1% to 24%, although positive displacement devices and an open-top bailer resulted in the lowest losses and the highest precision in that study. A field study by Schuller et al. (1981) found that, as a result of CO<sub>2</sub> stripping, an air-lift pump and a nitrogen-lift pump produced pH values up to 1.0 pH unit higher than a peristaltic pump and opentop bailer. Other field studies concluded that open-top and dual-valve bailers produced no more error in field parameter values than bladder pumps (Houghton and Berger, 1984). In that study, which used bladder pump values as a standard for comparison, a peristaltic pump and a high-speed submersible centrifugal pump had increases in pH of about 0.06 pH units and approximately 20% declines in dissolved oxygen (DO) concentrations. A gas-driven piston pump had an increase in DO of 8% to 36%. Temperatures increased up to 5% in samples collected with the peristaltic and piston pumps and 14% in samples collected with the high-speed submersible centrifugal pump.

Most major dissolved ions are relatively stable and not greatly affected by collection method. Schuller et al. (1981) determined that concentrations of calcium, chloride, fluoride, potassium, magnesium, and sodium collected at two field sites were not significantly affected by the choice of suction, gas-contact, or bailer device. Dissolved metals, on the other hand, are very sensitive to sample aeration and degassing during sampling. Schuller et al. (1981) found that iron and zinc concentrations in samples collected with two gas contact devices were, at most, 30% of those collected with either a peristaltic pump or a bailer. Field studies of 18 wells with seven sampling devices by Houghton and Berger (1984) showed significant declines in metals concentrations for a gas contact device when compared to positive displacement pumps, grab samplers, and a peristaltic pump. Houghton and Berger (1984) also found that coprecipitation of arsenic and zinc with iron led to significant losses of these constituents in samples collected with a high-speed submersible centrifugal pump.

Sampling device impact on VOC concentrations is of particular importance because of the high sensitivity of these compounds to sample aeration and degassing and the critical need for accurate VOC data in many site investigations. Several laboratory experiments have shown that positive displacement devices (bladder, piston, and helical-rotor pumps) and conven-

tional grab samplers (open-top and dual-valve bailers) provide the most accurate VOC concentrations (Barcelona et al. 1984; Unwin, 1984; Schalla et al., 1988; Unwin and Maltby, 1988). Although the bladder pump and bailers that Barcelona et al. (1984) tested produced less than 3% losses in VOC concentrations, these same devices produced up to 10% losses in other studies, even under carefully-controlled conditions. Suction and gas-contact devices tested in these studies, and a study of peristaltic pumps by Ho (1983), resulted in 4% to 30% losses in VOC concentrations. Of those devices that performed well, no relation was found between sampler accuracy and VOC concentration over a range of 80 to 8000  $\mu\text{g/L}$  (Barcelona et al., 1984; Unwin, 1984). The devices that performed poorly, however, often revealed significant increases in error as concentration increased (Barcelona et al., 1984). From these laboratory studies it appears that certain classes of samplers, specifically suction and gas-contact, can lead to significant error in VOC concentrations as a result of volatilization from the sample during collection.

A positive relation between increased losses of VOCs from solution with increase in Henry's law constant was predicted by Pankow (1986) based on theoretical considerations of the factors leading to bubble formation in water during sampling. Physical experiments have shown a strong positive correlation between compound volatility and Henry's law constant for a peristaltic pump, some correlation for a helical-rotor pump, but no correlation for a bailer and bladder pump (Unwin and Maltby, 1988). On the other hand, Barker et al. (1987) found no clear correlation for a peristaltic pump and gas-drive sampler and Barker and Dickhout (1988) found no clear correlation for a peristaltic, bladder, or inertial-lift pump, although the range of Henry's law constants was small. These findings suggest that compound volatility may not be an important source of bias for some positive displacement and grab samplers but there may be potential for losses for samplers that impose a suction on the sample.

Many field comparisons of sampler effectiveness verify the findings of laboratory experiments, despite the increased number of variables involved in the field studies. Investigations involving a variety of field conditions by Muska et al. (1986), Pearsall and Eckhardt (1987), Imbrigiotta et al. (1988), Liikala et al. (1988), Yeskis et al. (1988), and Pohlmann et al. (1990) concluded that positive displacement devices produced the highest VOC concentrations, and therefore introduced the least error into VOC determinations. The accuracy of grab samplers was more variable: some studies showed little difference between the VOC recoveries of bailers and positive displacement pumps (Muska et al. (1986); Imbrigiotta et al. (1988); Liikala et al. (1988)), but Imbrigiotta et al. (1987), Yeskis et al. (1988), and Pohlmann et al. (1990) reported that bailer VOC concentrations were significantly lower than positive displacement pumps; 46% to 84% lower in the work of Yeskis et al. (1988). Pearsall and Eckhardt (1987) found that a bailer was as accurate as a positive displacement pump at concentrations in the range of 76 to 79  $\mu\text{g/L}$  but recovered 12% to 15% lower concentrations in the range 23 to 29  $\mu\text{g/L}$ .

Another grab sampler, the syringe sampler, also produced mixed results. Muska et al. (1986) concluded that syringe sampler accuracy and precision were not significantly different from those of the positive displacement pumps while Imbrigiotta

et al. (1988) concluded that syringe sampler accuracy was lower than the pumps but that precision was comparable. Other samplers field-tested produced significant error: a peristaltic pump and surface centrifugal pump were found by Pearsall and Eckhardt (1987) to be less accurate, but not necessarily less precise than the other samplers tested. Imbrigiotta et al. (1988) found the same for a peristaltic pump.

In ground-water environments charged with dissolved gases, collection of accurate VOC samples can be even more problematic. VOC losses of 9% to 33% were produced by a peristaltic pump in laboratory and field studies of water containing high  $\text{CO}_2$  (laboratory study) and  $\text{CH}_4$  (field study) concentrations (Barker and Dickhout, 1988). Losses of 13% to 20% were produced by a bladder pump in the laboratory study, while an inertial-lift pump produced no losses. No differences between results from these two pumps were observed in the field. The  $\text{CO}_2$  concentrations used in the laboratory investigation were higher than under environmental conditions, but this study nonetheless suggests that degassing during sample collection, even with a positive displacement pump, can lead to significant error in VOC concentrations (Barker and Dickhout, 1988).

Several "in situ" devices have been developed to alleviate some of the problems inherent to conventional monitoring wells and sampling devices. These devices generally utilize sample containers under reduced pressure to collect samples directly from the water-bearing zone, without exposure to the atmosphere or excessive agitation. In a field study, Pohlmann et al. (1990) found that two types of in situ devices delivered samples with VOC concentrations that were not significantly different from those collected by a bladder pump in a conventional monitoring well.

Although the field studies outlined above cannot provide values of absolute sample error, they do provide information on the effectiveness of various devices under actual operating conditions. The results of the laboratory studies, in conjunction with field studies, indicate that suction pumps are very likely to introduce significant error into VOC determinations. Grabsamplers, especially bailers, are also likely to produce errors if not operated with great care because their successful operation is closely related to operator skill. Under certain conditions, for certain parameters, and if operated by skilled personnel, bailers can produce representative samples. However, much of the research outlined here indicates that positive displacement pumps consistently provide the lowest potential for sample error. Appropriate application of most types of positive displacement pumps can reduce sampling device contribution to error well below the levels of some other aspects of ground-water sampling protocol.

A summary of the impacts that some commonly-used sampling devices have on ground-water sample quality is shown in Table 4 which was compiled from the sources referenced in this section and Nielsen and Yeates (1985).

### ***Collection Depth and Time after Purging***

The length of time between well purging and sample collection may influence the representativeness of samples by exposing ground water to the effects of atmospheric diffusion, interaction with well materials, and contaminant volatilization. Smith et al.

**TABLE 4. SOME IMPACTS THAT THE OPERATING PRINCIPLES OF GROUND-WATER SAMPLING DEVICES MAY HAVE ON GROUND-WATER SAMPLE QUALITY (WITH THE EXCEPTION OF GRAB SAMPLERS, IT IS ASSUMED THAT THESE DEVICES REMAIN IN THE WELL DURING THE SAMPLING PROCESS).**

Operating Principle	Impacts
Gas Contact	<p>Contact with drive gas may cause loss of dissolved gases and increase pH.</p> <p>Contact with drive gas may volatilize sensitive solutes.</p> <p>Exposure to driving gas may introduce contaminants or oxidize sensitive constituents.</p>
Grab	<p>Contact with atmosphere during sample recovery and transfer may cause loss of dissolved gases and increase pH.</p> <p>Contact with atmosphere during sample recovery and transfer may volatilize sensitive solutes.</p> <p>Exposure to atmosphere during sample recovery and transfer may introduce contaminants or oxidize sensitive constituents.</p> <p>May be contaminated when passing through zone of stagnant water.</p>
Positive Displacement	Minimal if discharge rate is low.
Suction Lift	<p>Application of suction to sample may cause loss of dissolved gases and increase pH.</p> <p>Application of suction to sample may volatilize sensitive solutes.</p>
High-Speed Submersible Centrifugal	<p>Suction applied at pump intake may cause loss of dissolved gases and increase pH.</p> <p>Suction applied at pump intake may cause volatilization of sensitive solutes.</p> <p>Application of excessive head to the sample may cause degassing or volatilization.</p> <p>Heat produced by pump motor may increase sample temperature.</p>

(1988) found that trichloroethane concentrations in a well declined from 170 µg/L immediately after purging to 10 µg/L 24 hours later. To ensure consistency and to reduce potential errors when sampling in high-yield wells, it is generally recommended that samples be collected immediately following completion of well bore purging. In low-yield wells, however, low water level recovery rates may require that sampling be delayed

until sufficient volume is available. Determination of sample collection time in low-yield wells is more problematic and may require site-specific sampling experiments.

To reduce potential errors caused by mixing with stagnant well water during sampling, research has suggested that the sampler intake be located either within the screened interval (Giddings, 1983; Bryden et al., 1986; Robin and Gillham, 1987) or at the top of the screened interval (Unwin, 1982; Barcelona and Helfrich, 1986) so samples can be obtained soon after fresh ground water enters the well bore. However, in cases where wells are screened over a long interval, it is important to determine if contaminants are vertically stratified in the well. Pearsall and Eckhardt (1987) found that TCE concentrations of samples collected at the top of a 10-foot screened interval were 30% lower than those collected at the bottom and attributed the difference to vertical stratification of VOCs within the screened interval. Errors associated with sampler intake placement have not been quantified to date but are likely strongly controlled by conditions at each well.

The use of samplers that must pass through the zone of stagnant water that invariably remains near the water level, even in a properly-purged well, may also introduce error. For example, grab samplers, which often require repeated entry and retrieval from the well during sampling, may be contaminated by this zone of stagnant water or may mix stagnant water into the water column. Likewise, if the purging device is not used for sampling, removal of the purging device and installation of the sampling device may have a similar effect. The use of a dedicated device for both purging and sampling would significantly reduce this source of error but may introduce others.

## SAMPLE FILTRATION

Ground-water samples collected for analysis of certain constituents are often filtered in the field prior to transfer to the appropriate container. Reasons for filtration include prevention of geochemical reactions that might occur with particulates during sample shipment and storage, removal of suspended sediments so as to analyze only dissolved constituents, and removal of fine-grained sediments which might interfere with laboratory analyses. Because filtration may contribute to sample error by the method employed or by the choice to filter, it is of the utmost importance to confirm the objectives of the sampling program and the implications of filtering when choosing whether to filter and, if so, the filtration technique.

Puls and Barcelona (1989) point out that if mobile trace metal species are of interest to the investigation filtration may remove metals adsorbed onto some colloidal particles, leading to underestimates of dissolved metals concentrations and, therefore, concentrations of mobile species. Conversely, if the objective of metals analysis is to quantify total dissolved metals concentrations, colloids with sorbed metals that pass through the filter material may result in overestimates of dissolved metals concentrations (Puls and Barcelona, 1989). These workers indicate that filtration should not be used as a means of removing from the sample particulates that result from poor well construction, purging, or sampling procedures because the misapplication of filtration may introduce substantial bias to trace metal determinations. If filtration is deemed necessary, it should be conducted soon after sample collection as temperature changes, CO<sub>2</sub>

invasion, or the presence of particulates may have adverse effects on trace metal concentrations or dissolved solids content (Unwin, 1982). Factors important to proper field filtration include filter pore size, material, and method, and holding time prior to filtration.

Filter pore size has very important implications for determinations of metal species and major ions in ground-water samples as a result of the inclusion of undissolved material. Constituents showing the greatest sensitivity to filter pore size include iron and zinc (Gibb et al., 1981), iron and aluminum (Wagemann and Brunskill, 1975), and iron, aluminum, manganese, and titanium (Kennedy et al., 1974). In all cases, larger filter pore sizes produced higher concentrations of these constituents because the larger pore-size filters allowed more particulates to pass. In fact, Kennedy et al. (1974) found that concentrations of some metal species in samples filtered through 0.45  $\mu\text{m}$  filters were up to five times higher than in samples filtered through 0.10  $\mu\text{m}$  filters. These results suggest that if field-filtration is deemed necessary, smaller pore size filters may reduce sample error.

Sorptive losses of trace metals during filtration can also introduce error into metals determinations. Truitt and Weber (1979) found that both cellulose acetate and polycarbonate 0.4  $\mu\text{m}$  filter membranes sorbed copper and lead from solution. For example, losses of copper averaged 8.6% with cellulose acetate membranes and 1.1% with polycarbonate membranes. Gardner and Hunt (1981) found that sorption of lead onto cellulose acetate membranes resulted in losses of 20 to 44% from a synthetic solution. These losses were reduced to 5 to 24% by pre-rinsing the filter apparatus with the test solution (Gardner and Hunt, 1981). Studies by Jay (1985) found that virtually all filters require pre-rinsing to avoid sample contamination by leaching of anions from the filter material.

Although filter material and pore size have been the subject of considerable research, less effort has been directed toward understanding the effects of filtration method on dissolved constituents. Of the few studies available, Stolzenburg and Nichols (1985) investigated the effects of sampling and filtration method on concentrations of iron and arsenic. Their laboratory study showed that samples that were vacuum-filtered after a 10-minute holding time delay experienced iron losses of 20% to 90% and arsenic losses of 45% to 100% compared to in-line filtered samples. The ranges of percentages were due to the use of several types of sampling devices. Later experiments by Stolzenburg and Nichols (1986) added immediate vacuum filtering of samples. Both immediate and delayed vacuum-filtration produced similar iron concentrations but these concentrations were 17% to 67% lower than concentrations produced by in-line filtration. In both the 1985 and 1986 reports, in-line filtering produced concentrations that were comparable to the source concentrations of approximately 8 mg/L iron and 0.05 mg/L arsenic suggesting that in-line filtration methods were the most effective of those tested. These experiments also suggested that filtration method may cause greater losses of certain constituents than the type of sampling device used. Unfortunately, commonly-used pressure filtration methods were not compared to in-line and vacuum filtration methods in these experiments.

Clearly, sample filtration can lead to substantial error in trace metal determinations even if procedures are carefully followed. Because of this great potential for error, filtration should not be

used to correct for sedimentation problems that result from poorly designed or constructed wells or incomplete development. If filtration is deemed necessary, pre-cleaning the filters can reduce error. In addition, the limited research into filtration methods in ground-water investigations suggests that in-line methods may result in the least sample error. However, even under ideal conditions, sample filtration may lead to significant error in determinations of metals concentrations, suggesting that analysis of both filtered and non-filtered samples should be considered.

## EQUIPMENT DECONTAMINATION

Contaminants on equipment that contacts ground water and samples, including drilling equipment, well materials, sampling devices, and sample bottles may be another source of sample error. Error may be introduced by the addition of contaminants to ground water or samples (contamination) or by the conveyance of ground water and/or contaminants from one sampling installation or zone to another (cross-contamination). Cross-contamination is most often a problem when equipment, particularly sampling devices, is used portably but not properly cleaned between installations. The process of cleaning equipment before installation or after sampling is generally referred to as decontamination.

Drilling equipment can be a source of gasoline, diesel fuel, hydraulic fluid, lubricating oils and greases, and paint, all of which can be introduced into the subsurface during drilling operations. In addition, contaminated soil, scale, or water from the site may enter the borehole directly or by adhering to drilling pipe or other down-hole equipment. If these contaminants originate from other sites or boreholes, cross-contamination may result (Fetter, 1983). Steam cleaning is often recommended as a method of decontaminating the drilling rig and equipment before use and between boreholes. In addition, placing down-hole drilling equipment on plastic sheeting or other appropriate material while not in use may reduce contamination from soils or other sources of contaminants at ground surface.

Well casing and screen materials may contain residues of the manufacturing process including cutting oils, cleaning solvents, lubricants, and waxes (Aller et al., 1989). These residues must be removed prior to well installation to prevent contamination or other chemical impacts on samples. A procedure generally recommended is to wash the casing in a strong detergent solution followed by a tap water rinse (Barcelona et al., 1983; Curran and Tomson, 1983) although steam cleaning or a high-pressure hot water wash may be required for removal of some oils, lubricants, and solvents (Aller et al., 1989).

Equipment used portably can lead to cross-contamination by transferring water and contaminants from one installation to another. In a survey of state and federal environmental regulatory agencies, Mickham et al. (1989) found that procedures for decontamination of sampling equipment generally include a tap water rinse, acid or solvent rinse (depending on type of contamination), organic-free water rinse, and air drying. The survey also showed that equipment that does not directly contact samples is generally cleaned by detergent washes and steam cleaning. These workers found little research into the effectiveness of decontamination procedures.

Korte and Kearl (1985) suggest that high-volume pumping may sufficiently clean sampling pumps. In contrast, field experiments conducted by Matteoli and Noonan (1987) determined that 90 minutes of pumping clean water through 200 feet of PTFE tubing was required to reduce the concentrations of several organic and inorganic constituents to below detection levels. These workers found that the time required for effective decontamination was generally related to the type of constituent. Freon was still detectable after 120 minutes of pumping.

The effects of cross-contamination can be reduced or eliminated by utilizing equipment dedicated to individual monitoring wells. As discussed previously, a potential disadvantage of this approach may be interactions between the device and ground water in the well between sampling events.

The use of plastic sample bottles may be another potential source of contamination through leaching of organic and inorganic constituents from the bottle materials (Gillham et al., 1983). An experiment comparing acid-washed and water-washed plastic sample containers determined that the risk of contamination from trace elements in the bottles was greatest for cadmium, copper, and zinc (Ross, 1986). In some cases copper concentrations were 50 times higher in samples collected in bottles that were not acid-washed. Moody and Lindstrom (1977) suggested that plastic sample containers are most effectively cleaned with rinses in both hydrochloric acid and nitric acid to leach impurities from the plastics. Their study further determined that, after acid-washing, PTFE and PE containers were the least contaminating plastic or polymeric materials.

Interference of ground-water sample chemistry may result from direct introduction of foreign materials to ground water and samples or from crosscontamination. Although it appears that currently used decontamination procedures are adequate in a general way, little research has been conducted to determine the effectiveness of specific procedures for individual contaminants. Because they are not standardized, the contribution to sample error of a particular procedure must be evaluated, perhaps on a case-by-case basis.

To prevent crosscontamination when using sampling devices portably, rinsate blanks (also referred to as equipment blanks) should be collected to ensure the effectiveness of decontamination procedures. This may be accomplished by flushing or filling the device with Type II reagentgrade water and collecting a sample of the rinsate water. Analysis of rinsate blanks for the contaminants being sampled will provide an indication of the effectiveness of the cleaning method (U.S. EPA, 1986) and indicate if modifications of the procedures are required.

## **SAMPLE TRANSPORT AND STORAGE**

Ground-water samples require proper containers, treatment, transport, and storage to ensure the chemical and physical state of the sample is preserved until analysis. Factors that could potentially lead to error include volatilization, adsorption, diffusion, precipitation, photodegradation, biodegradation, and cross-contamination (Parr et al., 1988). Methods developed, and widely accepted, to minimize these effects are summarized in U.S. EPA (1986) and Herzog et al. (1991).

To reduce the potential for bias during sample handling, appropriate chemical preservation of samples should take place immediately upon collection. Increases in pH of 0.3 to 0.4 units and declines in iron and zinc concentrations of several orders of magnitude have been observed within seven hours of sample collection (Schuller et al., 1981). These investigators also noted slight declines in the concentrations of calcium, potassium, magnesium, manganese, and sodium in unpreserved samples within 48 hours of collection. To ensure immediate preservation, it may be advisable in some cases to add chemical preservatives to bottles immediately before sample collection. If this method is utilized it is important to prevent the bottle from overflowing which might cause the loss of some of the preservative.

Plastic bottles are usually used for metals and major ions samples to avoid the sorption effects that may occur with glass. Most types of plastic bottles can be cleaned with hydrochloric acid and nitric acid rinses which effectively leach impurities from the material. PTFE and PE bottles tend to not leach impurities to samples (Moody and Lindstrom, 1977) and therefore are the easiest to clean and have the lowest potential to contaminate samples. The quantities of impurities leached in these studies are in the very low ng/cm<sup>2</sup> range, generally below the levels in most site investigations. Sorption of metals onto plastic bottles, although normally not a problem, is reduced by acidifying the sample and thereby keeping the metals ions in solution (Parr et al., 1988). Clearly, if adequate cleaning is carried out and pre-analysis holding times are not exceeded, contamination of major ion and trace metal samples by sample bottles is unlikely.

Organic samples are usually placed in glass containers to avoid the chemical interferences that may occur with plastic bottles. The borosilicate glass used in bottles for water samples for organic analyses is easily cleaned and has very little potential for contamination of samples or sorption from samples.

Cross-contamination of VOC samples during transport and storage can be minimized if accepted procedures are carefully followed. The evidence presently available indicates that cross-contamination of VOC samples at concentrations typical of hazardous waste sites is negligible under conditions normally present during sample storage (Levine et al., 1983; Maskarinec and Moody, 1988). Levine et al. (1983) did note, however, the thickness of the PTFE lining under the VOC vial septum was critical to the prevention of cross-contamination and that contamination was evident when samples were stored near vials containing saturated aqueous solutions of VOCs. Trip blanks can be utilized to evaluate the potential for contamination of samples during shipment to the laboratory. These blanks, which consist of reagent-grade water in bottles of the same type used for sampling, can be shipped to the site and laboratory in the same shipping containers used for samples.

The length of time that a sample can be stored without degradation is related to the potential sources of error covered here. If adequate measures are taken to reduce these errors, chemical alteration of the sample during storage can be minimized. Using commonly-accepted storage methods, concentrations of VOCs have been shown to be stable after 34 days (Friedman et al., 1986) and 56 days (Maskarinec and Moody, 1988).

## ANALYTICAL TECHNIQUES

To gain perspective into the relative magnitude and importance of errors introduced during ground-water sampling, it is useful to quantify the errors involved in laboratory analysis. Potential sources of error in the laboratory include glassware, reagents, laboratory preparation techniques, and analytical equipment and apparatus (Lewis, 1988). It is beyond the scope of this document to discuss how each of these aspects of laboratory operation can impact sample quality except to say that errors can be detected and controlled by the use of various quality-control checks. Vitale et al., (1991) describe the blanks, duplicate samples, and spikes that ensure the identification of laboratory error. Through the use of these checks, analytical errors often can be quantified, unlike many aspects of sampling protocol where comparison to 'true' concentrations is usually impossible.

In a review of the EPA Contract Laboratory Program (CLP) database for gas chromatograph/mass spectrometer (GC/MS) analysis of VOCs, Flotard et al. (1986) analyzed the deviations in reported concentrations from actual concentrations in blind performance evaluation samples. These deviations can be considered measures of analytical errors, with underreported concentrations considered negative error and overreported concentrations considered positive error. The Flotard et al. (1986) study found errors in reported concentrations of 22 VOCs from -48.4% for 1,1-dichloroethane to +6.5% for bromoform. The results for methylene chloride exhibited an apparent error of +36.6% but this value was attributed to laboratory contamination of samples and not analysis error. Their review indicated that 55% of the 22 evaluated VOCs resulted in reported concentrations that were more than 20% lower than actual concentrations. Interlaboratory errors from 35 laboratories were found to be from -3.9% to zero, although data from only three compounds were analyzed.

A similar review of the CLP database for semi-volatile analyses conducted by Wolff et al. (1986) concluded that the greatest analytical errors were associated with phenolic compounds, whose concentrations were consistently underreported. Other classes of semi-volatiles showed no general trends. In that study, analytical errors ranged from -48% for 1,3-dichlorobenzene and 2,6-dinitrotoluene to +12% for 4-chlorophenylphenylether. The review indicated that 60% of the 33 compounds evaluated showed analytical errors in excess of -20%, slightly more than for VOC analyses. Interlaboratory errors for six compounds ranged from -51% for phenol- $d_6$  to -16% for p-terphenyl, considerably greater than for the volatile analyses.

The CLP database has also been evaluated for errors introduced by inorganic analytical methods (Aleckson et al., 1986). These workers found that analytical errors ranged from -26.5% to +10.0%, with most errors falling in the range -10.0% to zero. The greatest negative errors were found for selenium, silver, and thallium.

Barcelona et al. (1989) tabulated laboratory errors for inorganic constituents during an intensive time-series investigation of ground-water chemistry variation. They found that errors in determinations of major ions in external performance samples ranged from -8.1% (potassium) to +12.1% (total iron). An evaluation of eight analytical laboratories was conducted by

Rice et al. (1988) as part of a uranium mill tailings ground-water quality investigation. Constituents of interest included total dissolved solids, major ions, trace metals, and radionuclides. Analysis of external performance samples during the study showed that 67% of all analyses were within the acceptable range but that 60% of the reported values were higher than the known concentrations. Iron and aluminum were among the constituents showing the highest analytical errors.

## SUMMARY AND CONCLUSIONS

As shown here, many aspects of ground-water investigations may introduce error into determinations of concentrations of hydrochemical constituents. The potential errors associated with many of these aspects are summarized in Table 5.

Errors produced during certain aspects of sampling programs can be identified, quantified, and controlled through the use of accepted procedures in conjunction with performance evaluation samples. For example, equipment decontamination and sample transport and storage have considerable potential for introducing sample error if not conducted in a careful and consistent manner. In the case of equipment decontamination, collection and analysis of rinse blanks from cleaned equipment can be useful for evaluating the effectiveness of decontamination procedures. Likewise, errors that may occur during sample transport can be identified by the use of trip blanks that are transported to the site and laboratory in the same shipping containers as field samples. An aspect that may require particular attention and further research is the effectiveness of decontamination of flexible tubing used for conveying samples from the sampler to sample bottle.

The potential errors associated with other aspects of sampling programs are relatively well understood and can be minimized through appropriate choice of equipment and materials. For instance, advances in sampling device design and construction have resulted in the development and widespread use of positive displacement sampling devices whose operation generally introduces little sample error. For most compounds, including VOCs, positive displacement devices allow collection of accurate and precise samples, with concentrations of VOCs typically within 10% of true concentrations. Some grab samplers, particularly bailers, may also produce representative samples but their effectiveness is highly dependent on mode of operation and the constituents of interest. Under unfavorable field conditions or when operated improperly, bailers may produce errors in VOC concentrations from -10% to -80% or more. Most other types of samplers produce errors of unpredictable magnitude but show VOC errors of at least -20% in controlled laboratory experiments. The unpredictable magnitude of errors associated with many of these devices also means that they often cannot provide the precise, or repeatable, measurements usually associated with positive displacement devices. As a result, the use of positive displacement sampling devices may minimize the introduction of error into determinations of the concentrations of sensitive hydrochemical constituents. Use of other types of devices may introduce error of unpredictable magnitude.

Potential impacts of materials used in well and sampler construction have been demonstrated, but the implications of these effects in a field setting remain unclear. Laboratory comparison studies conducted under static conditions have demonstrated



the potential for rigid PTFE, PVC, and metallic materials to introduce error into concentrations of some trace metals and hydrocarbon compounds. However, little work has been conducted under conditions simulating dynamic ground- or sample-water flow or, more importantly, well-purging effects. Despite these unresolved issues, materials' impacts can be minimized by choosing well materials compatible with the objectives of the sampling program and the hydrogeologic and hydrochemical conditions of the site. The proper choice of materials can reduce chemical effects on water stored in the well between sampling events and make removal of stagnant water during well purging less difficult. When monitoring for low hydrocarbon concentrations in non-corrosive ground water, SS and PVC casing may be the most appropriate choices. Because PTFE has been shown to introduce error into hydrocarbon determinations, it may be most applicable under conditions where SS and PVC are not considered appropriate. For example, SS would probably not be considered an appropriate material in corrosive ground water or where determinations of trace metal concentrations are of primary concern. Likewise, PVC probably would not be considered an appropriate material in situations where solvents in moderate to high concentrations might dissolve the PVC material.

Flexible tubing can introduce significant error through sorption of contaminants onto tubing material, leaching of constituents of the tubing material into sampled water, and possibly transmission of organic compounds and gases through tubing walls. These errors are generally greater than for rigid materials and may be particularly important during site remediation efforts when declines in ground-water concentrations may be masked by desorption of previously sorbed compounds. Laboratory research has demonstrated the potential for errors under static conditions, but further research is required to understand how sorption/desorption mechanisms can impact samples during the dynamic sampling process. These studies suggest, however, that sample error can be minimized by substituting PTFE for other types of flexible materials.

Filtration of samples for trace metals determinations may introduce sample error either by the equipment and methods utilized or by the actual decision to filter. Due to the presence of colloidal sized particles in ground water, filtration can have dramatic impacts on determinations of the concentrations of both mobile and total dissolved metals. Indiscriminate filtration of metals samples may lead to gross errors in these concentrations and result in erroneous conclusions about ground-water transport of metals. In view of this, the objectives of the sampling program must be carefully considered before samples are filtered. If it is decided to filter samples, in-line filtration with pre-cleaned, lower pore-size filters can reduce errors associated with filtration.

In contrast to most aspects of the sampling process, errors introduced during laboratory analysis may be relatively well quantified. Analysis of the CLP database has shown errors in reported concentrations of performance samples of -20% to -30% for volatile and semivolatile compounds and -10% to zero for inorganic constituents. Errors in analytical methods, as with sample transport, sample storage, and equipment decontamination, can be quantified for individual investigations by analyzing standards and blind quality evaluation samples. Although the magnitude of analytical error may be greater than the error

introduced during some aspects of sample collection, analysis of quality evaluation samples leads to easier identification and quantification of analytical error.

Errors associated with other aspects of site investigations, including well drilling and construction, are more difficult to identify because true concentrations of hydrochemical constituents are unknown in field investigations. During the drilling phase of site investigations, hydrogeologic disturbances can be minimized by utilizing appropriate drilling methods. Likewise, drilling-related hydrochemical disturbances can be reduced by avoiding the use of fluids that might alter ground-water chemistry through ion exchange reactions or exposure to organic polymers. Well construction and development methods appropriate to the site hydrogeologic conditions are capable of removing artifacts from the drilling process and improving the hydraulic efficiency of the well with minimal impact on subsequent samples. Proper design, installation, and isolation of cement or bentonite seals reduces the potential for chemical alterations from these materials. Any of these aspects of drilling and well construction can lead to large errors if not carefully controlled, however, the magnitude of error is directly related to site conditions and the extent to which methods have been misapplied. Careful consideration and application of methods and materials during well drilling and construction can significantly reduce sample error.

Well purging method, purging rate, and the volume purged prior to sample collection all possess great potential for introducing significant error when sampling for sensitive constituents. For example, setting the purging device far below the air-water interface and using a high purge rate may contaminate samples by allowing stagnant water to mix with sampled water. However, it is possible to identify these potential sources of error and modify purging procedures to minimize the errors. Conducting a preliminary purge test may aid in identification of the depth and rate that results in the most representative samples, however, determination of when purging is complete (purge volume) may be more difficult. Although purge volume can be calculated by several indirect methods, this volume may not directly correlate with the volume of water required to provide representative samples. In particular, stabilization of the values of field chemical indicator parameters such as temperature, pH, and EC may not coincide with stabilization of other hydrochemical parameters and constituents. Due to the often complex three-dimensional distribution of many contaminants, concentrations of individual constituents may not stabilize at the same time, or may never stabilize. Despite these possibilities, the potential for sample error can be reduced by choosing indicator parameters that are sensitive to the purging process and relate to the constituents of interest.

To reduce error when sampling for constituents that may be associated with colloids, or other very sensitive constituents, it is particularly important to minimize disturbance of the samples and the sampling environment during the purging and sampling process. To this end, reducing or eliminating purging, minimizing purging and sampling flow rates, and using dedicated sampling devices placed within the well intake interval should all be considered. Because this issue remains unresolved, general recommendations are not possible and it may be necessary to conduct preliminary purge tests to determine how indicator



parameters and concentrations of important constituents vary with purging rate, volume, method, and distribution of contaminants around the well. Inadequate determination of these factors may lead to order-of-magnitude, or more, errors in concentration determinations, especially in low-yield wells.

The errors most critical to sampling programs are those that are difficult or impossible to identify because important conclusions may be unknowingly based on erroneous or inadequate data. Well location and design are aspects of sampling that are very likely to produce undetected errors. Errors produced by well location are virtually impossible to identify because their magnitude is entirely specific to that particular location. The appropriate placement of a well can mean the difference between detection of a contaminant plume or missing it entirely, so the potential for error is virtually infinite. Even if a well is located in the targeted zone of contamination or plume, little can be deduced about small-scale hydrogeologic properties or contaminant distribution without a well-designed monitoring network that accounts for individual site characteristics and program objectives.

Well design, particularly the depth and interval of the well intake, can also be a large potential source of undetectable errors. To delineate the vertical distribution of contaminants at a single location, samples must be collected at specific depths, hence, wells must be screened over short intervals and adequately

sealed between sampling zones. Dilution and cross-contamination resulting from long-screened wells or poor well seals may produce order-of-magnitude errors in concentrations that far outweigh errors produced in all other aspects of the sampling process. For example, dilution of samples collected from long-screened remediation wells may mask true contaminant concentrations, leading to erroneous conclusions about the effectiveness of remedial efforts.

In conclusion, it can be stated that virtually all aspects of groundwater investigations, from well location to laboratory analysis, have the potential to introduce error into the determinations of concentrations of hydrochemical constituents. General definition of the magnitude of potential errors is difficult because errors will be influenced by the complex interaction of geologic, hydraulic, and hydrochemical conditions unique to each site, as well as the design and performance of the sampling program. Potential sources of error related to site conditions must be identified during early phases of the remedial investigation (RI) and then minimized by careful design of the sampling program. Modifications to the program design may then be necessary to address issues that might arise as the RI proceeds. Methods of detecting errors that may be introduced during the performance of the sampling program must be utilized so that these errors can be identified and minimized. However, errors that are difficult or impossible to detect may provide the greatest obstacles to the collection of representative data.

**TABLE 5. POTENTIAL SOURCES OF ERROR ASSOCIATED WITH ELEMENTS OF GROUND-WATER SAMPLING PROGRAMS AT HAZARDOUS WASTE SITES.**

Program Element	Type of Error	Ability to Avoid Error	Methods for Error Avoidance	Ability to Detect Error	Methods for Error Detection
Well Intake Length	Long-screened and multi-screened wells may lead to cross-contamination or contamination dilution.	Easy to Moderate	Identify specific zones of interest. Use intake length appropriate to program objectives and hydrogeologic and hydrochemical conditions.	Difficult	Compare with data from short-screen wells or field-screening methods.
Well Intake Depth	Well intake may miss zone of interest.	Easy to Moderate	Identify specific zones of interest. Use intake length appropriate to program objectives and hydrogeologic and hydrochemical conditions.	Difficult	Compare with data from other wells or field-screening methods.
Well Intake Design	Presence of particulates in samples.	Easy to Moderate	Design in conjunction with filter pack for hydrogeologic conditions.	Easy to Moderate	Turbid samples.
Filter Pack	Presence of particulates in samples. Reaction with filter pack materials or introduced contaminants may alter hydrochemistry. Vertical connection of naturally isolated zones if filter pack too long. Invasion of borehole seal materials if filter pack too short.	Easy to Moderate	Design in conjunction with well intake for hydrogeologic conditions. Use clean, non-reactive materials. Install with tremie pipe and measure depths and volumes during installation to ensure correct placement.	Easy to Moderate	Turbid samples. Sorption/leaching studies of materials before installation.

(Continued)

TABLE 5. CONTINUED.

Program Element	Type of Error	Ability to Avoid Error	Methods for Error Avoidance	Ability to Detect Error	Methods for Error Detection
Borehole Seals	If improperly placed, bentonite materials may alter hydrochemistry through ion exchange. If improperly placed, cement may elevate values of ground-water pH, EC, alkalinity, calcium concentration.	Moderate	Design for hydrogeologic conditions. Isolate seals from sampling zone. Install with tremie pipe and measure depths and volumes during installation to ensure correct placement.	Moderate to Difficult	Bentonite: High sodium concentrations if sodium bentonite used and samples are highly contaminated. Cement: Sample pH over 10, and high EC, alkalinity, and calcium concentrations.
Well Location	Inadequate coverage of area of investigation.	Moderate	Careful design of monitoring well network.	Difficult	Compare with data from nearby wells or field-screening methods.
Drilling	Depends on method. Contamination by drilling or other fluids may alter hydrochemistry. Smearing and mixing of fluids and sediments at borehole wall. Cross-contamination within borehole.	Moderate	Careful consideration and application of methods that are appropriate for program objectives and hydrogeologic and hydrochemical conditions. Minimize use of water-based drilling fluids and additives. If constituents sensitive to atmospheric exposure will be sampled, minimize use of air-based drilling fluids. Determine the chemical quality of drilling fluids used. Use appropriate development methods to minimize impacts of drilling.	Moderate to Difficult	Drilling fluid contamination: Depends on composition of fluid. Compare with data from nearby wells and field-screening methods. Evaluate chemical quality of fluids used.
Well Development	Depends on method. Incomplete development may lead to turbid samples or poor hydraulic efficiency. Alteration of hydrochemistry by development action. Introduction of contaminants (including air and water).	Easy to Moderate	Careful consideration and application of methods that are appropriate for program objectives and hydrogeologic and hydrochemical conditions. Avoid adding fluids to well. If adding fluids is necessary, determine the chemical quality of the fluids used.	Moderate	Turbid samples and production of sediments during pumping may indicate incomplete development or inadequate design of filter pack and well intake. If fluids were added, evaluate chemical quality of fluids used.
Materials	Depends on material, contaminants, hydrochemical conditions, and time of contact. Sorption/desorption of chemical constituents. Leaching of constituents from materials' matrix. Biologic activity. Possible transmission through flexible materials.	Easy to Moderate	Select materials that are appropriate for program objectives and hydrogeologic and hydrochemical conditions. Use appropriate well purging techniques.	Difficult	Sorption/leaching studies of materials before installation. Detection after installation depends on material, contaminants, hydrochemical conditions, and time of contact.

(Continued)

TABLE 5. CONTINUED.

Program Element	Type of Error	Ability to Avoid Error	Methods for Error Avoidance	Ability to Detect Error	Methods for Error Detection
Well Purging	Incomplete removal of stagnant water (water affected by contact with atmosphere and well and sampling device materials). Disturbance of ambient hydrochemical conditions.	Easy to Moderate (Moderate to Difficult under low-yield conditions)	Choose indicator parameters that are sensitive to purging process and relate to the chemical constituents of interest. Conduct purge-volume test to determine when parameters or constituents of interest reach stable values. Determine if low flow-rate and/or low volume purging is appropriate. If not, minimize volume of stagnant water above device intake by purging near water surface or lower device during purging or before sampling. Avoid drawing water level below top of well intake.	Easy to Moderate (Moderate to Difficult under low-yield conditions)	Conduct purge-volume test to determine when parameters or constituents of interest reach stable values
Sampling Device	Depends on operating principle of sampling device. Sorption, desorption, and leaching from materials. Degassing or volatilization from sample. Atmospheric contamination.	Easy	Select device that is appropriate for sample type, hydrochemical conditions, and program objectives.	Moderate to Difficult	Depends on sampler type. Compare with data collected with other devices.
Sample Collection Time and Depth	Mixing with stagnant water in well. As time after purging increases, water in well becomes more stagnant.	Easy	Collect samples from within or immediately above well intake. Use appropriate sampling rate. Avoid moving sampler within water column during sampling. High-yield wells: Sample immediately after purging. Low-yield wells: Determine appropriate time based on response of well and purge-volume test.	Moderate to Difficult	Test different scenarios and compare results, although may be very difficult to determine which results are the most representative.
Sample Filtration	Type of filter system used and length of pre-filtration holding time determines extent of temperature changes, atmospheric contamination, degassing, and sorption onto particulates. Filter pore size may affect passage of certain constituents and suspended material. Filter material and filter pre-cleaning may affect results. Erroneous conclusions about metals concentrations may result from association of metals with colloids.	Easy to Moderate	Determine if filtration is necessary for the objectives of the program. Minimize pre-filtration holding time. Use pre-cleaned in-line filters. Some situations may warrant use of pore sizes other than 0.45 $\mu$ m.	Moderate	Compare analytical results of filtered and unfiltered samples. Compare analytical results of different filtration methods.

(Continued)

TABLE 5. CONTINUED.

Program Element	Type of Error	Ability to Avoid Error	Methods for Error Avoidance	Ability to Detect Error	Methods for Error Detection
Equipment Decontamination	Cross-contamination between wells if sampling equipment is used portably. Incomplete removal of residues from manufacture or contaminants from storage, transport, or use.	Easy	Use appropriate cleaning and decontamination procedures.	Easy	Collect rinsate blanks after cleaning.
Sample Preservation	Changes in hydrochemistry during sample shipment and storage.	Easy	Use appropriate physical and chemical preservation procedures.	Moderate to difficult.	Indirectly identified by evaluating how well procedures are being followed.
Sample Transport and Storage	Cross-contamination between sample bottles. Materials' effects from sample bottles. Loss of volatile constituents.	Easy	Use appropriate sample bottle type and cleaning procedure. Do not exceed sample holding times.	Easy	Transport trip blanks with samples.
Laboratory Analysis	Deviation from true concentrations.	Moderate	Use appropriate analytical methods and laboratory procedures.	Easy to Moderate	Analyze blind performance evaluation samples, blanks, and standards.

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# Ground-Water Issue

## SOIL SAMPLING AND ANALYSIS FOR VOLATILE ORGANIC COMPOUNDS

T. E. Lewis, A. B. Crockett, R. L. Siegrist, and K. Zarrabi

The Regional Superfund Ground Water Forum is a group of ground-water scientists that represents EPA's Regional Superfund Offices. The forum was organized to exchange up-to-date information related to ground-water remediation at Superfund sites. Sampling of soils for volatile organic compounds (VOCs) is an issue identified by the Ground Water Forum as a concern of Superfund decision makers.

A group of scientists actively engaged in method development research on soil sampling and analysis for VOCs gathered at the Environmental Monitoring Systems Laboratory in Las Vegas to examine this issue. Members of the committee were R. E. Cameron (LESC), A. B. Crockett (EG&G), C. L. Gerlach (LESC), T. E. Lewis (LESC), M. P. Maskarinec (ORNL), B. J. Mason (ERC), C. L. Mayer (LESC), C. Ramsey (NEIC), S. R. Schroedl (LESC), R. L. Siegrist (ORNL), C. G. Urcin (Rutgers University), L. G. Wilson (University of Arizona), and K. Zarrabi (ERC). This paper was prepared by The Committee for EMSL-LV's Monitoring and Site Characterization Technical Support Center, under the direction of T. E. Lewis, with the support of the Superfund Technical Support Project. For further information contact Ken Brown, Center Director at EMSL-LV, FTS 545-2270, or T. E. Lewis at (702) 734-3400.

### PURPOSE AND SCOPE

Concerns over data quality have raised many questions related to sampling soils for VOCs.

This paper was prepared in response to some of these questions and concerns expressed by Remedial Project Managers (RPMs) and On-Scene Coordinators (OSCs). The following questions are frequently asked:

1. Is there a specific device suggested for sampling soils for VOCs?
2. Are there significant losses of VOCs when transferring a soil sample from a sampling device (e.g., split spoon) into the sample container?
3. What is the best method for getting the sample from the split spoon (or other device) into the sample container?
4. Are there smaller devices such as subcore samplers available for collecting aliquots from the larger core and efficiently transferring the sample into the sample container?
5. Are certain containers better than others for shipping and storing soil samples for VOC analysis?
6. Are there any reliable preservation procedures for reducing VOC losses from soil samples and for extending holding times?

This paper is intended to familiarize RPMs, OSCs, and field personnel with the current state of the science and the current thinking concerning sampling soils for VOC analysis. Guidance is provided for selecting the most effective sampling device for collecting

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samples from soil matrices. The techniques for sample collection, sample handling, containerizing, shipment, and storage described in this paper reduce VOC losses and generally provide more representative samples for volatile organic analyses (VOA) than techniques in current use. For a discussion on the proper use of sampling equipment the reader should refer to other sources (Acker, 1974; U.S. EPA, 1983; U.S. EPA, 1986a).

Soil, as referred to in this report, encompasses the mass (surface and subsurface) of unconsolidated mantle of weathered rock and loose material lying above solid rock. Further, a distinction must be made as to what fraction of the unconsolidated material is soil and what fraction is not. The soil component here is defined as all mineral and naturally occurring organic material that is 2 mm or less in size. This is the size normally used to differentiate between soils (consisting of sands, silts, and clays) and gravels.

Although numerous sampling situations may be encountered, this paper focuses on three broad categories of sites that might be sampled for VOCs:

1. Open test pit or trench
2. Surface soils (< 5 ft in depth)
3. Subsurface soils (> 5 ft in depth)

## INTRODUCTION

VOCs are the class of compounds most commonly encountered at Superfund and other hazardous waste sites (McCoy, 1985; Plumb and Pitchford, 1985; Plumb, 1987; Ameth et al., 1988). Table 1 ranks the compounds most commonly encountered at Superfund sites. Many VOCs are considered hazardous because they are mutagenic, carcinogenic, or teratogenic, and they are commonly the controlling contaminants in site restoration projects. Decisions regarding the extent of contamination and the degree of cleanup have far-reaching effects; therefore, it is essential that they be based on accurate measurements of the VOC concentrations present. VOCs, however, present sampling, sample handling, and analytical difficulties, especially when encountered in soils and other solid matrices.

Methods used for sampling soils for volatile organic analysis (VOA) vary widely within and between EPA Regions, and the recovery of VOCs from soils has been highly variable. The source of variation in analyte recovery may be associated with any single step in the process or all steps, including sample collection, transfer from the sampling device to the sample container, sample shipment, sample preparation for analysis, and sample analysis. The strength of the sampling chain is only as strong as its weakest link; soil sampling and transfer to the container are often the weakest links.

Sample collection and handling activities have large sources of random and systematic errors compared to the analysis itself (Barcelona, 1989). Negative bias (i.e., measured value less than true value) is perhaps the most significant and most difficult to delineate and control. This error is caused primarily by loss through volatilization during soil sample collection, storage, and handling.

TABLE 1. RANKING OF GROUND WATER CONTAMINANTS BASED ON FREQUENCY OF DETECTION AT 358 HAZARDOUS WASTE DISPOSAL SITES

Contaminant	Detection Frequency
Trichloroethene (V)	51.3
Tetrachloroethene (V)	36.0
1,2-trans Dichloroethene (V)	29.1
Chloroform (V)	28.4
1,1-Dichloroethene (V)	25.2
Methylene chloride (V)	19.2
1,1,1-Trichloroethane (V)	18.9
1,1-Dichloroethane (V)	17.9
1,2-Dichloroethane (V)	14.2
Phenol (A)	13.6
Acetone (V)	12.4
Toluene (V)	11.6
bis-(2-Ethylhexyl) phthalate (B)	11.5
Benzene (V)	11.2
Vinyl chloride	8.7

V = volatile, A = acid extractable, B = base/neutral  
Source: Plumb and Pitchford (1985).

There are currently no standard procedures for sampling soils for VOC analyses. Several types of samplers are available for collecting intact (undisturbed) samples and bulk (disturbed) samples. The selection of a particular device is site-specific. Samples are usually removed from the sampler and are placed in glass jars or vials that are then sealed with Teflon-lined caps. Practical experience and recent field and laboratory research, however, suggest that procedures such as these may lead to significant VOC losses (losses that would affect the utility of the data). Hanisch and McDevitt (1984) reported that any headspace present in the sample container will lead to desorption of VOCs from the soil particles into the headspace and will cause loss of VOCs upon opening of the container. Siegrist and Jennsen (1990) found that 81% of the VOCs were lost from samples containerized in glass jars sealed with Teflon-lined caps compared to samples immersed in methanol in jars.

## FACTORS AFFECTING VOC RETENTION AND CONCENTRATION IN SOIL SYSTEMS

Volatile organic compounds in soil may coexist in three phases: gaseous, liquid (dissolved), and solid (sorbed). [Note: "Sorbed" is used throughout this paper to encompass physical and chemical adsorption and phase partitioning.] The sampling, identification, and quantitation of VOCs in soil matrices are complicated because VOC molecules can coexist in these

three phases. The interactions between these phases are illustrated in Figure 1. The phase distribution is controlled by VOC physicochemical properties (e.g., solubility, Henry's constant), soil properties, and environmental variables (e.g., soil temperature, water content, organic carbon content).

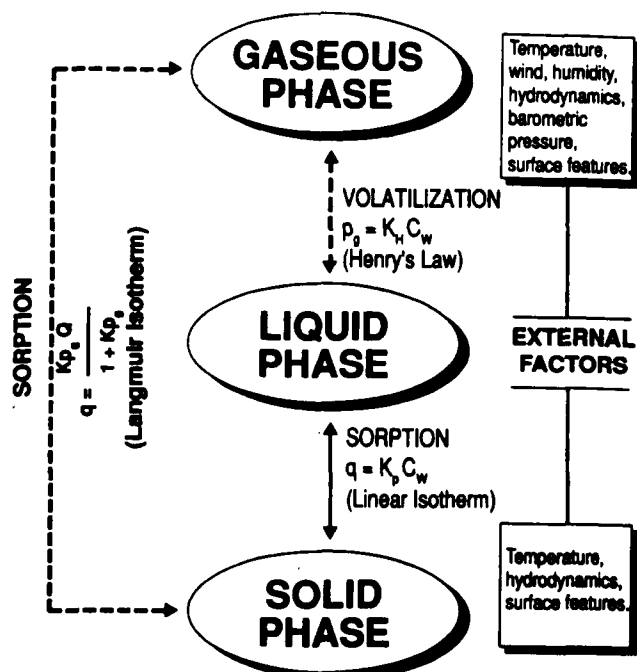


Figure 1. Equilibrium relationships for phase partitioning of VOCs in soil systems. See Table 2 for definitions of abbreviations.

The factors that affect the concentration and retention of VOCs in soils can be divided into five categories: VOC chemical properties, soil chemical properties, soil physical properties, environmental factors, and biological factors. A brief summary of VOC, soil, and environmental factors is presented in Table 2, which provides an overview of the factors that interact to control VOCs in the soil environment at the time a sample is collected. The cited references provide a more detailed discussion. The chemical and physical properties of selected VOCs are further described in Table 3. Note that many of these properties have been determined in the laboratory under conditions (e.g., temperature, pressure) that may differ from those encountered in the field. Devitt et al. (1987) offers a more exhaustive list.

Many VOCs exhibit extreme mobilities, particularly in the vapor phase, where their gas diffusion coefficients can be four times greater than their liquid diffusion coefficients. The vapor phase migration is influenced by the moisture content of the soil which alters the air-filled to water-filled pore volume ratio. The retention of VOCs by soil is largely controlled by reactions with the solid phase. This retention is especially true for the finer particles of silts and clays. The fine-grained particles (<2 mm) have a large surface-to-volume ratio, a large number of reactive sites, and high sorption capacities (Richardson and Epstein, 1971; Boucher and Lee, 1972; Lotse et al., 1988). Some investigators attribute the greater sorption of VOCs onto fine-grained particles to the greater organic carbon content of smaller particles (Karickhoff et al., 1979).

Soil-moisture content affects the relative contributions of mineral and organic soil fractions to the retention of VOCs (Smith et al., 1990). Mineral clay surfaces largely control sorption when soil moisture is extremely low (<1%), and organic carbon

(Continued on page 7)

TABLE 2. FACTORS AFFECTING VOC CONCENTRATIONS IN SOILS

Factor	Common Abbr.	Units	Effects on VOC Concentrations in Soil	References
<b>VOC Chemical Properties</b>				
Solubility	$C_w$	mg/L	Affects fate and transport in water, effects water/air partit., influences organic carbon partit.	Roy and Griffin (1985)
Henry's Constant	$K_H$	(atm-m <sup>3</sup> )/mole	Constant of proportionality between the water and gas phase concentrations; temperature and pressure dependent.	Shen and Sewell (1982) Spencer et al. (1988)
Vapor pressure	v.p.	mm Hg	Affects rate of loss from soil.	Shen and Sewell (1982)
Organic carbon part. coeff.	$K_{oc}$	mg VOC/g C	Adsorption coefficient normalized for soil organic content.	Farmer et al. (1980)
Octanol/water part. coeff.	$K_{ow}$	mg VOC/ mg octanol	Equilibrium constant for distribution of VOC between water and an organic (octanol) phase. Gives estimate of VOC partitioning into organic fraction of soil.	Voice and Weber (1983)
Boiling point	b.p.	°C	Affects co-evaporation of VOC and water from soil surface.	Voice and Weber (1983)
Soil/water distribution coefficient	$K_d$	[1]	Equilibrium constant for distribution of contaminant between solid and liquid phases.	Voice and Weber (1983)

(Continued)

TABLE 2. (CONTINUED)

Factor	Common Abbr.	Units	Effects on VOC Concentrations in Soil	References
<b>Soil Chemical Properties</b>				
Cation exchange capacity	CEC	meq/100 g	Estimates the number of negatively charged sites on soil particles where charged VOC may sorb; pH dependent.	
Ion concentration (activity)	pH	-log[H <sup>+</sup> ]	Influences a number of soil processes that involve non-neutral organic partitioning; affects CEC and solubility of some VOCs.	
Total organic carbon content	TOC	mg C/g soil	An important partitioning medium for non-polar, hydrophobic (high $K_{ow}$ ) VOCs; sorption of VOCs in this medium may be highly irreversible.	Chiou et al. (1988) Farmer et al. (1980)
<b>Soil Physical Properties</b>				
Particle size or texture	A	% sand, silt, clay	Affects infiltration, penetration, retention, sorption, and mobility of VOCs. Influences hydraulics as well as surface-area-to-volume ratio (s.a. $\propto$ Kd).	Richardson and Epstein (1971)
Specific surface area	s.a.	m <sup>2</sup> /g	Affects adsorption of VOCs from vapor phase; affects soil porosity and other textural properties.	Karickhoff et al. (1979)
Bulk density	$\rho_b$	g/cm <sup>3</sup>	Used in estimating mobility and retention of VOCs in soils; will influence soil sampling device selection.	Spencer et al. (1988)
Porosity	$n$	%	Void volume to total volume ratio. Affects volume, concentration, retention, and migration of VOCs in soil voids.	Farmer et al. (1980) Shen and Sewell (1982)
Percent moisture	$\Theta$	% (w/w)	Affects hydraulic conductivity of soil and sorption of VOCs. Determines the dissolution and mobility of VOCs in soil.	Farmer et al. (1980) Chiou and Shoup (1985)
Water potential	$pF$	m	Relates to the rate, mobility, and concentration of VOCs in water or liquid chemicals.	
Hydraulic conductivity	K	m/d	Affects viscous flow of VOCs in soil water depending on degree of saturation, gradients, and other physical factors.	
<b>Environmental Factors</b>				
Relative humidity	R.H.	%	Could affect the movement, diffusion, and concentration of VOCs; interrelated factors; could be site specific and dependent upon soil surface - air interface differentials.	Chiou and Shoup (1985)
Temperature	T	°C		
Barometric pressure		mm Hg		
Wind speed		knots	Relevant to speed, movement, and concentration of VOCs exposed, removed, or diffusing from soil surface.	
Ground cover		%	Intensity, nature, and kind, and distribution of cover could affect movement, diffusion rates, and concentration of VOCs.	

TABLE 3. CHEMICAL PROPERTIES OF SELECTED VOLATILE ORGANIC COMPOUNDS†

Compound	m.w. (g/mole)	Solubilities (mg/L @ 20°C)	log K <sub>oc</sub> <sup>a</sup>	log K <sub>ow</sub> <sup>b</sup>	K <sub>H</sub> <sup>c</sup>	Vapor Pressure (mm @ 20°C)
Acetone	58	Miscible		-0.22	-0.24	270 (@ 30°)
Benzene	78	1780	1.91	2.11	0.22	76
Bromodichloromethane	164	7500	2.18	2.10		50
Bromoform	253	3190 (@ 30°)				6 (@ 25°)
Bromomethane	95	900	1.34	1.19	1.50	1250
2-Butanone	72	270000	1.56	0.26		76
Carbon disulfide	76	2300	1.80			260
Carbon tetrachloride	154	800	2.04	2.64	0.94	90
Chlorobenzene	113	500	2.18	2.84	0.16	9
Chloroethane	65	5740	1.40	1.54	0.61	1000
2-Chloroethylvinyl ether	107					
Chloroform	120	8000	1.46	1.97	0.12	160
Chloromethane	51	8348	0.78	0.91	1.62	3800
Dibromochloromethane	208	3300	2.45	2.24		15 (@10.5°)
1,2-Dichlorobenzene	147	100	2.62	3.38		1
1,3-Dichlorobenzene	147	123 (@ 25°)		3.38		
1,4-Dichlorobenzene	147	49 (@ 22°)		3.39		1
1,1-Dichloroethane	99	5500	1.66	1.79	0.18	180
1,2-Dichloroethane	99	8690	1.34	1.48	0.04	61
1,1-Dichloroethene	97	400				500
trans-1,2-Dichloroethene	97	600	1.56	2.06		200 (@ 14°)
1,2-Dichloropropane	113	2700		1.99		42
cis-1,3-Dichloropropene	110	2700				34 (@ 25°)
trans-1,3-Dichloropropene	111	2800				43 (@ 25°)
Ethylbenzene	106	152	2.60	3.15		7
2-Hexanone	100	3500		1.38		2
Methylene chloride	85	20000	1.40	1.25		349
Methylisobutylketone	100	17000	1.34	1.46	0.002	6
Perchloroethylene	166	150	2.60	2.60	0.85	14
Styrene	104	300	2.61	2.95		5
1,1,2,2-Tetrachloroethane	168	2900	2.07	2.60		5
Tetrachloroethene	166	150	2.78	3.40		18 (@ 25°)
Toluene	92	515	2.18	2.69	0.27	22
1,1,1-Trichloroethane	133	4400	2.19	2.50	1.46	100
1,1,2-Trichloroethane	133	4500	2.14	2.07		19
Trichloroethylene	132	700	2.09	2.29	0.37	60
Trichlorofluoromethane	137	1100 (@ 25°)	2.68			687
Vinyl acetate	86	25000	1.59	0.73		115 (@ 25°)
Vinyl chloride	63	1100 (@ 25°)	2.60	1.38	97.0	2660 (@ 25°)
Total xylenes	106	198	2.46		9400.0	

† From Veracruz 1983, July 1984.

<sup>a</sup> Organic carbon partitioning coefficient.<sup>b</sup> Octanol/water partitioning coefficient.<sup>c</sup> Henry's Gas Law constant (dimensionless) @ 20°C.

TABLE 4. MICROBIOLOGICAL FACTORS AFFECTING VOCs IN SOIL SYSTEMS

Organism(s)	Compound(s)	Conditions	Remarks/metabolite(s)
Various soil microbes	Pentachlorophenol	Aerobic	tetra-, tri-, di-, and m-Chlorophenol (Kobayashi and Rittman, 1982)
	1,2,3- and 1,2,4-Trichlorobenzene	Aerobic	2,6-; 2,3-Dichlorobenzene; 2,4- and 2,5-dichlorobenzene; CO <sub>2</sub> (Kobayashi and Rittman, 1982)
Various soil bacteria	Trichloroethane, trichloromethane, methylchloride, chloroethane, dichloroethane, vinylidene chloride, trichloroethene, tetrachloroethene, methylene chloride, dibromochloromethane, bromochloromethane	Anaerobic	Reductive dehalogenation under anoxic conditions, (i.e., < 0.35 V) (Kobayashi and Rittman, 1982)
Various soil microbes	Tetrachloroethene	Anaerobic	Reductive dehalogenation to trichloroethene, dichloroethene, and vinyl chloride, and finally CO <sub>2</sub> (Vogel and McCarty, 1985)
Various soil microbes	<sup>13</sup> C-labeled trichloroethene	Anaerobic	Dehalogenation to 1,2-dichloroethene and not 1,1-dichloroethene (Kleopfer et al., 1985)
Various soil bacteria	Trichloroethene	Aerobic	Mineralized to CO <sub>2</sub> in the presence of a mixture of natural gas and air
Actinomycetes	chlorinated and non-chlorinated aromatics	aerobic	Various particle breakdown products mineralized by other microorganisms (Lechevalier and Lechevalier, 1976)
Fungi	DDT	Aerobic	Complete mineralization in 10-14 days (Johnsen, 1976)
<i>Pseudomonas</i> sp. <i>Acinetobacter</i> sp. <i>Micrococcus</i> sp.	Aromatics	Aerobic	Organisms were capable of sustaining growth in these compounds with 100% biodegradation (Jamison et al., 1975)
Acetate-grown biofilm	Chlorinated aliphatics	Aerobic	No biodegradation observed (Bouwer, 1984)
		Methanogenic	Nearly 100% biodegradation observed (Bouwer, 1984)
	Chlorinated and nonchlorinated aromatics	Aerobic	Nearly 100% biodegradation (Bouwer, 1984)
		Methanogenic	No biodegradation observed (Bouwer, 1984)
Blue-green algae (cyanobacteria)	Oil wastes	Aerobic	Biodegradation of automobile oil wastes, crankcase oil, etc. (Cameron, 1963)

partitioning is favored when moisture content is higher (Chiu and Shoup, 1985).

Biological factors affecting VOC retention in soil systems can be divided into microbiological and macrobiological factors. On the microbiological level, the indigenous microbial populations present in soil systems can alter VOC concentrations. Although plants and animals metabolize a diversity of chemicals, the activities of the higher organisms are often minor compared to the transformations affected by heterotrophic bacteria and fungi residing in the same habitat. The interactions between environmental factors, such as dissolved oxygen, oxidation-reduction potential (Eh), temperature, pH, availability of other compounds, salinity, particulate matter, and competing organisms, often control biodegradation. The physical and chemical characteristics of the VOC, such as solubility, volatility, hydrophobicity, and  $K_{ow}$ , also influence the ability of the compound to biodegrade. Table 4 illustrates some examples of the microbiological alterations of some commonly encountered soil VOCs. In general, the halogenated alkanes and alkenes are metabolized by soil microbes under anaerobic conditions (Kobayashi and Rittman, 1982; Bouwer, 1984), whereas the halogenated aromatics are metabolized under aerobic conditions. To avoid biodegradation and oxidation of VOCs in soils, scientists at the U.S. EPA Robert S. Kerr Environmental Research Laboratory in Ada, OK, extrude the sample in a glove box.

On a macro scale, biological factors can influence the migration of VOCs in the saturated, vadose, and surface zones (Table 5). Biofilms may accumulate in the saturated zone and may biodegrade and bioaccumulate VOCs from the ground water. The biofilm, depending on its thickness, may impede ground-water flow. Plant roots have a complex microflora associated with

**TABLE 5. MACROBIOLOGICAL FACTORS AFFECTING VOCs IN SOIL SYSTEMS**

Factor	Zone	Effects
Biofilms	Saturated	Biodegradation, bioaccumulation, formation of metabolites that are more or less toxic than parent compound, thick biofilm may retard saturated flow
Plant roots	Capillary fringe to vadose	Mycorrhizal fungi may biodegrade or bioaccumulate VOC, root channels may serve as conduits for VOC migration
Animal burrows holes	Vadose	May act as entry point for and downward migration of surface spills and serve as conduit for upward VOC migration
Vegetative cover	Soil surface	Serve as barrier to volatilization from soil surface and retard infiltration of surface spills

them known as mycorrhizae. The mycorrhizae may enhance VOC retention in the soil by biodegradation or bioaccumulation. The root channels may act as conduits for increasing the migration of VOCs through the soil. Similarly, animal burrows and holes may serve as paths of least resistance for the movement of VOCs through soil. These holes may range from capillary-size openings, created by worms and nematodes, to large-diameter tunnels excavated by burrowing animals. These openings may increase the depth to which surface spills penetrate the soil. A surface covering consisting of assorted vegetation is a significant barrier to volatilization of VOCs into the atmosphere. Some ground-water and vadose-zone models (e.g., RUSTIC) include subroutines to account for a vegetative cover (Dean et al., 1989).

## SOIL SAMPLING AND ANALYSIS DESIGN

Prior to any sampling effort, the RPM or OSC must establish the intended purpose of the remedial investigation/feasibility study (RI/FS). The goals of collecting samples for VOA may include source identification, spill delineation, fate and transport, risk assessment, enforcement, remediation, or post-remediation confirmation. The intended purpose of the sampling effort drives the selection of the appropriate sampling approach and the devices to be used in the investigation.

The phase partitioning of the VOC can also influence which sampling device should be employed. Computer models generally are used only at the final stages of a RI/FS. However, modeling techniques can be used throughout the RI/FS process to assist in sampling device selection by estimating the phase partitioning of VOCs. The RPM is the primary data user for a RI/FS led by a federal agency. As such, the RPM must select the sampling methodology to be employed at the site. Figure 2 illustrates the sequence of events used to plan a VOC sampling and analysis activity.

The domains of interest also must be determined. The target domains may include surface (two dimensions) or subsurface (three dimensions) environments, hot spots, a concentration greater or less than an action limit, or the area above a leaking underground storage tank. Statistics that may be generated from the target domain data must be considered before a sample and analysis design is developed. Possible statistics of interest may include average analyte concentration and the variance about the mean (statistics that compare whether the observed level is significantly above or below an action level) as well as temporal and spatial trends. Data must be of sufficiently high quality to meet the goals of the sampling activity. The level of data quality is defined by the data quality objectives (DQOs). In RI/FS activities, sites are so different and information on overall measurement error (sampling plus analytical error) is so limited that it is not practical to set universal or generic precision, accuracy, representativeness, completeness, and comparability (PARCC) goals. The reader is referred to a user's guide on quality assurance in soil sampling (Barth et al., 1989) and a guidance document for the development of data quality objectives for remedial response activities (U.S. EPA, 1987).

DQOs are qualitative and quantitative statements of the level of uncertainty a decision maker is willing to accept in making decisions on the basis of environmental data. It is important to realize that if the error associated with the sample collection or



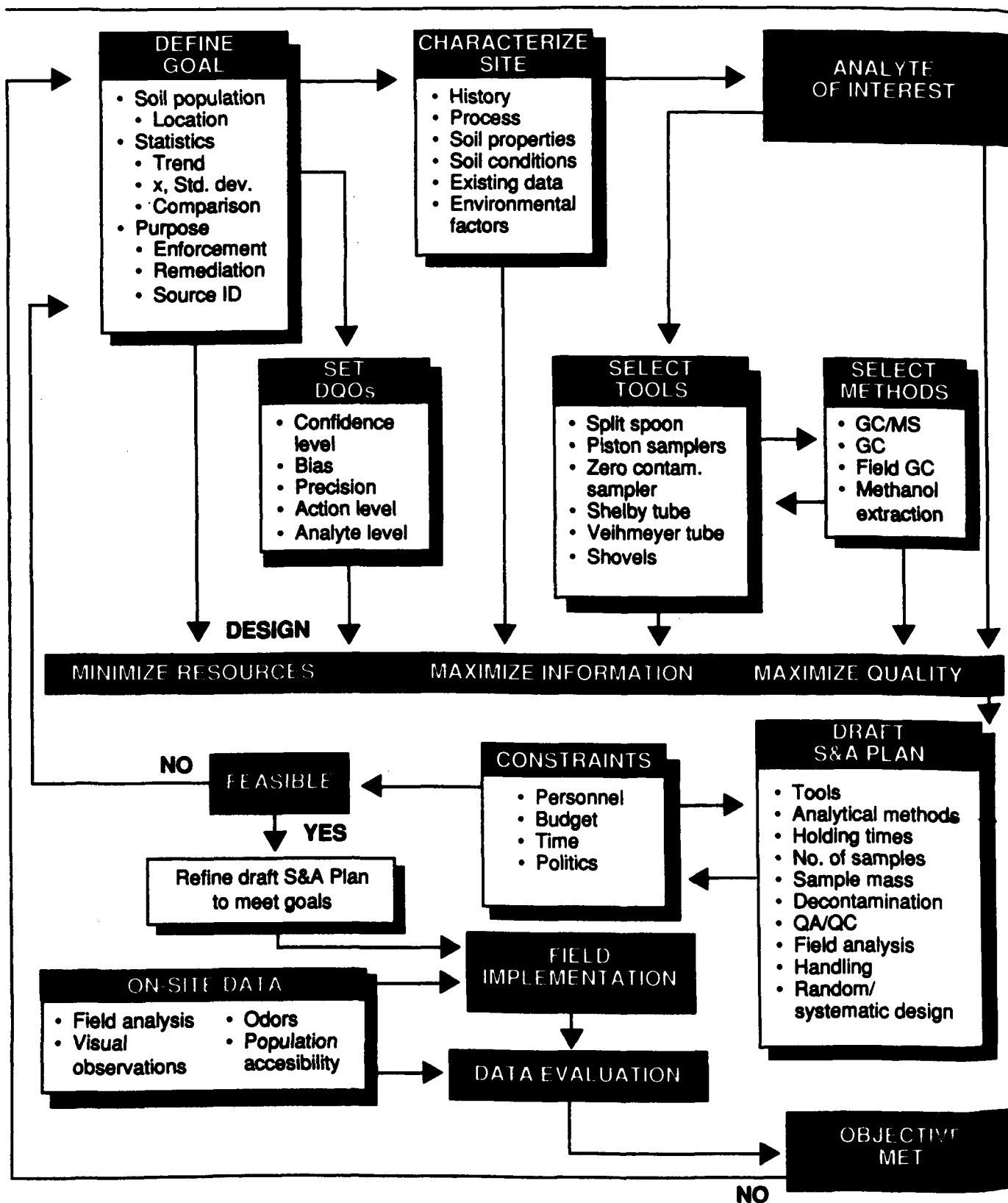


Figure 2. Flowchart for planning and implementation of a soil sampling and analysis activity.

preparation step is large, then the best laboratory quality assurance program will be inadequate (van Ee et al., 1990). The greatest emphasis should be placed on the phase that contributes the largest component of error. For the analysis of soils for VOCs, the greatest sources of error are the sample collection and handling phases.

The minimum confidence level (CL) required to make a decision from the data is defined by the DQOs. The minimum CL depends on the precision and accuracy in sampling and analysis and on the relative analyte concentration. Relative error may be reduced by increasing either the number or the mass of the samples to be analyzed. For instance, although 5-g aliquots collected in the field might exhibit unacceptable errors, 100-g samples will yield smaller errors and might therefore meet study or project requirements. Compositing soil samples in methanol in the field also can reduce variance by attenuating short-range spatial variability.

Field sampling personnel should coordinate with laboratory analysts to ensure that samples of a size appropriate to the analytical method are collected. For example, if the laboratory procedure for preparing aliquots calls for removing a 5-g aliquot from a 125-mL wide-mouth jar, as per SW-846, Method 8240 (U.S. EPA 1986b), then collecting a larger sample in the field will not reduce total measurement error, because additional errors will be contributed from opening the container in the laboratory and from subsequent homogenization. Aliquoting of a 5-g sample in the field into a 40-mL VOA vial that can be directly attached to the laboratory purge-and-trap unit significantly reduces loss of VOCs from the sample (U.S. EPA, 1991a). Significant losses of VOCs were observed when samples were homogenized as per Method 8240 specifications. Smaller losses were observed for smaller aliquots (1 to 5 g) placed in 40-mL VOA vials that had modified caps that allowed direct attachment to the purge-and-trap device. The procedure of collecting an aliquot in the field eliminates the need for sample preparation and eliminates subsequent VOC loss in the laboratory.

Field-screening procedures are gaining recognition as an effective means of locating sampling locations and obtaining real-time data. The benefits of soil field-screening procedures are: (1) near real-time data to guide sampling activities, (2) concentration of Contract Laboratory Program (CLP) sample collection in critical areas, (3) reduced need for a second visit to the site, and (4) reduced analytical load on the laboratory. Limitations of field-screening procedures are: (1) a priori knowledge of VOCs present at the site is needed to accurately identify the compounds, (2) methodologies and instruments are in their infancy and procedures for their use are not well documented and (3) a more stringent level of quality assurance and quality control (QA/QC) must be employed to ensure accurate and precise measurements. The potential benefits and limitations associated with soil-screening procedures must be carefully weighed and compared to the DQOs.

Certain sampling and analytical methods have inherent limitations on the type of QA/QC that is applicable. For example, splitting soil samples in the field would not be appropriate for VOA due to excessive analyte loss. The higher the minimum CL needed to make a decision, the more rigorous the QA/QC protocols must be. As VOC concentrations in the soil sample approach the action or detection limit, the quantity and fre-

quency of QA/QC samples must be increased, or the number of samples must be increased, to ensure that the data quality obtained is appropriate to satisfy project objectives.

One critical element in VOC analysis is the appropriate use of trip blanks. If a sample consists of a silty clay loam, a trip blank of washed sand may not be realistic, for such a blank would not retain VOC cross contaminants in the same way as the sample. The trip blank soil matrix should have a sorptive capacity similar to the actual sample. In addition, high-concentration and low-concentration samples should be shipped in separate coolers.

## DEVICE SELECTION CRITERIA

The selection of a sampling device and sampling procedures requires the consideration of many factors including the number of samples to be collected, available funds, soil characteristics, site limitations, ability to sample the target domain, whether or not screening procedures are to be used, the size of sample needed, and the required precision and accuracy as given in the DQOs. The number of samples to be collected can greatly affect sampling costs and the time required to complete a site characterization. If many subsurface samples are needed, it may be possible to use soil-gas sampling coupled with on-site analysis as an integrated screening technique to reduce the area of interest and thus the number of samples needed. Such a sampling approach may be applicable for cases of near-surface contamination.

Ultimately, the sampling, sample handling, containerizing, and transport of the soil sample should minimize losses of volatiles and should avoid contamination of the sample. Soil sampling equipment should be readily decontaminated in the field if it is to be reused on the job site. Decontamination of sampling equipment may require the use of decontamination pads that have impervious liners, wash and rinse troughs, and careful handling of large equipment. Whenever possible, a liner should be used inside the sampling device to reduce potential cross contamination and carryover. Decontamination procedures take time, require extra equipment, and ultimately increase site characterization costs. Ease and cost of decontamination are thus important factors to be considered in device selection.

Several soil-screening procedures are in use that include headspace analysis of soils using organic vapor analyzers: water (or NaCl-saturated water) extraction of soil, followed by static headspace analysis using an organic vapor analyzer (OVA) or gas chromatograph (GC); colorimetric test kits; methanol extraction followed by headspace analysis or direct injection into a GC; and soil-gas sampling (U.S. EPA, 1988). Field measurements may not provide absolute values but often may be a superior means of obtaining relative values. These procedures are gaining acceptance.

## Site Characteristics

The remoteness of a site and the physical setting may restrict access and, therefore, affect equipment selection. Such factors as vegetation, steep slopes, rugged or rocky terrain, overhead power lines or other overhead restrictions, and lack of roads can contribute to access problems.

The presence of underground utilities, pipes, electrical lines, tanks and leach fields can also affect selection of sampling

equipment. If the location or absence of these hazards cannot be established, it is desirable to conduct a nonintrusive survey of the area and select a sampling approach that minimizes hazards. For example, hand tools and a backhoe are more practical under such circumstances than a large, hollow-stem auger. The selection of a sampling device may be influenced by other contaminants of interest such as pesticides, metals, semivolatile organic compounds, radionuclides, and explosives. Where the site history indicates that the matrix is other than soil, special consideration should be given to device selection. Concrete, reinforcement bars, scrap metal, and lumber will affect sampling device selection. Under some circumstances, it may not be practical to collect deep soil samples. The presence of ordnance, drums, concrete, voids, pyrophoric materials, and high-hazard radioactive materials may preclude some sampling and may require development of alternate sampling designs, or even reconsideration of project objectives.

### Soil Characteristics

The characteristics of the soil material being sampled have a marked effect upon the selection of a sampling device. An investigator must evaluate soil characteristics, the type of VOC, and the depth at which a sample is to be collected before selection of a proper sampling device. Specific characteristics that must be considered are:

1. Is the soil compacted, rocky, or rubble filled? If the answer is yes, then either hollow stem augers or pit sampling must be used.
2. Is the soil fine grained? If yes, use split spoons, Shelby tubes, liners, or hollow stem augers.

3. Are there flowing sands or water saturated soils? If yes, use samplers such as piston samplers that can retain these materials.

### SOIL-GAS MEASUREMENTS

Soil-gas measurements can serve a variety of screening purposes in soil sampling and analysis programs, from initial site reconnaissance to remedial monitoring efforts. Soil-gas measurements should be used for screening purposes only, and not for definitive determination of soil-bound VOCs. Field analysis is usually by hand-held detectors, portable GC or GC/MS, infrared detectors, ion mobility spectrometers (IMS), industrial hygiene detector tubes, and, recently, fiber optic sensors.

At some sites, soil-gas sampling may be the only means of acquiring data on the presence or absence of VOCs in the soil. For example, when the size and density of rocks and cobbles at a site prevent insertion and withdrawal of the coring device and prevent sampling with shovels and trowels, unacceptable losses of VOCs would occur. Soil-gas measurements, which can be made on site or with collected soil samples, can be used to identify volatile contaminants and to determine relative magnitudes of concentration. Smith et al. (1990) have shown a disparity in soil-gas VOC concentrations and the concentration of VOCs found on the solid phase.

Soil-gas measurements have several applications. These include in situ soil-gas surveying, measurement of headspace concentrations above containerized soil samples, and scanning of soil contained in cores collected from different depths. These applications are summarized in Table 6. Currently, no

TABLE 6. APPLICATIONS OF SOIL-GAS MEASUREMENT TECHNIQUES IN SOIL SAMPLING FOR VOCs

Application	Uses	Methods	Benefits/limitations
Soil vapor surveying	Identify sources and extent of contamination. Distinguish between soil and ground water contamination. Detect VOCs under asphalt, concrete, etc.	Active sampling from soil probes into canisters, glass bulbs, gas sampling bags. Passive sampling onto buried adsorptive substrates. Followed by GC or other analysis.	BENEFITS: Rapid, inexpensive screening of large areas, avoid sampling uncontaminated areas. LIMITATIONS: False positives and negatives, miss detecting localized surface spills, disequilibrium between adsorbed and vapor phase VOC concentrations.
Soil headspace measurements	Screen large numbers of soil samples.	Measure headspace above containerized soil sample. Containers range from plastic sandwich bags to VOA vials. Use GC, vapor detectors, IMS, etc.	BENEFITS: More representative of adsorbed solid phase concentration. LIMITATIONS: Losses of vapor phase component during sampling and sample transfer.
Screening soil cores	Soil cores scanned to locate depth where highest VOC levels are located.	Collect core sample (e.g., unlined split spoon) and scan for vapors near core surface using portable vapor monitor.	BENEFITS: Locate and collect soil from hot spot in core for worst case. LIMITATIONS: False negatives and positives, environmental conditions can influence readings (e.g., wind speed and direction, temperature, humidity).

standard protocols exist for soil-gas analysis; many investigators have devised their own techniques, which have varying degrees of efficacy. Independently, the American Society for Testing and Materials (ASTM) and EPA EMSL-LV are preparing guidance documents for soil-gas measurement. These documents should be available late in 1991.

The required precision and accuracy of site characterization, as defined in the DQOs, affect the selection of a sampling device. Where maximum precision and accuracy are required, sampling devices that collect an intact core should be used, particularly for more volatile VOCs in nonretentive matrices. Augers and other devices that collect highly disturbed samples and expose the samples to the atmosphere can be used if lower precision and accuracy can be tolerated. Collection of a larger number of samples to characterize a given area, however, can compen-

sate for a less precise sampling approach. The closer the expected contaminant level is to the action or detection limit, the more efficient the sampling device should be for obtaining an accurate measurement.

## SOIL SAMPLING DEVICES

Table 7 lists selection criteria for different types of commercially available soil sampling devices based on soil type, moisture status, and power requirements. The sampling device needed to achieve a certain sampling and analysis goal can be located in Table 7 and the supplier of such a device can be identified in Table 8. Table 8 is a partial list of commercially available soil sampling devices that are currently in use for sampling soils for VOC analysis. The list is by no means exhaustive and inclusion

(Continued on page 14)

TABLE 7. CRITERIA FOR SELECTING SOIL SAMPLING EQUIPMENT†

Type of Sampler	Obtains Core Samples	Most Suitable Soil types	Operation in Stony Soils	Suitable Soil Moisture Conditions	Relative Sample Size	Labor Requirements (# of Persons)	Manual or Power Operation
<b>A. Mechanical Sample Recovery</b>							
1. Hand-held Power augers	No	Coh/coh'less	Unfavorable	Intermediate	Large	2+	Power
2. Solid stem flight augers	No	Coh/coh'less	Favorable	Wet to dry	Large	2+	Power
3. Hollow-stem augers	Yes	Coh/coh'less	Fav/unfav	Wet to dry	Large	2+	Power
4. Bucket augers	No	Coh/coh'less	Favorable	Wet to dry	Large	2+	Power
5. Backhoes	No	Coh/coh'less	Favorable	Wet to dry	Large	2+	Power
<b>B. Samplers</b>							
1. Screw-type augers	No	Coh	Unfavorable	Intermediate	Small	Single	Manual
2. Barrel augers							
a. Post-hole augers	No	Coh	Unfavorable	Wet	Large	Single	Manual
b. Dutch augers	No	Coh	Unfavorable	Wet	Large	Single	Manual
c. Regular barrel augers	No	Coh	Unfavorable	Intermediate	Large	Single	Manual
d. Sand augers	No	Coh'less	Unfavorable	Intermediate	Large	Single	Manual
e. Mud augers	No	Coh	Unfavorable	Wet	Large	Single	Manual
3. Tube-type samplers							
a. Soil samplers	Yes	Coh	Unfavorable	Wet to dry	Small	Single	Manual
b. Veihmeyer tubes	Yes	Coh	Unfavorable	Intermediate	Large	Single	Manual
c. Shelby tubes	Yes	Coh	Unfavorable	Intermediate	Large	2+*	Both
d. Ring-lined samplers	Yes	Coh'less	Favorable	Wet to intermediate	Large	2+*	Both
e. Continuous samplers	Yes	Coh	Unfavorable	Wet to dry	Large	2+	Power
f. Piston samplers	Yes	Coh	Unfavorable	Wet	Large	2+*	Both
g. Zero-contamination samplers	Yes	Coh	Unfavorable	Wet to intermediate	Small	2+*	Both
h. Split spoon samplers	Yes	Coh	Unfavorable	Intermediate	Large	2+*	Both
4. Bulk samplers	No	Coh	Favorable	Wet to dry	Large	Single	Manual

† Adapted from U.S. EPA, 1986a.

\* All hand-operated versions of samplers, except for continuous samplers, can be worked by one person.

Coh = cohesive.

**TABLE 8. EXAMPLES OF COMMERCIALY AVAILABLE SOIL SAMPLING DEVICES**

Manufacturers	Sampling Device	Specifications		Features
		Length (Inches) I.D. (Inches)	Sampler Material Liners	
Associated Design & Manufacturing Co. 814 North Henry Street Alexandria, VA 22314 703-549-5999	Purge and Trap Soil Sampler	3 0.5 Stainless steel		Will rapidly sample soils for screening by "Low Level" Purge and Trap methods.
	Heavy Duty "Lynac" Split Tube Sampler	18 & 24 1-1/2 to 4-1/2 Steel	Brass, stainless	Split tube allows for easy sample removal.
Acker Drill Co. P.O. Box 830 Scranton, PA 717-586-2061	Dennison Core Barrel	24 & 60 1-7/8 to 6-5/16	Brass	Will remove undisturbed sample from cohesive soils.
	Core Soil Sampler	2 to 12 1-1/2 to 3 Alloy, stainless	Stainless, plastic aluminum, bronze teflon	Good in all types of soils.
AMS Harrison at Oregon Trail American Falls, ID 83211	Dual Purpose Soil Recovery Probe	12, 18 & 24 3/4 and 1 4130 Alloy, stainless	Butyrate, Teflon stainless	Adapts to AMS "up & down" hammer attachment. Use with or without liners.
	Soil Recovery Auger	8 to 12 2 & 3 Stainless	Plastic, stainless Teflon, aluminum	Adaptable to AMS extension and cross-handles.
Concord, Inc. 2800 7th Ave. N. Fargo, ND 58102 701-280-1260	Speedy Soil Sampler	48 & 72 3/16 to 3-1/2 Stainless	Acetate	Automated system allows retrieval of 24 in soil sample in 12 sec.
	Zero Contamination Unit Hand-Held Sampler			
CME Central Mine Equip. Co. 6200 North Broadway St. Louis, MO 63147 800-325-8827	Continuous Sampler	60 2-1/2 to 5-3/8 Steel, stainless	Butyrate	May not be suitable in stony soils. Adapts to CMS auger.
	Bearing Head Continuous Sample Tube System	60 2-1/2 Steel, stainless	Butyrate	Versatile system. Adapts to all brands of augers.
Diedrich Drilling Equip. P.O. Box 1670 Laporte, IN 46350 800-348-8809	Heavy Duty Split Tube Sampler	18 & 24 2, 2-1/2, 3 Steel	Brass, plastic stainless, Teflon	Full line of accessories are available.
	Continuous Sampler	60 3, 3-1/2	Brass, plastic stainless, Teflon	Switch-out device easily done.

*(Continued)*

TABLE 8. (CONTINUED)

Manufactures	Sampling Device	Specifications		Features
		Length (Inches) I.D. (Inches)	Sampler Material	
Geoprobe Systems 607 Barney St. Salina, KS 913-825-1842	Probe Drive Soil Sampler	11-1/4 0.96 Alloy steel		Remains completely sealed while pushed to depth in soil.
Giddings Machine Co. P.O. Drawer 2024 Fort Collins, CO 80522 303-485-5586	Coring Tubes	48 & 60 7/8 to 2-3/8 4130 Molychrome	Butyrate	A series of optional 5/8 in slots permit observation of the sample.
JMC Clements and Associates R.R. 1 Box 186 Newton, IA 50208 800-247-6630	Environmentalists' Sub-soil Probe	36 & 48 0.9 Nickel plated	PETG plastic, stainless	Adapts to drop-hammer to penetrate the hardest of soils.
	Zero Contamination Tubes	12, 18 & 24 0.9 Nickel plated	PETG plastic, stainless	Adapts to power probe.
Mobile Drilling Co. 3807 Madison Ave. Indianapolis, IN 46227 800-428-4475	"Lynac" Split Barrel Sampler	18 & 24 1-1/2	Brass, plastic	Adapts to Mobile wireline sampling system.
Solitest, Inc. 66 Albrecht Drive Lake Bluff, IL 800-323-1242	Zero Contamination Sampler	12, 18 & 24 0.9 Chrome plated	Stainless, acetate	Hand sampler good for chemical residue studies.
	Thin Wall Tube Sampler (Shelby)	30 2-1/2, 3, 3-1/2 Steel		Will take undisturbed samples in cohesive soils and clays.
	Split Tube Sampler	24 1-1/2 to 3 Steel	Brass	Forced into soil by jacking, hydraulic pressure or driving. Very popular type of sampler.
	Veihmeyer Soil Sampling Tube	48 & 72 3/4 Steel		Adapts to drop hammer for sampling in all sorts of soils.
Sprague & Henwood, Inc. Scranton, PA 18501 800-344-8506	S & H Split Barrel Sampler	18 & 24 2 to 3-1/2	Brass, plastic	A general all-purpose sampling device designed for driving into material to be sampled.

Note: This list is not exhaustive. Inclusion in this list should not be construed as endorsement for use.

in the list should not be construed as an endorsement for their use.

Commonly, soil samples are obtained from the near surface using shovels, scoops, trowels, and spatulas. These devices can be used to extract soil samples from trenches and pits excavated by back hoes. A precleaned shovel or scoop can be used to expose fresh soil from the face of the test pit. A thin-walled tube or small-diameter, hand-held corer can be used to collect soil from the exposed face. Bulk samplers such as shovels and trowels cause considerable disturbance of the soil and expose the sample to the atmosphere, enhancing loss of VOCs. Siegrist and Jenssen (1990) have shown that sampling procedures that cause the least amount of disturbance provide the greatest VOC recoveries. Therefore, sampling devices that obtain undisturbed soil samples using either hand-held or mechanical devices are recommended. Sampling devices that collect undisturbed samples include split-spoon samplers, ring samplers, continuous samplers, zero-contamination samplers, and Shelby tubes. These sampling devices can be used to collect surface soil samples or they can be used in conjunction with hollow-stem augers to collect subsurface samples. The soil sampling devices discussed above are summarized in Table 9. Devices where the soil samples can be easily and quickly removed and containerized with the least amount of disturbance and exposure to the atmosphere are highly recommended. U.S. EPA (1986a) gives a more detailed discussion on the proper use of drill rigs and sampling devices.

Liners are available for many of the devices listed in Table 9. Liners make soil removal from the coring device much easier and quicker. Liners reduce cross contamination between samples and the need for decontamination of the sampling device. The liner can run the entire length of the core or can be precut into sections of desired length.

When sampling for VOCs, it is critical to avoid interactions between the sample and the liner and between the sample and the sampler. Such interactions may include either adsorption of VOCs from the sample or release of VOCs to the sample. Gillman and O'Hannesin (1990) studied the sorption of six monoaromatic hydrocarbons in ground water samples by seven materials. The hydrocarbons included benzene, toluene, ethylbenzene, and o-, m-, and p-xylene. The materials examined were stainless steel, rigid PVC, flexible PVC, PTFE Teflon, polyvinylidene fluoride, fiberglass, and polyethylene. Stainless

steel showed no significant sorption during an 8-week period. All polymer materials sorbed all compounds to some extent. The order of sorption was as follows: rigid PVC < fiberglass < polyvinylidene fluoride < PTFE < polyethylene < flexible PVC. Stainless steel or brass liners should be used since they exhibit the least adsorption of VOCs. Other materials such as PVC or acetate may be used, provided that contact time between the soil and the liner material is kept to a minimum. Stainless steel and brass liners have been sealed with plastic caps or paraffin before shipment to the laboratory for sectioning and analysis. VOC loss can result from permeation through the plastic or paraffin and volatilization through leaks in the seal. Acetate liners are available, but samples should not be held in these liners for any extended period, due to adsorption onto and permeation through the material. Alternatively, the soil can be extruded from the liner, and a portion can be placed into a wide-mouth glass jar. Smaller aliquots can be taken from the center of the precut liner using subcoring devices and the soil plug extruded into VOA vials.

## TRANSFER OF SOIL SAMPLES FROM DEVICE TO CONTAINER

The sample transfer step is perhaps the most critical and least understood step in the sampling and analysis procedure. The key point in sample transfer, whether in the field or in the laboratory, is to minimize disturbance and the amount of time the sample is exposed to the atmosphere. It is more important to transfer the sample rapidly to the container than to accurately weigh the aliquot which is transferred, or to spend considerable time reducing headspace. Therefore, a combination of a device for obtaining the appropriate mass of sample and placement of the aliquot into a container that can be directly connected to the analytical device in the laboratory is recommended. Several designs are available for obtaining a 5-g aliquot (or other size). Most subcoring devices consist of a plunger/barrel design with an open end. The device shown in Figure 3 was constructed by Associated Design & Manufacturing Company (Alexandria, VA). Other designs include syringes with the tips removed, and cork borers (Table 8). The device is inserted into the sample and an aliquot is withdrawn. The aliquot, which is of a known volume and approximate weight, can then be extruded into a tared 40-mL VOA vial. Routinely, the vial is then sealed with a Teflon-lined septum cap. Teflon, however, may be permeable to VOCs. Aluminum-lined caps are available to reduce losses due to permeation. At the laboratory, the vial must be opened and the contents of the vial must be transferred to a sparger tube. The transfer procedure will result in significant losses of VOCs from the headspace in the vial. The modified purge-and-trap cap shown in Figure 4 eliminates the loss of VOCs due to container opening and sample transfer. The soil is extruded from the subcorer into a tared 40-mL VOA vial and the modified cap is attached in the field. In the laboratory, the vial is attached directly to a purge-and-trap device without ever being opened to the ambient air.

Use of subcoring devices should produce analytical results of increased accuracy. In order to test this hypothesis, an experiment was conducted in which a bulk soil sample was spiked with 800 µg/kg of different VOCs (Maskarinec, 1990). Three aliquots were withdrawn by scooping, and three aliquots were withdrawn by using the sub-corer approach. The results are presented in Table 10. Although neither method produced quantitative recovery, the subcorer approach produced results that were generally

TABLE 9. SOIL SAMPLERS FOR VOC ANALYSIS

Recommended	Not Recommended
Split spoon w/liners	Solid flight liners
Shelby tube (thin wall tubes)	Drilling mud auger
Hollow-stem augers	Air drilling auger
Veihmeyer or King tubes	Cable tool
w/liners	Hand augers
Piston samplers*	Barrel augers
Zero contamination samplers*	Scoop samplers
Probe-drive samplers	Excavating tools, e.g., shovels, backhoes

\* May sustain VOC losses if not used with care

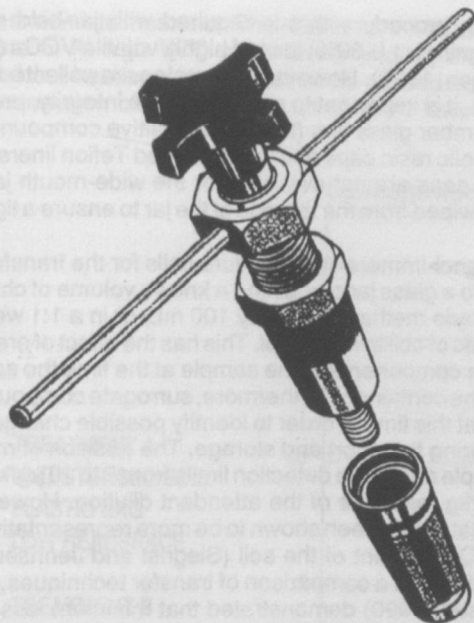


Figure 3. Small-diameter hand-held subcoring device made by Associated Design & Manufacturing Company (Alexandria, VA).

TABLE 10. LABORATORY COMPARISON OF STANDARD METHOD AND SUBCORER METHOD

Compound	Standard Method <sup>a</sup>	Subcorer Method <sup>b</sup>	Standard Method % of Recovery of Spike	Subcorer % of Recovery of Spike
Chloromethane	50	1225	6	153
Bromomethane	31	536	4	67
Chloroethane	78	946	10	118
1,1-Dichloroethene	82	655	10	82
1,1-Dichloroethane	171	739	21	92
Chloroform	158	534	20	67
Carbon tetrachloride	125	658	16	82
1,2-Dichloropropane	147	766	18	96
Trichloroethene	120	512	15	64
Benzene	170	636	21	80
1,1,2-Trichloroethane	78	477	10	60
Bromoform	30	170	4	21
1,1,2,2-Trichloroethane	46	271	6	34
Toluene	129	656	16	82
Chlorobenzene	57	298	7	37
Ethylbenzene	68	332	8	42
Styrene	30	191	4	24

<sup>a</sup> µg/kg (n=3)

<sup>b</sup> µg/kg (n=3)

Note: Standard method of sample transfer consists of scooping and subcorer method uses device shown in Figure 3. Soil samples were spiked with 800 µg/kg of each VOC.

five times higher than the standard approach, whereby the contents of a 125-mL wide-mouth jar are poured into an aluminum tray and homogenized with a stainless steel spatula. A 5-g sample is then placed in the sparger tube (SW-846, Method 8240). Several compounds presented problems with both approaches: styrene polymerizes, bromoform purges poorly, and 1,1,2,2-tetrachloroethane degrades quickly.

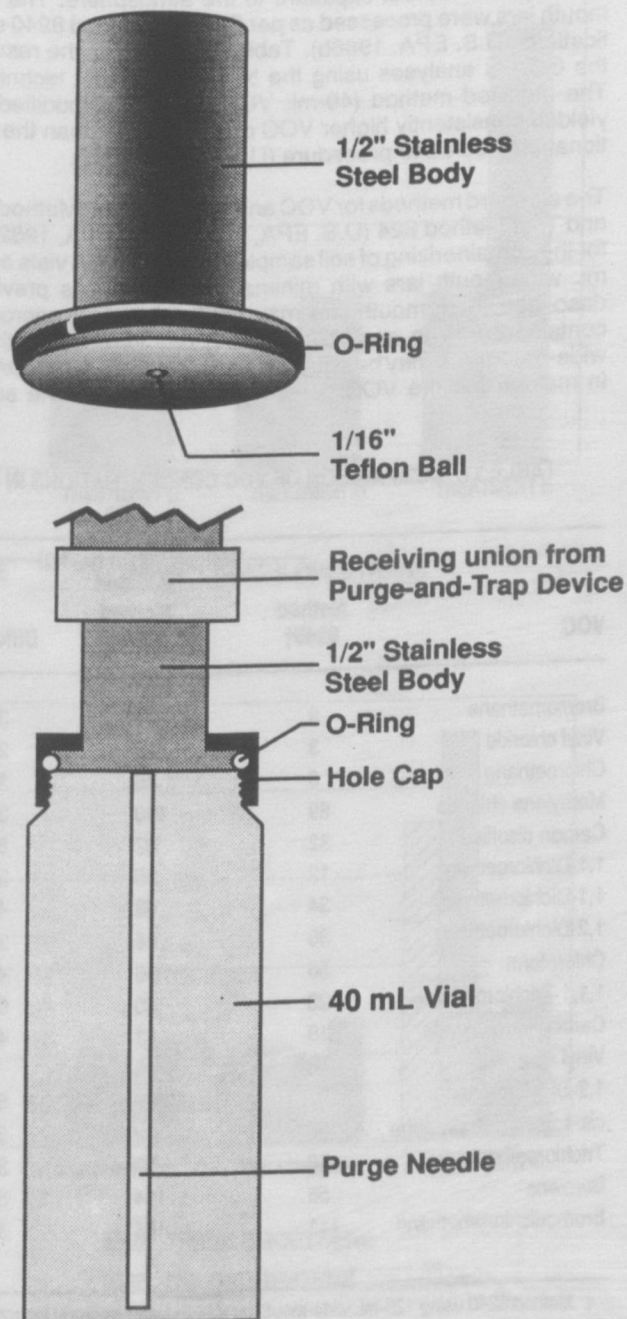


Figure 4. Modified purge-and-trap 40-mL VOA vial cap for containerizing samples in the field. Vial is attached directly to a purge-and-trap system without exposure of sample to the atmosphere.



In another study (U.S. EPA, 1991a), a large quantity of well characterized soil was spiked with 33 VOCs and was homogenized. From the homogenized material, a 5-g aliquot of soil was placed in a 40-mL VOA vial and sealed with a modified purge-and-trap cap (Figure 4). The remaining soil was placed in 125-mL wide-mouth jars. The samples were shipped via air carrier and were analyzed by GC/MS with heated purge and trap. The 40-mL VOA vials were connected directly to a Tekmar purge-and-trap unit without exposure to the atmosphere. The wide-mouth jars were processed as per SW-846 Method 8240 specifications (U.S. EPA, 1986b). Table 11 compares the results of the GC/MS analyses using the two pretreatment techniques. The modified method (40-mL VOA vial with a modified cap) yielded consistently higher VOC concentrations than the traditional Method 8240 procedure (U.S. EPA, 1986b).

The standard methods for VOC analysis, SW-846, Method 8240 and Test Method 624 (U.S. EPA, 1986b; U.S. EPA, 1982), call for the containerizing of soil samples in 40-mL VOA vials or 125-mL wide-mouth jars with minimal headspace. As previously described, wide-mouth jars may not be the most appropriate containers due to sample aliquoting requirements. Although wide-mouth jars may be equally as effective as 40-mL VOA vials in maintaining the VOC content of soil samples, the sample

preparation procedure that is required with jar-held samples causes significant (>80%) loss of highly volatile VOCs (Siegrist and Jennsen, 1990). However, if samples are collected in such containers, it is important to ensure sample integrity, preferably by using amber glass jars (for photosensitive compounds) with solid phenolic resin caps and foam-backed Teflon liners. Aluminum-lined caps are not available for the wide-mouth jars. Soil should be wiped from the threads of the jar to ensure a tight seal.

The methanol-immersion procedure calls for the transfer of the sample into a glass jar containing a known volume of chromatographic-grade methanol (usually 100 mL) or in a 1:1 weight-to-volume ratio of soil to methanol. This has the effect of preserving the volatile components of the sample at the time the sample is placed in the container. Furthermore, surrogate compounds can be added at this time in order to identify possible changes in the sample during transport and storage. The addition of methanol to the sample raises the detection limits from 5 to 10 µg/kg to 100 to 500 µg/kg, because of the attendant dilution. However, the resulting data have been shown to be more representative of the original VOC content of the soil (Siegrist and Jennsen, 1990; Siegrist, 1990). In a comparison of transfer techniques, Siegrist and Jennsen (1990) demonstrated that minimum losses were obtained by using an undisturbed sample followed by immediate

TABLE 11. COMPARISON OF VOC CONCENTRATIONS IN SPIKED SOIL ANALYZED BY METHOD 8240 AND MODIFIED METHOD 8240

VOC	Concentration (µg/kg)			VOC	Concentration (µg/kg)		
	Method 8240†	Modified Method 8240††	Difference		Method 8240†	Modified Method 8240††	Difference
Bromomethane	9	44	35**	Dibromochloromethane	121	159	38
Vinyl chloride	3	32	29**	1,1,2-Trichloroethane	142	193	51
Chloroethane	6	36	30**	trans-1,3-Dichloropropene	154	203	49
Methylene chloride	69	100	31**	Bromoform	116	140	24
Carbon disulfide	32	82	50**	Tetrachloroethene	62	124	62**
1,1-Dichloroethene	12	35	23**	1,1,2,2-Tetrachloroethane	137	162	25
1,1-Dichloroethane	34	83	49**	Toluene	85	161	76*
1,2-Dichloroethene	36	66	30**	Chlorobenzene	91	132	41**
Chloroform	56	96	40**	Ethylbenzene	85	135	50**
1,1,1-Trichloroethane	26	80	54**	Styrene	86	114	28*
Carbon tetrachloride	18	61	43**	Total xylenes	57	85	28**
Vinyl acetate	18	26	8				
1,2-Dichloroethane	101	159	58**	KETONES			
cis-1,3-Dichloropropene	136	189	53*	Acetone	336	497	161*
Trichloroethene	48	87	39**	2-Butanone	290	365	75
Benzene	56	114	58*	2-Hexanone	200	215	15
Bromodichloromethane	111	166	55*	4-Methyl-2-pentanone	264	288	24

† Method 8240 using 125-mL wide-mouth jar mixing subsampling in laboratory purge/trap analysis.

†† Method 8240 using 40-mL vial. 5-g sampled in the field, shipped to laboratory purge/trap analysis.

\*\* Difference significantly greater than 0, with P-value <0.01.

\* Difference significantly greater than 0, with P-value between 0.01 and 0.05.

Note: Spike concentration was 300 µg/kg.

immersion into methanol. The results for six VOCs are shown in Figure 5. At high VOC spike levels (mg/kg) the investigators found that headspace within the bottle caused a decrease in the concentration of VOCs in the sample. At lower spike levels,

however, headspace did not seem to be a major contributor to VOC losses (Maskarinec, 1990). In another study (U.S. EPA, 1991a), it was found that a 5-g sample collected from a soil core and placed in a 40-mL VOA vial provided consistently higher

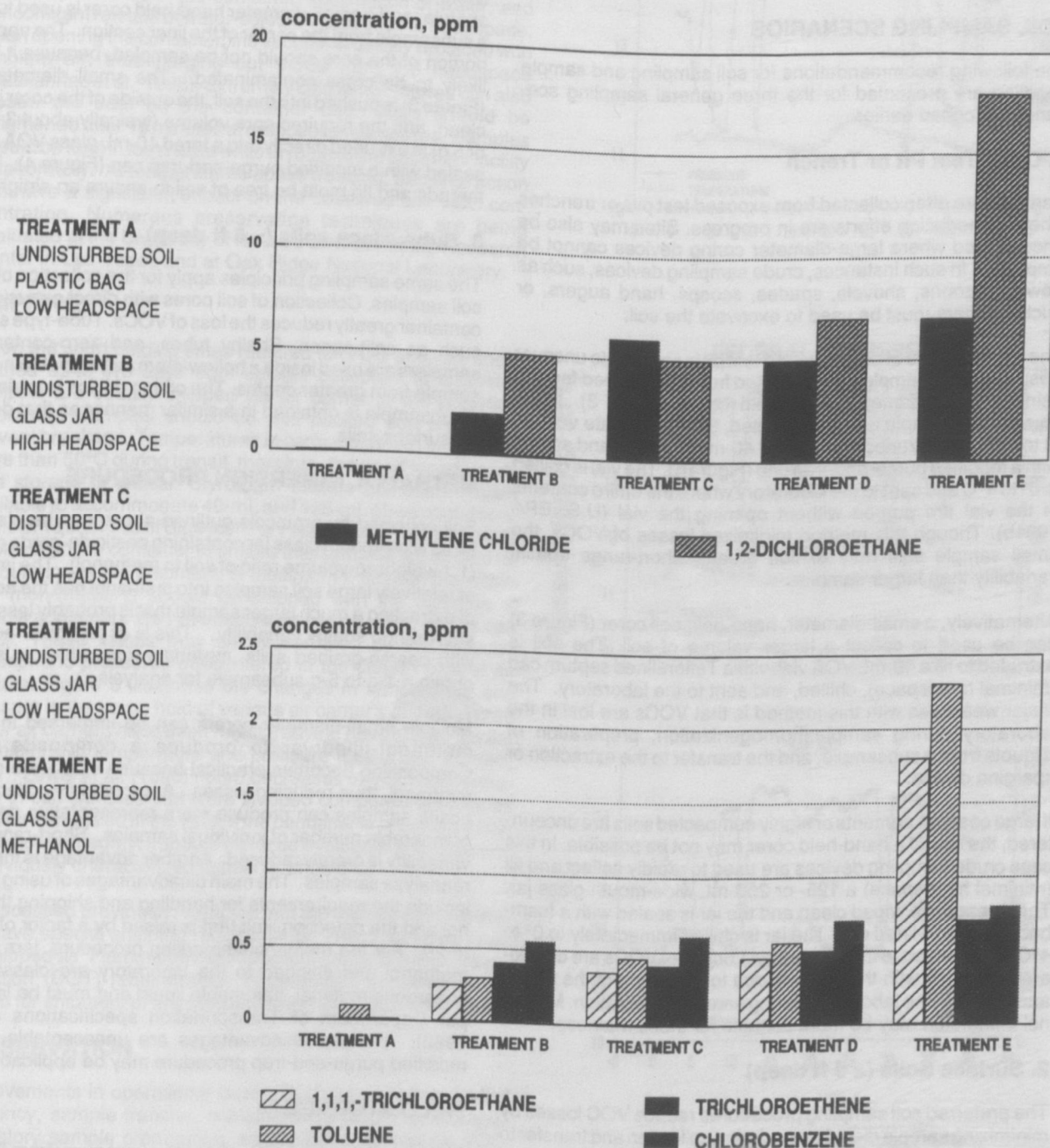


Figure 5. VOC recovery as a function of sample treatment.

VOC levels than a sample taken from the same core, placed in a 125-mL wide-mouth jar, and later poured out, homogenized, and a 5-g aliquot taken from the bulk material as per Method 8240 specifications.

## SOIL SAMPLING SCENARIOS

The following recommendations for soil sampling and sample handling are presented for the three general sampling scenarios described earlier.

### 1. Open Test Pit or Trench

Samples are often collected from exposed test pits or trenches where remediation efforts are in progress. Sites may also be encountered where large-diameter coring devices cannot be employed. In such instances, crude sampling devices, such as trowels, spoons, shovels, spades, scoops, hand augers, or bucket augers must be used to excavate the soil.

The exposed face of an excavated test pit is scraped to uncover fresh material. Samples are collected from the scraped face by using a small-diameter, hand-held corer (Figure 3). If the nominal 5-g sample is to be collected, the appropriate volume (3 to 4 mL) is extruded into a tared 40-mL VOA vial and sealed with a modified purge-and-trap cap (Figure 4). The vial is chilled to 0° to 4°C and sent to the laboratory where the entire contents of the vial are purged without opening the vial (U.S. EPA 1991b). Though this method minimizes losses of VOCs, the small sample size may exhibit greater short-range spatial variability than larger samples.

Alternatively, a small-diameter, hand-held soil corer (Figure 3) can be used to collect a larger volume of soil. The soil is extruded to fill a 40-mL VOA vial with a Teflon-lined septum cap (minimal headspace), chilled, and sent to the laboratory. The major weakness with this method is that VOCs are lost in the laboratory during sample homogenization, preparation of aliquots from a subsample, and the transfer to the extraction or sparging device.

If large coarse fragments or highly compacted soils are encountered, the use of a hand-held corer may not be possible. In this case crude sampling devices are used to rapidly collect and fill (minimal headspace) a 125- or 250-mL wide-mouth glass jar. The threads are wiped clean and the jar is sealed with a foam-backed Teflon-lined cap. The jar is chilled immediately to 0° to 4°C for shipment to the laboratory. Losses of VOCs are considerably greater with this method due to disruption of the matrix and losses in the laboratory during sample preparation. Methanol immersion may be more suitable for these matrices.

### 2. Surface Soils (< 5 ft deep)

The preferred soil sampling procedures reduce VOC losses by minimizing sample disturbance during collection and transfer to a container. The collection of soil cores with direct extrusion into a container accomplishes this goal. A larger-diameter coring device (e.g., split-spoon sampler, Shelby tube, zero-contamination sampler) is used to collect an intact sample from the surface soil or from an augered hole. Many of these samplers can be used with liners, an insert that greatly reduces the time required to remove the soil and obtain a subsample. For

subsamples collected from split spoons or extruded large-diameter cores, the section to be subsampled is scraped and laterally subcored, or the extruded soil is cut or broken to expose fresh material at the depth or zone of interest, then longitudinally subcored. For large-diameter cores that are collected in precut liners, the liner sections are separated with a stainless steel spatula, and a small-diameter hand-held corer is used to collect a subsample from the center of the liner section. The uppermost portion of the core should not be sampled, because it is more likely to be cross contaminated. The small diameter corer (Figure 3) is pushed into the soil, the outside of the corer is wiped clean, and the required core volume (typically about 3 to 4 mL or 5 g) is extruded directly into a tared 40-mL glass VOA vial and sealed with a modified purge-and-trap cap (Figure 4). The vial threads and lip must be free of soil to ensure an airtight seal.

### 3. Subsurface soils (> 5 ft deep)

The same sampling principles apply for the collection of deeper soil samples. Collection of soil cores with direct extrusion into a container greatly reduces the loss of VOCs. Tube-type samplers such as split-spoon, Shelby tubes, and zero-contamination samplers are used inside a hollow-stem auger to obtain an intact sample from greater depths. The coring device is retrieved and a subsample is obtained in a similar manner as that described for surface soils.

## METHANOL IMMERSION PROCEDURE

Soil collected by protocols outlined above can be placed in a tared wide-mouth glass jar containing pesticide-grade methanol (1:1 weight-to-volume ratio of soil to methanol). The immersion of relatively large soil samples into methanol has the advantage of extracting a much larger sample that is probably less prone to short-range spatial variability. This is of particular advantage with coarse-grained soils, materials from which it is hard to obtain a 1-g to 5-g subsample for analysis.

Multiple small-diameter corers can be immersed in a single methanol-filled jar to produce a composite sample. Compositing becomes practical because VOCs are soluble in methanol, thus reducing losses. Appropriately collected composite samples can produce more representative data than a comparable number of individual samples. Short-range spatial variability is greatly reduced. Another advantage is the ability to reanalyze samples. The main disadvantages of using methanol include the requirements for handling and shipping the methanol and the detection limit that is raised by a factor of about 10 to 20. For the methanol-immersion procedure, jars filled with methanol and shipped to the laboratory are classified as a hazardous material, flammable liquid and must be labelled as per Department of Transportation specifications (49 CFR, 1982). If these disadvantages are unacceptable, then the modified purge-and-trap procedure may be applicable.

## FIELD STORAGE

Material containing VOCs should be kept away from the sample and the sample container. Hand lotion, labeling tape, adhesives, and ink from waterproof pens contain VOCs that are often analytes of interest in the sample. Samples and storage containers should be kept away from vehicle and generator exhaust and other sources of VOCs. Any source of VOCs may cause contamination that may compromise the resulting data.

Once samples are removed from the sampling device and placed in the appropriate storage container, the containers should be placed in the dark at reduced temperatures (0° to 4°C). Excessively cold temperatures (<-10°C) should be avoided; studies have shown greater losses of analytes due to reduced pressures in the container, sublimation of water, and concomitant release of water-soluble VOCs into the headspace. Upon opening the container, the vacuum is quickly replaced with ambient air, thus purging out VOCs from the headspace (Maskarinec et al., 1988). Extremely cold temperatures can also loosen the seal on the container cap. Caps should be retightened after 15 minutes at reduced temperatures. Samples should be kept in ice chests while in route to the shipment facility or laboratory. At temperatures above freezing, bacterial action can have a significant impact on the observed soil VOC concentration. Numerous preservation techniques are being evaluated at the University of Nevada Environmental Research Center in Las Vegas and at Oak Ridge National Laboratory.

## SHIPPING

Given the short holding times required for VOC analysis under Method 8240 (10 days from sample collection to analysis), samples are usually shipped via air carrier to the analytical laboratory. Samples should be well packed and padded to prevent breakage. Temperatures in cargo holds can increase to more than 50°C during transit, therefore, the need for adequate cold storage is critical. Styrofoam coolers are commercially available to accommodate 40-mL and 125-mL glass containers. Sufficient quantities of Blue Ice™ or Freeze-Gel™ packs should be placed in the container to ensure that samples are cooled for the duration of the shipment. A maximum-minimum thermometer (non-mercury) should be shipped with the samples. If sample containers are not adequately sealed, VOC losses can occur. These losses may be exacerbated by the reduced atmospheric pressures encountered in the cargo holds of air carriers. Figure 6 illustrates the changes in temperature and pressure in the cargo hold of various air carrier's aircraft. Three major air carriers have been monitored and have shown similar fluctuations in temperature and pressure (Lewis and Parolini, 1991). Lewis et al. (1990) noted decreases in VOC concentrations in soil samples that were shipped compared to samples that were analyzed in the field. If the container is of questionable or unknown integrity, it should either be evaluated prior to use or a previously characterized container should be used.

As discussed previously, samples that are immersed in methanol have special shipping requirements. These samples must be shipped as "Flammable Liquids" under Department of Transportation (DOT) requirements. A secondary container is required for shipment of any item classified as a flammable liquid.

## PRESERVATION

Improvements in operational factors such as sampling device efficiency, sample transfer, containerizing, shipping, storage, laboratory sample preparation, and analysis will reduce VOC losses from soils. Two principal matrix-specific factors that can contribute to the loss of VOC in soils are biodegradation and volatilization. An effective preservation technique should act on these matrix-specific factors to reduce losses of VOCs.

The required preservation technique for soil samples is storage at 0° to 4°C in the dark. This technique retards biodegradation

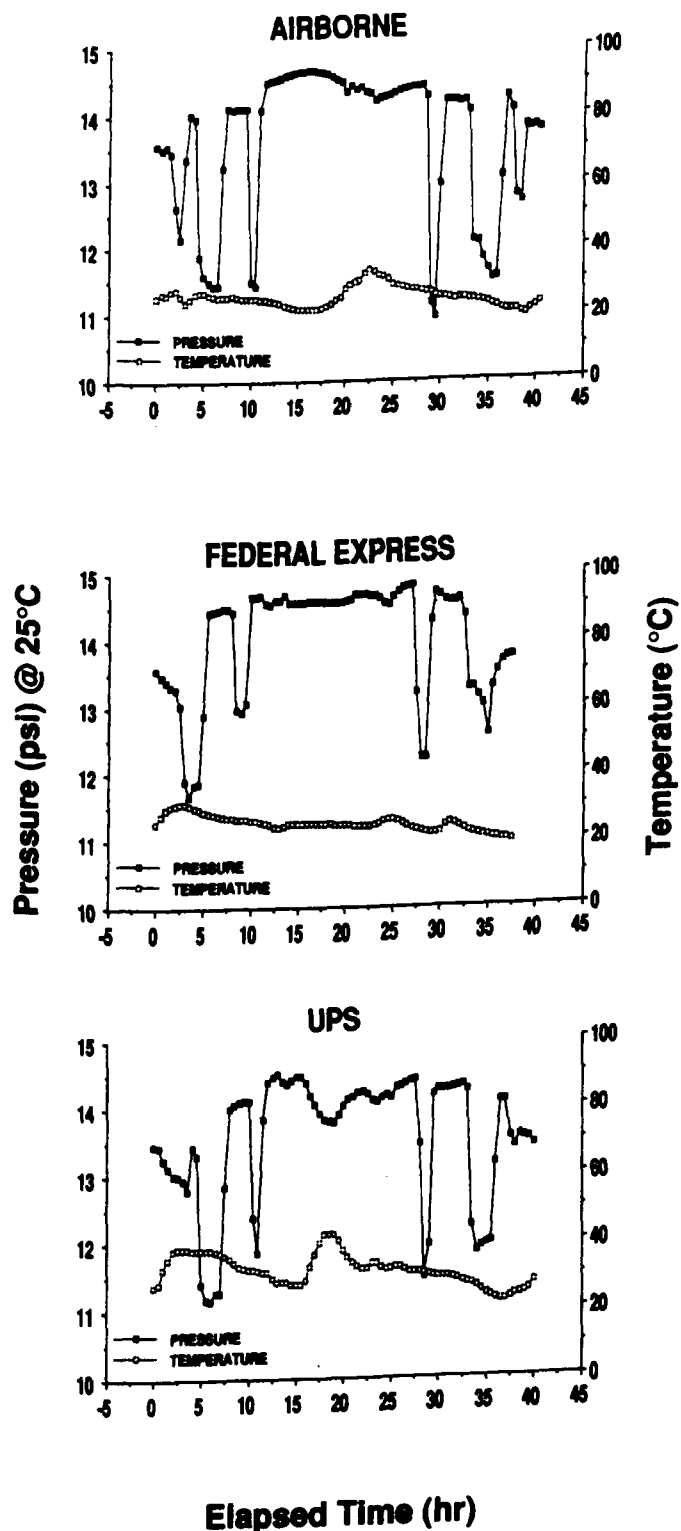


Figure 6. Temperature and pressure fluctuations recorded in the cargo hold of various air carriers. Recording device was shipped from Las Vegas, NV, to Pearl River, NY, and returned.

processes mediated by soil microorganisms. Some microorganisms, however, such as fungi, are biologically active even at 4°C. Wolf et al. (1989) investigated several methods (i.e., chemical and irradiation) for sterilizing soil and concluded that mercuric chloride is one of the most effective preservatives that causes minimal changes to the chemical and physical properties of the soil. Stuart et al. (1990) utilized mercuric chloride as an antimicrobial preservative to stabilize ground-water samples contaminated with gasoline. Other researchers (U.S. EPA 1991a) have used mercuric chloride to retard biodegradation of VOCs in soil samples. The soils were spiked with 150 µg/kg of Target Compound List (TCL) VOCs and were preserved with 2.5 mg of mercuric chloride per 5 g of soil. The results indicated that the amount of mercuric chloride needed to reduce biodegradation was directly related to the soil's organic carbon content. In addition, the levels of mercuric chloride added to samples did not interfere with sample handling or analysis. Currently, research is underway to quantitate the required mercuric chloride concentration as a function of soil organic content.

The loss of VOCs through volatilization is reduced by optimizing sample handling procedures. When samples require laboratory pretreatment, severe losses of VOCs (up to 100%) have been observed. In order to minimize volatilization losses, several preservatives have been examined (U.S. EPA 1991a), including solid adsorbents, anhydrous salts, and water/methanol extraction mixtures. The most efficient preservatives for reducing volatilization of VOCs from soils have been two solid adsorbents, Molecular Sieve - 5A™ (aluminum silicate desiccant) and Florasil™ (magnesium silicate desiccant). The addition of 0.2 mg per 5 g of soil greatly increased the recovery of VOCs from spiked samples. The mechanism is believed to involve the displacement of water from adsorption sites on the soil particle and binding of VOCs to these freed sites. Currently, research is in progress with soils obtained from actual contaminated sites.

## LABORATORY PROCEDURES

### Sample Storage

Most regulatory procedures specify storage of samples for VOA at 4°C in the dark. Sample coolers should be opened under chain-of-custody conditions, and the temperature inside the cooler should be verified and noted. Samples should be transferred to controlled-temperature (4°C) refrigerators until analysis. In many cases, insufficient cooling is provided during transport. In these cases, data quality may be compromised.

### Sample Preparation

The two most commonly used methods that satisfy regulatory requirements for the analysis of soil samples for VOCs are direct purge and trap and methanol extraction. Each procedure has benefits and limitations with respect to sample preparation prior to VOC analysis of soils.

The modified purge-and-trap procedure has the following characteristics:

- Homogenization of contents of wide-mouth jar will cause significant VOC losses. The collection of a 5-g aliquot in the field and placement into a tared vial sealed with a modified purge-and-trap cap is recommended.

- Surrogate addition should be made to the soil in the field, if possible.
- May be more susceptible to short-range spatial variability.
- Samples should be brought to ambient temperature before purging.
- May be more suitable for low-level samples.

The methanol-immersion procedure has the following characteristics:

- The key is to minimize the time samples are exposed to the atmosphere prior to immersion into methanol.
- Minimum detection limits can be raised by a factor of 10 to 20.
- The best option for sample archival because VOCs are highly soluble in methanol.
- Large-mass samples can be extracted in the field in a 1:1 ratio and the methanol extract shipped to the laboratory for analysis.
- Can collect composite samples.

The analytical methods that can be used for the analysis of soils for VOCs are summarized in Table 12. An analytical method should be selected that is compatible with the recommended sample collection and containerizing procedure discussed earlier.

## CONCLUSIONS AND RECOMMENDATIONS

Current research on sampling soils for VOC analyses answers many of the questions asked by RPMs and OSCs who conduct site characterization and restoration.

1. There is no specific method or process that can be recommended for sampling soils for VOA. A wide variety of sampling devices are currently used for collecting soil samples for VOA. Sampling device selection is site-specific, and no single device can be recommended for use at all sites. Several different samplers, which cover a broad range of sampling conditions and circumstances, are recommended for obtaining representative samples for VOC analysis (Table 7). Procedures may vary for different VOCs. Experiments have shown that a procedure that collects an undisturbed, intact sample with a device that allows direct transfer to a sample container (e.g., split-spoon, Shelby tube, or zero-contamination sampler) is superior to a more disruptive procedure that uses a crude bulk sampler (e.g., shovel, trowel, scoop, or spade) for maintaining the integrity of VOCs in a soil sample. Large-diameter tube-type sampling devices are recommended for collection of near-surface samples. The same types of devices can be used in conjunction with hollow-stem augers for collecting subsurface samples.
2. Transfer of the sample from the sampling device to the container is a critical step in the process. Losses of as much as 80% have been observed during this step. The faster the soil can be removed from the sampling device and

TABLE 12. METHODS FOR VOC ANALYSIS OF SOIL

Method Extraction/analysis	Sample Size (g)	Sample Preparation Procedure	Sensitivity (µg/kg)	Data Quality Objective	Program	Comments
5030 / 8240 / 8010 / 8015 / 8020 / 8030 / 8260	5	Purge and trap	5-10	Litigation	RCRA <sup>a</sup>	Sample transfer to purge and trap is critical.
5380 / 8240 / 8010 / 8015 / 8020 / 8030 / 8260	5-100	Methanol extraction	500-1000	Litigation	RCRA	Sensitivity loss but sample transfer facilitated.
5031 / 8240 / 8010 / 8015 / 8020 / 8030 / 8260	5	Field purge	5-10	Semi- quantitative	RCRA	Sample can only be analyzed once, transfer and shipping facilitated.
3810 / 8240 / 8010 / 8015 / 8020 / 8030 / 8260	10	Heat to 90°C in water bath and analyze headspace	1000	Screening for purgeable organics	RCRA	Can be performed in the field.
3820	10	Hexadecane extraction followed by GC/FID	500-1000	Screening prior to GC or GC/MS analysis	RCRA	FID responses vary with type of VOC.
624	5	Purge and trap	5-10	Litigation	CLP <sup>b</sup>	Similar to method 5030/8240 in RCRA SW-846.

<sup>a</sup> U.S. EPA, 1986b

<sup>b</sup> U.S. EPA, 1982

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transferred into an airtight sample container, the smaller the VOC loss. Liners make the removal and subsampling of soil from the collection device more efficient.

3. The best method for transferring a sample from a large-diameter coring device (or exposed test pit) into a sample container is by collecting the appropriate size aliquot (for laboratory analysis) with a small-diameter, hand-held corer and extruding the subsample into a 40-mL VOA vial, then sealing the vial with a modified purge-and-trap cap. Alternatively, contents of the large-diameter coring device can be sectioned and immersed in methanol.
4. Small-diameter, hand-held corers can be used for collecting samples from a freshly exposed face of a trench or test pit, or for obtaining a subsample from a large-diameter coring device. The use of a small-diameter, hand-held corer is recommended for obtaining subsamples from liner-held soil. Collection of a sample of the appropriate size for a particular analytical procedure is optimal. The required size of aliquot can be extruded into a 40-mL VOA vial and sealed with a modified purge-and-trap cap. The possibility exists of compositing several small-diameter core samples by immersing them in a single jar containing methanol.
5. Sample containers vary in terms of air-tightness. Data are available to indicate that there is a decrease in pressure

and an increase in temperature in the cargo holds of certain air carriers. This is the worst possible set of conditions for maintaining VOCs in containerized soil samples. Intact seals on storage containers and adequate cooling is thus critical for maintaining VOCs in soil samples. Shipping and holding-time studies have shown that vials and jars may be equally suited for containing VOCs in soil samples, the laboratory pretreatment step needed to obtain an aliquot from a jar-held sample causes significant losses of VOCs. Commercially available shipping packages with built-in cooling materials (e.g., Freeze Gel Packs® or Blue Ice®) are available. Whenever possible, an integrated sampling approach should be employed to obtain the most representative samples possible. Soil-gas surveying coupled with on-site soil sampling and analyses followed by the Resource Conservation and Recovery Act (RCRA) or CLP laboratory analyses may provide valuable information on the partitioning of VOCs at a site.

6. The current preservation technique for soil samples is storage at 4°C in the dark. Biological activity may continue at this temperature. The addition of mercuric chloride to the soil may reduce biodegradation of VOCs. The amount of mercuric chloride to be added, however, is a function of the organic carbon content in the soil. The most promising preservatives for reducing losses of VOCs through volatilization are solid adsorbents such as Molecular Sieve - 5A™ and Florasil™.



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# Ground-Water Issue

## CHARACTERIZING SOILS FOR HAZARDOUS WASTE SITE ASSESSMENTS

R. P. Breckenridge<sup>1</sup>, J. R. Williams<sup>2</sup>, and J. F. Keck<sup>1</sup>

### INTRODUCTION

The Regional Superfund Ground Water Forum is a group of ground-water scientists representing EPA's Regional Offices, organized to exchange up-to-date information related to ground-water remediation at hazardous waste sites. Soil characterization at hazardous waste sites is an issue identified by the forum as a concern of CERCLA decision-makers.

To address this issue, this paper was prepared through support from EMSL-LV and RSKERL, under the direction of R. P. Breckenridge, with the support of the Superfund Technical Support Project. For further information contact Ken Brown, EMSL-LV Center Director, at FTS 545-2270 or R. P. Breckenridge at FTS 583-0757.

Site investigation and remediation under the Superfund program is performed using the CERCLA remedial investigation/feasibility study (RI/FS) process. The goal of the RI/FS process is to reach a Record of Decision (ROD) in a timely manner. Soil characteriza-

tion provides data types required for decision making in three distinct RI/FS tasks:

1. Determination of the nature and extent of soil contamination.
2. Risk assessment, and determination of risk-based soil clean-up levels.
3. Determination of the potential effectiveness of soil remediation alternatives.

Identification of data types required for the first task, determination of the nature and extent of contamination, is relatively straightforward. The nature of contamination is related to the types of operations conducted at the site. Existing records, if available, and interviews with personnel familiar with the site history are good sources of information to help determine the types of contaminants potentially present. This information may be used to shorten the list of target analytes from the several hundred contaminants of concern in the 40 CFR Part 264 list (Date 7-1-89). Numerous guidance documents are available for planning all

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aspects of the subsequent sampling effort (US EPA, 1987a, 1988a, 1988b, and Jenkins et al., 1988).

The extent of contamination is also related to the types of operations conducted at the site. Existing records, if available, and interviews with personnel familiar with the site history are also good sources of information to help determine the extent of contamination potentially present. The extent of contamination is dependent on the nature of the contaminant source(s) and the extent of contaminant migration from the source(s). Migration routes may include air, via volatilization and fugitive dust emissions; overland flow; direct discharge; leachate migration to ground water and surface runoff and erosion. Preparation of a preliminary site conceptual model is therefore an important step in planning and directing the sampling effort. The conceptual model should identify the most likely locations of contaminants in soil and the pathways through which they move.

The data type requirements for tasks 2 and 3 are frequently less well understood. Tasks 2 and 3 require knowledge of both the nature and extent of contamination, the environmental fate and transport of the contaminants, and an appreciation of the need for quality data to select a viable remedial treatment technique.

Contaminant fate and transport estimation is usually performed by computer modeling. Site-specific information about the soils in which contamination occurs, migrates, and interacts with, is required as input to a model. The accuracy of the model output is no better than the accuracy of the input information.

The purpose of this paper is to provide guidance to Remedial Project Managers (RPM) and On-Scene Coordinators (OSC) concerning soil characterization data types required for decision-making in the CERCLA RI/FS process related to risk assessment and remedial alternative evaluation for contaminated soils. Many of the problems that arise are due to a lack of understanding the data types required for tasks 2 and 3 above. This paper describes the soil characterization data types required to conduct model based risk assessment for task 2 and the selection of remedial design for task 3. The information presented in this paper is a compilation of current information from the literature and from experience combined to meet the purpose of this paper.

EMSL-Las Vegas and RSKERL-Ada convened a technical committee of experts to examine the issue and provide technical guidance based on current scientific information. Members of the committee were Joe R. Williams, RSKERL-Ada; Robert G. Baca, Robert P. Breckenridge, Alan B. Crockett, and John F. Keck from the Idaho National Engineering Laboratory, Idaho Falls, ID; Gretchen L. Rupp, PE, University of Nevada-Las Vegas; and Ken Brown, EMSL-LV.

This document was compiled by the authors and edited by the members of the committee and a group of peer reviewers.

Characterization of a hazardous waste site should be done using an integrated investigative approach to determine quickly and cost effectively the potential health effects and appropriate response measures at a site. An integrated approach involves consideration of the different types and sources of contaminants, their fate as they are transported through and are partitioned, and their impact on different parts of the environment.

## CONCERNS

This paper addresses two concerns related to soil characterization for CERCLA remedial response. The first concern is the applicability of traditional soil classification methods to CERCLA soil characterization. The second is the identification of soil characterization data types required for CERCLA risk assessment and analysis of remedial alternatives. These concerns are related, in that the Data Quality Objective (DQO) process addresses both. The DQO process was developed, in part, to assist CERCLA decision-makers in identifying the data types, data quality, and data quantity required to support decisions that must be made during the RI/FS process. *Data Quality Objectives for Remedial Response Activities: Development Process* (US EPA, 1987b) is a guidebook on developing DQOs. This process as it relates to CERCLA soil characterization is discussed in the Data Quality Objective section of this paper.

Data types required for soil characterization must be determined early in the RI/FS process, using the DQO process. Often, the first soil data types related to risk assessment and remedial alternative selection available during a CERCLA site investigation are soil textural descriptions from the borehole logs prepared by a geologist during investigations of the nature and extent of contamination. These boreholes might include installation of ground-water monitoring wells, or soil boreholes. Typically, borehole logs contain soil lithology and textural descriptions, based on visual analysis of drill cuttings.

Preliminary site data are potentially valuable, and can provide modelers and engineers with data to begin preparation of the conceptual model and perform scoping calculations. Soil texture affects movement of air and water in soil, infiltration rate, porosity, water holding capacity, and other parameters. Changes in lithology identify heterogeneities in the subsurface (i.e., low permeability layers, etc.). Soil textural classification is therefore important to contaminant fate and transport modeling, and to screening and analysis of remedial alternatives. However, unless collected properly, soil textural descriptions are of limited value for the following reasons:

1. There are several different systems for classification of soil particles with respect to size. To address this problem it is important to identify which system has been or will be used to classify a soil so that data can be properly compared. Figure 1 can be used to compare the different systems (Gee and Bauder, 1986). *Keys to Soil Taxonomy* (Soil Survey Staff, 1990) provides details to one of the more useful systems that should be consulted prior to classifying a site's soils.
2. The accuracy of the field classification is dependent on the skill of the observer. To overcome this concern RPMs and OSCs should collect soil textural data that are quantitative rather than qualitative. Soil texture can be determined from a soil sample by sieve analysis or hydrometer. These data types are superior to qualitative description based on visual analysis and are more likely to meet DQOs.
3. Even if the field person accurately classifies a soil (e.g., as a silty sand or a sandy loam), textural descriptions do not afford accurate estimations of actual physical properties required for modeling and remedial alternative evaluation,

such as hydraulic conductivity. For example, the hydraulic conductivity of silty-sand can range from  $10^{-5}$  to  $10^{-1}$  cm/sec (four orders of magnitude).

These ranges of values may be used for bounding calculations, or to assist in preparation of the preliminary conceptual model. These data may therefore meet DQOs for initial screening of remedial alternatives, for example, but will likely not meet DQOs for detailed analysis of alternatives.

## DATA QUALITY OBJECTIVES

EPA has developed the Data Quality Objective (DQO) process to guide CERCLA site characterization. The relationship between CERCLA RI/FS activities and the DQO process is shown in Figure 2 (US EPA, 1988c, 1987a). The DQO process occurs in three stages:

- **Stage 1. Identify Decision Types.** In this stage the types of decisions that must be made during the RI/FS are identified.

The types of decisions vary throughout the RI/FS process, but in general they become increasingly quantitative as the process proceeds. During this stage it is important to identify and involve the data users (e.g. modelers, engineers, and scientists), evaluate available data, develop a conceptual site model, and specify objectives and decisions.

- **Stage 2. Identify Data Uses/Needs.** In this stage data uses are defined. This includes identification of the required data types, data quality and data quantity required to make decisions on how to:

- Perform risk assessment
- Perform contaminant fate and transport modeling
- Identify and screen remedial alternatives

- **Stage 3. Design Data Collection Program.** After Stage 1 and 2 activities have been defined and reviewed, a data collection program addressing the data types, data quantity (number of samples) and data quality required to make these decisions needs to be developed as part of a sampling and analysis plan.

Although this paper focuses on data types required for decision-making in the CERCLA RI/FS process related to soil contamination, references are provided to address data quantity quality issues.

## Data Types

The OSC or RPM must determine which soil parameters are needed to make various RI/FS decisions. The types of decisions to be made therefore drive selection of data types. Data types required for RI/FS activities including risk assessment, contaminant fate and transport modeling and remedial alternative selection are discussed in Soil characteristics Data Types Required for Modeling Section, and the Soil Characterization Data Type Required for Remedial Alternative Selection Section.

## Data Quality

The RPM or OSC must decide "How good does the data need to be in order for me to make a given decision?". EPA has assigned quality levels to different RI/FS activities as a guideline. *Data Quality Objectives for Remedial Response Activities* (US EPA, 1987a) offers guidance on this subject and contains many useful references.

## Data Quantity

The RPM or OSC must decide "How many samples do I need to determine the mean and standard deviation of a given parameter at a given site?", or "How does a given parameter vary spatially across the site?". Decisions of this type must be addressed by statistical design of the sampling effort. The *Soil Sampling Quality Assurance Guide* (Barth et al., 1989) and *Data Quality Objectives for Remedial Response* (US EPA, 1987a) offer guidance on this subject and contain many useful references.

		PARTICLE SIZE LIMIT CLASSIFICATION			
		USDA	CSSC	ISSS	ASTM (unified)
0.0002	ASTM SIEVE NUMBER OR SIZE (Openings/inch)	CLAY	FINE CLAY	COARSE CLAY	FINES (SILT AND CLAY)
0.001			COARSE CLAY		
0.002			FINE SILT		
0.003		SILT	MEDIUM SILT	SILT	
0.004			COARSE SILT		
0.006					
0.008		VERY FINE SAND	VERY FINE SAND	FINE SAND	
0.01			FINE SAND		
0.02			MEDIUM SAND		
0.03		COARSE SAND	COARSE SAND	COARSE SAND	MEDIUM SAND
0.04	VERY COARSE SAND				
0.06					
0.08	FINE GRAVEL	GRAVEL	GRAVEL	COARSE SAND	
0.1				FINE GRAVEL	
0.2				COARSE GRAVEL	
0.3	COBBLES	COBBLES	COBBLES	COBBLES	
0.4					
0.6					

USDA - U.S. DEPARTMENT OF AGRICULTURE, (SOIL SURVEY STAFF, 1975)  
 CCS - CANADA SOIL SURVEY COMMITTEE (McKEAGUE, 1978)  
 ISSS - INTERNATIONAL SOIL SCI. SOC. (YONG AND WARKENTIN, 1966)  
 ASTM - AMERICAN SOCIETY FOR TESTING & MATERIALS (ASTM, D-2487, 1985a)

Figure 1. Particle-size limits according to several current classification schemes (Gee and Bauder, 1986).

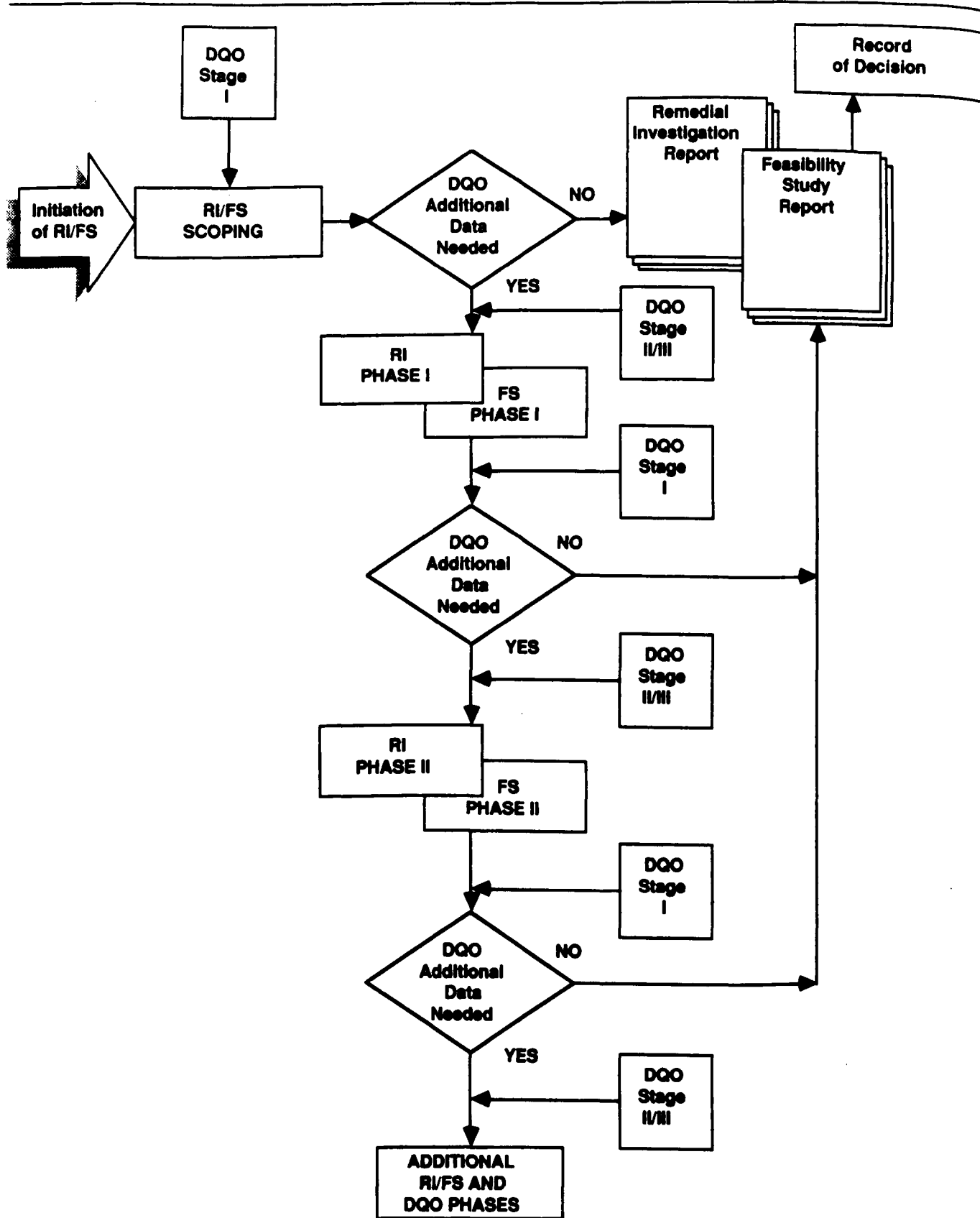


Figure 2. Phased RI/FS approach and the DQO process (EPA, 1987a).

## IMPORTANT SOIL CHARACTERISTICS IN SITE EVALUATION

Tables 1 and 2 identify methods for collecting and determining data types for soil characteristics either in the field, laboratory, or by calculation. Soil characteristics in Table 1 are considered the primary indicators that are needed to complete Phase I of the RI/FS process. This is a short, but concise list of soil data types that are needed to make CERCLA decisions and should be planned for and collected early in the sampling effort. These primary data types should allow for the initial screening of remedial treatment alternatives and preliminary modeling of the site for risk assessment. Many of these characteristics can be obtained relatively inexpensively during periods of early field work when the necessary drilling and sampling equipment are already on site. Investigators should plan to collect data for all the soil characteristics at the same locations and times soil boring is done to install monitoring wells. Geophysical logging of the well should also be considered as a cost effective method for collecting lithologic information prior to casing the well. Data quality and quantity must also be considered before beginning collection of the appropriate data types.

The soil characteristics in Table 2 are considered ancillary only because they are needed in the later stages and tasks of the DQO process and the RI/FS process. If the site budget allows, collection of these data types during early periods of field work will improve the database available to make decisions on remedial treatment selection and model-based risk assessments. Advanced planning and knowledge of the need for the ancillary soil characteristics should be factored into early site work to reduce overall costs and the time required to reach a ROD. A small additional investment to collect ancillary data during early site visits is almost always more cost effective than having to send crews back to the field to conduct additional soil sampling.

Further detailed descriptions of the soil characteristics in Tables 1 and 2 can be found in *Fundamentals of Soil Physics and Applications of Soil Physics* (Hillel, 1980) and in a series of articles by Dragun (1988, 1988a, 1988b). These references provide excellent discussions of these characteristics and their influence on water movement in soils as well as contaminant fate and transport.

## SOIL CHARACTERISTICS DATA TYPES REQUIRED FOR MODELING

The information presented here is not intended as a review of all data types required for all models, instead it presents a sampling of the more appropriate models used in risk assessment and remedial design.

### *Uses of Vadose Zone Models for Cercla Remedial Response Activities*

Models are used in the CERCLA RI/FS process to estimate contaminant fate and transport. These estimates of contaminant behavior in the environment are subsequently used for:

- **Risk assessment.** Risk assessment includes contaminant release assessment, exposure assessment, and determining risk-based clean-up levels. Each of these activities requires estimation of the rates and extents of contaminant movement

in the vadose zone, and of transformation and degradation processes.

- **Effectiveness assessment of remedial alternatives.** This task may also require determination of the rates and extents of contaminant movement in the vadose zone, and of rates and extents of transformation and degradation processes. Technology-specific data requirements are cited in the Soil Characterization Data Type Required for Remedial Alternative Selection Section.

The types, quantities, and quality of site characterization data required for modeling should be carefully considered during RI/FS scoping. Several currently available vadose zone fate and transport models are listed in Table 3. Soil characterization data types required for each model are included in the table. Model documentation should be consulted for specific questions concerning uses and applications.

The Superfund Exposure Assessment Manual discusses various vadose zone models (US EPA, 1988e). This document should be consulted to select codes that are EPA-approved.

### *Data Types Required for Modeling*

Soil characterization data types required for modeling are included in Tables 1 and 2. Most of the models are one- or two-dimensional solutions to the advection-dispersion equation, applied to unsaturated flow. Each is different in the extent to which transformation and degradation processes may be simulated; various contaminant release scenarios are accommodated; heterogeneous soils and other site-specific characteristics are accounted for. Each, therefore, has different data type input requirements.

All models require physicochemical data for the contaminants of concern. These data are available in the literature, and from EPA databases (US EPA, 1988c,d). The amount of physicochemical data required is generally related to the complexity of the model. The models that account for biodegradation of organics, vapor phase diffusion and other processes require more input data than the relatively simpler transport models.

### *Data Quality and Quantity Required for Modeling*

DQOs for the modeling task should be defined during RI/FS scoping. The output of any computer model is only as valid as the quality of the input data and code itself. Variance may result from the data collection methodology or analytical process, or as a result of spatial variability in the soil characteristic being measured.

In general, the physical and chemical properties of soils vary spatially. This variation rarely follows well defined trends; rather it exhibits a stochastic (i.e., random) character. However, the stochastic character of many soil properties tends to follow classic statistical distributions. For example, properties such as bulk density and effective porosity of soils tend to be normally distributed (Campbell, 1965). Saturated hydraulic conductivity, in contrast, is often found to follow a log-normal distribution. Characterization of a site, therefore, should be performed in such a manner as to permit the determination of the statistical characteristics (i.e., mean and variance) and their spatial correlations.

(Continued on page 8)

**TABLE 1. MEASUREMENT METHODS FOR PRIMARY SOIL CHARACTERISTICS  
NEEDED TO SUPPORT CERCLA DECISION-MAKING PROCESS**

Soil Characteristic*	Measurement Technique/Method (w/Reference)		
	Field	Laboratory	Calculation or Lookup Method
Bulk density	Neutron probe (ASTM, 1985), Gamma radiation (Blake and Hartage, 1986, Blake, 1965).	Coring or excavation for lab analysis (Blake and Hartage, 1986).	Not applicable.
Soil pH	Measured in field in same manner as in laboratory.	Using a glass electrode in an aqueous slurry (ref. EPRI EN-6637) Analytical Method - Method 9045, SW-846, EPA.	Not applicable.
Texture	Collect composite sample for each soil type. No field methods are available, except through considerable experience of "feeling" the soil for an estimation of % sand, silt, and clay.	ASTM D 522-63 Method for Particle Analysis of Soils. Sieve analysis better at hazardous waste sites because organics can effect hydrometer analysis (Kuate, 1986).	Not applicable.
Depth to ground water	Ground-water monitoring wells or piezometers using EPA approved methods (EPA 1985a).	Not applicable.	Not applicable.
Horizons or stratigraphy	Soil pits dug with backhoe are best. If safety and cost are a concern, soil bores can be collected with either a thin wall sample driver and veilmayer tube (Brown et al., 1990).	Not applicable.	May be possible to obtain information from SCS soil survey for the site.
Hydraulic conductivity (saturated)	Auger-hole and piezometer methods (Amoozegeer and Warrick, 1986) and Guelph permeameter (Reynolds & Elrick, 1985; Reynolds & Elrick, 1986).	Constant head and falling head methods (Amoozegeer and Warrick, 1986).	Although there are tables available that list the values for the saturated hydraulic conductivity, it should be understood that the values are given for specific soil textures that may not be the same as those on the site.
Water retention (soil water characteristic curves)	Field methods require a considerable amount of time, effort, and equipment. For a good discussion of these methods refer to Bruce and Luxmoore (1986).	Obtained through wetting or drainage of core samples through a series of known pressure heads from low to high or high to low, respectively (Klute, 1986).	Some look-up and estimation methods are available, however, due to high spatial variability in this characteristic they are not generally recommended unless their use is justified.
Air permeability and water content relationships	None	Several methods have been used, however, all use disturbed soil samples. For field applications the structure of soils are very important. For more information refer to Corey (1986).	Estimation methods for air permeability exist that closely resemble the estimation methods for unsaturated hydraulic conductivity. Example models those developed by Brooks and Corey (1964) and van Genuchten (1980).
Porosity (pore volume)		Gas pycnometer (Danielson and Sutherland, 1986).	Calculated from particle and bulk densities (Danielson and Sutherland, 1986).
Climate	Precipitation measured using either Sacramento gauge for accumulated value or weighing gauge or tipping bucket gauge for continuous measurement (Finkelstein et al., 1983; Kite, 1979). Soil temperature measured using thermocouple.	Not applicable.	Data are provided in the Climatic Atlas of the United States or are available from the National Climatic Data Center, Asheville, NC Telephone (704) 259-0882.

\* Soil characteristics are discussed in general except where specific cases relate to different waste types (i.e., metals, hydrophobic organics or polar organics).

**TABLE 2. MEASUREMENT METHODS FOR ANCILLARY SOIL PARAMETERS  
NEEDED TO SUPPORT CERCLA DECISION-MAKING PROCESS**

Soil Characteristic*	Measurement Technique/Method (w/Reference)		
	Field	Laboratory	Calculation or Lookup Method
Organic carbon	Not applicable.	High temperature combustion (either wet or dry) and oxidation techniques (Powell et al., 1989) (Powell, 1990).	Not applicable.
Capacity Exchange Capacity (CEC)	See Rhoades for field methods.	(Rhoades, 1982).	
Erodibility			Estimated using standard equations and graphs (Israelsen et al., 1980) field data for slope, field length, and cover type required as input. Soils data can be obtained from the local Soil Conservation Service (SCS) office.
Water erosion Universal Soil Loss Equation (USLE) or Revised USLE (RUSLE)	Measurement/survey of slope (in ft rise/ft run or %), length of field, vegetative cover.	Not applicable.	A modified universal soil loss equation (USLE) (Williams, 1975) presented in Mills et al., (1982) and US EPA (1988d) source for equations.
Wind erosion	Air monitoring for mass of containment. Field length along prevailing wind direction.	Not applicable.	The SCS wind loss equation (Israelsen et al., 1980) must be adjusted (reduced) to account for suspended particles of diameter $\leq 10\mu\text{m}$ Cowherd et al., (1985) for a rapid evaluation ( $\leq 24$ hr) of particle emission from a Superfund site.
Vegetative cover	Visual observation and documented using map. USDA can aid in identification of unknown vegetation.	Not applicable.	
Soil structure	Classified into 10 standard kinds – see local SCS office for assistance (Soil Survey Staff, 1990) or Taylor and Ashcroft (1972), p. 310.	Not applicable.	See local soil survey for the site.
Organic carbon partition coefficient ( $K_{oc}$ )	<i>In situ</i> tracer tests (Freeze and Cherry, 1979).	(ASTM E 1195-87, 1988)	Calculated from $K_{oc}$ , water solubility (Mills et al., 1985; Sims et al., 1986).
Redox couple ratios of waste/soil system	Platinum electrode used on lysimeter sample (ASTM, 1987).	Same as field.	Can be calculated from concentrations of redox pairs or $O_2$ (Stumm and Morgan, 1981).
Liner soil/water partition coefficient	<i>In situ</i> tracer tests (Freeze and Cherry, 1979)	Batch experiment (Ash et al., 1973); column tests (van Genuchten and Wierenga, 1986).	Mills et al., 1985.
Soil oxygen content (aeration)	$O_2$ by membrane electrode $O_2$ diffusion rate by Pt microelectrode (Phene, 1986). $O_2$ by field GC (Smith, 1983).	Same as field.	Calculated from pE (Stumm and Morgan, 1981) or from $O_2$ and soil-gas diffusion rate.

(Continued)



TABLE 2. (CONTINUED)

Soil Characteristic*	Measurement Technique/Method (w/Reference)		
	Field	Laboratory	Calculation or Lookup Method
Soil temperature (as it affects volatilization)	Thermotery (Taylor and Jackson, 1986).	Same as field.	Brown and Associates (1980).
Clay mineralogy	Parent material analysis.	X-ray diffraction (Whittig and Allardice, 1986).	
Unsaturated hydraulic conductivity	Unsteady drainage-flux (or instantaneous profile) method and simplified unsteady drainage flux method (Green et al., 1986). The instantaneous profile method was initially developed as a laboratory method (Watson, 1966), however it was adapted to the field (Hillel et al., 1972). Constant-head borehole infiltration (Amoozegar and Warrick, 1986).	Not usually done; results very difficult to obtain.	A number of estimation methods exists, each with their own set of assumptions and requirements. Reviews have been presented by Mualem (1986), and van Gehuchten (in press).
Moisture content	Two types of techniques – indirect and direct. Direct methods, (i.e., gravimetric sampling), considered the most accurate, with no calibration required. However, methods are destructive to field systems. Methods involve collecting samples, weighing, drying and re-weighing to determine field moisture. Indirect methods rely on calibration (Klute, 1986).		
Soil biota	No standard method exists (see model or remedial technology for input or remedial evaluation procedures).	No standard method exists; can use agar plate count using MOSA method 99-3 p. 1462 (Klute, 1986).	

\* Soil characteristics are discussed in general except where specific cases relate to different waste types (i.e., metals, hydrophobic organics or polar organics).

Significant advances have been made in understanding and describing the spatial variability of soil properties (Neilsen and Bouma, 1985). Geostatistical methods and techniques (Clark, 1982; Davis, 1986) are available for statistically characterizing soil properties important to contaminant migration. Information gained from a geostatistical analysis of data can be used for three major purposes:

- Determining the heterogeneity and complexity of the site;
- Guiding the data collection and interpretation effort and thus identifying areas where additional sampling may be needed (to reduce uncertainty by estimating error); and
- Providing data for a stochastic model of fluid flow and contaminant migration.

One of the geostatistical tools useful to help in the interpolation or mapping of a site is referred to as kriging (Davis, 1986). General kriging computer codes are presently available. Application of this type of tool, however, requires an adequate

sample size. As a rule of thumb, 50 or more data points are needed to construct the semivariogram required for use in kriging. The benefit of using kriging in site characterization is that it allows one to take point measurements and estimate soil characteristics at any point within the domain of interest, such as grid points, for a computer model. Geostatistical packages are available from the US EPA, Geo-EAS and GEOPACK (Englund and Sparks, 1988 and Yates and Yates, 1990).

The use of stochastic models in hydrogeology has increased significantly in recent years. Two stochastic approaches that have been widely used are the first order uncertainty method (Dettinger and Wilson, 1981) and Monte Carlo methods (Clifton et al., 1985; Sagar et al., 1986; Esslinger and Sagar, 1988). Andersson and Shapiro (1983) have compared these two approaches for the case of steady-state unsaturated flow. The Monte Carlo methods are more general and easier to implement than the first order uncertainty methods. However, the Monte Carlo method is more computationally intensive, particularly for multidimensional problems.

(Continued on page 10)

TABLE 3. SOIL CHARACTERISTICS REQUIRED FOR VADOSE ZONE MODELS

Properties and Parameters	Model Name [Reference(s)]									
	Help (A,B)	Sesoi (C,D)	Creams (E,F)	PRZM (G,H,I)	Vadof (H,J)	Minteq (J)	Fowl <sup>TM</sup> (K)	Ritz (L)	Vip (M)	Chemflo (N)
Soil bulk density	○	●	●	●	●	○	●	●	●	●
Soil pH	○	●	○	○	○	●	●	○	○	○
Soil texture	●	○	●	●	●	○	○	●	●	○
Depth to ground water	○	●	○	○	●	○	○	○	○	○
Horizons (soil layering)	●	●	●	●	●	○	○	○	○	○
Saturated hydraulic conductivity	●	●	●	●	●	○	●	●	●	●
Water retention	●	●	●	●	●	○	●	○	○	●
Air permeability	○	●	○	○	○	○	○	○	●	○
Climate (precipitation)	●	●	●	●	○	○	●	●	●	●
Soil porosity	●	●	●	●	●	○	○	●	●	○
Soil organic content	○	●	●	●	●	●	○	●	●	○
Cation Exchange Capacity (CEC)	○	●	○	○	○	●	○	○	○	○
Degradation parameters	●	●	●	●	●	○	○	●	●	●
Soil grain size distribution	○	○	○	○	○	○	○	○	○	○
Soil redox potential	○	○	○	○	○	●	○	○	○	○
Soil/water partition coefficients	○	●	●	●	●	●	●	●	●	●
Soil oxygen content	○	○	○	○	○	○	○	○	●	○
Soil temperature	○	●	○	●	●	●	○	●	●	○
Soil mineralogy	○	●	○	○	○	○	○	○	○	○
Unsaturated hydraulic conductivity	●	●	●	●	●	○	●	○	○	●
Saturated soil moisture content	●	●	●	●	●	○	●	●	●	●
Microorganism population	○	○	○	○	○	○	○	○	○	○
Soil respiration	○	○	○	○	○	○	○	○	○	○
Evaporation	●	●	●	●	○	○	○	●	●	●
Air/water contaminant densities	○	○	○	○	○	○	●	●	●	○
Air/water contaminant viscosities	○	○	○	○	○	○	○	○	○	○

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- A. Schroeder, et al., 1984.  
 B. Schroeder, et al., 1984a.  
 C. Bonazountas and Wagner, 1984.  
 D. Chen, Wollman, and Liu, 1987.  
 E. Leonard and Ferreira, 1984.  
 F. Devaurs and Springer, 1988.  
 G. Carsel et al., 1984.  
 H. Dean et al., 1989.  
 I. Dean et al., 1989a.  
 J. Brown and Allison, 1987.  
 K. Hostettler, Erickson, and Rai, 1988.  
 L. Nofziger and Willaims, 1988.  
 M. Stevens et al., 1989.  
 N. Nofziger et al., 1989.

● Required ○ Not required ○ Used indirectly\*

\* Used in their estimation of other required characteristics or the interpretation of the models, but not directly entered as input to models.

Application of stochastic models to hazardous waste sites has two main advantages. First, this approach provides a rigorous way to assess the uncertainty associated with the spatial variability of soil properties. Second, the approach produces model predictions in terms of the likelihood of outcomes, i.e., probability of exceeding water quality standards. The use of models at hazardous waste sites leads to a thoughtful and objective treatment of compliance issues and concerns.

In order to obtain accurate results with models, quality data types must be used. The issue of quality and confidence in data can be partially addressed by obtaining as representative data as possible. Good quality assurance and quality control plans must be in place for not only the acquisition of samples, but also for the application of the models (van der Heijde, et al., 1989).

Specific soil characteristics vary both laterally and vertically in an undisturbed soil profile. Different soil characteristics have different variances. As an example, the sample size required to have 95 percent probability of detecting a change of 20 percent in the mean bulk density at a specific site was 6; however, for saturated hydraulic conductivity the sample size would need to be 502 (Jury, 1986). A good understanding of site soil characteristics can help the investigators understand these variations. This is especially true for most hazardous waste sites because the soils have often been disturbed, which may cause even greater variability.

An important aspect of site characterization data and models is that the modeling process is dynamic, i.e., as an increasing number of "simplifying" assumptions are needed, the complexity of the models must increase to adequately simulate the additional processes that must be included. Such simplifying assumptions might include an isotropic homogeneous medium or the presence of only one mobile phase (Weaver, et al., 1989). In order to decrease the number of assumptions required, there is usually a need to increase the number of site-specific soil characteristic data types in a model (see Table 2); thus providing greater confidence in the values produced. For complex sites, an iterative process of initial data collection and evaluation leading to more data collection and evaluation until an acceptable level of confidence in the evaluation can be reached can be used.

Table 3 identifies selected unsaturated zone models and their soil characteristic needs. For specific questions regarding use and application of the model, the reader should refer to the associated manuals. Some of these models are also reviewed by Donigan and Rao (1986) and van der Heijde et al. (1988).

## SOIL CHARACTERISTICS DATA TYPES REQUIRED FOR REMEDIAL ALTERNATIVE SELECTION

### Remedial Alternative Selection Procedure

The CERCLA process involves the identification, screening and analysis of remedial alternatives at uncontrolled hazardous waste sites (US EPA, 1988c). During screening and analysis, decision values for process-limiting characteristics for a given remedial alternative are compared to site-specific values of those characteristics. If site-specific values are outside the range required for effective use of a particular alternative, that alternative is less likely to be selected. Site soil conditions are critical process-limiting characteristics.

### Process-Limiting Characteristics

Process-limiting characteristics are site- and waste-specific data types that are critical to the effectiveness and ability to implement remedial processes. Often, process-limiting characteristics are descriptors of rate-limiting steps in the overall remedial process. In some cases, limitations imposed by process-limiting characteristics can be overcome by adjustment of soil characteristics such as pH, soil moisture content, temperature and others. In other cases, the level of effort required to overcome these limitations will preclude use of a remedial process.

Decision values for process limiting characteristics are increasingly available in the literature, and may be calculated for processes where design equations are known. Process limiting characteristics are identified and decision values are given for several vadose zone remedial alternatives in Table 4. For waste/site characterization, process-limiting characteristics may be broadly grouped in four categories:

1. Mass transport characteristics
2. Soil reaction characteristics
3. Contaminant properties
4. Engineering characteristics

Thorough soil characterization is required to determine site-specific values for process-limiting characteristics. Most remedial alternatives will have process-limiting characteristics in more than one category.

### Mass Transport Characteristics

Mass transport is the bulk flow, or advection of fluids through soil. Mass transport characteristics are used to calculate potential rates of movement of liquids or gases through soil and include:

Soil texture  
Unsaturated hydraulic conductivity  
Dispersivity  
Moisture content vs. soil moisture tension  
Bulk density  
Porosity  
Permeability  
Infiltration rate, stratigraphy and others.

Mass transport processes are often process-limiting for both *in situ* and extract-and-treat vadose zone remedial alternatives (Table 4). *In situ* alternatives frequently use a gas or liquid mobile phase to move reactants or nutrients through contaminated soil. Alternatively, extract-and-treat processes such as soil vapor extraction (SVE) or soil flushing use a gas or liquid mobile phase to move contaminants to a surface treatment site. For either type of process to be effective, mass transport rates must be large enough to clean up a site within a reasonable time.

### Soil Reaction Characteristics

Soil reaction characteristics describe contaminant-soil interactions. Soil reactions include bio- and physicochemical reactions that occur between the contaminants and the site soil. Rates of reactions such as biodegradation, hydrolysis, sorption/desorption, precipitation/dissolution, redox reactions, acid-base reactions, and others are process-limiting characteristics for

(Continued on page 12)

TABLE 4. SOIL CHARACTERIZATION CHARACTERISTICS REQUIRED FOR REMEDIAL TECHNOLOGY EVALUATION ,  
(US EPA, 1988a,f; 1989a,b; 1990; Sims et al., 1986; Sims, 1990; Towers et al., 1989)

Technology	Process Limiting Characteristics	Site Data Required	Technology	Process Limiting Characteristics	Site Data Required
Pretreatment/ materials handling	Large particles interfere Clayey soils or hardpan difficult to handle	Particle size distribution	Thermal treatment (continued)	Particle size affects feeding and residuals	Particle size distribution
	Wet soils difficult to handle	Soil moisture content		pH <5 and >11 causes corrosion	pH
Soil vapor extraction	Applicable only to volatile organics w/significant vapor pressure >1 mm Hg	Contaminants present	Solidification/ stabilization	Not equally effective for all contaminants	Contaminants present
	Low soil permeability inhibits air movement	Soil permeability		Fine particles < No. 200 mesh may interfere	Particle size distribution
	Soil hydraulic conductivity >1E-8 cm/sec required	Hydraulic conductivity		Oil and grease >10% may interfere	Oil and grease
	Depth to ground water >20 ft recommended	Depth to ground water	Chemical extraction (slurry reactors)	Not equally effective for all contaminants	Contaminants present
	High moisture content inhibits air movement	Soil moisture content		Particle size <0.25 in.	Particle size distribution
	High organic matter content inhibits contaminant removal	Organic matter content		pH <10	pH
<i>In situ</i> enhanced bioremediation	Applicable only to specific organics	Contaminants present	Soil washing	Not equally effective for all contaminants	Contaminants present
	Hydraulic conductivity >1E-4 cm/sec preferred to transport nutrients	Hydraulic conductivity		Silt and clay difficult to remove from wash fluid	Particle size distribution
	Stratification should be minimal	Soil stratigraphy	Soil flushing	Not equally effective for all contaminants	Contaminants present
	Lower permeability layers difficult to remediate	Soil stratigraphy		Required number of pore volumes	Infiltration rate and porosity
	Temperature 15-45°C required	Soil temperature	Glycolate dechlorination	Not equally effective for all contaminants	Contaminants present
	Moisture content 40-80% of that at -1/3 bars tension preferred	Soil moisture characteristic curves		Moisture content <20%	Moisture content
	pH 4.5-8.5 required	Soil pH		Low organic matter content required	Organic carbon
	Presence of microbes required	Plate count	Chemical oxidation/ reduction (slurry reactor)	Not equally effective for all contaminants	Contaminants present
Thermal treatment	Applicable only to organics	Contaminants present		Oxidizable organics interfere	Organic carbon
	Soil moisture content affects handling and heating requirements	Soil moisture content		pH <2 interferes	pH
<i>In situ</i> vitrification			<i>In situ</i> vitrification	Maximum moisture content of 25% by weight	Moisture content
				Particle size <4 inches	Particle size distribution
				Requires soil hydraulic conductivity <1E-5 cm/sec	Hydraulic conductivity

many remedial alternatives (Table 4). Soil reaction characteristics include:

- $K_d$ , specific to the site soils and contaminants
- Cation exchange capacity (CEC)
- Eh
- pH
- Soil biota
- Soil nutrient content
- Contaminant abiotic/biological degradation rates
- Soil mineralogy
- Contaminant properties, described below, and others.

Soil reaction characteristics determine the effectiveness of many remedial alternatives. For example, the ability of a soil to attenuate metals (typically described by  $K_d$ ) may determine the effectiveness of an alternative that relies on capping and natural attenuation to immobilize contaminants.

### Soil Contaminant Properties

Contaminant properties are critical to contaminant-soil interactions, contaminant mobility, and to the ability of treatment technologies to remove, destroy or immobilize contaminants. Important contaminant properties include:

- Water solubility
- Dielectric constant
- Diffusion coefficient
- $K_{oc}$
- $K_d$
- $K_{ow}$
- Molecular weight
- Vapor pressure
- Density
- Aqueous solution chemistry, and others.

Soil contaminant properties will determine the effectiveness of many treatment techniques. For example, the aqueous solution chemistry of metal contaminants often dictates the potential effectiveness of stabilization/solidification alternatives.

### Soil Engineering Characteristics and Properties

Engineering characteristics and properties of the soil relate both to implementability and effectiveness of the remedial action. Examples include the ability of the treatment method to remove, destroy or immobilize contaminants; the costs and difficulties in installing slurry walls and other containment options at depths greater than 60 feet; the ability of the site to withstand vehicle traffic (trafficability); costs and difficulties in deep excavation of contaminated soil; the ability of soil to be worked for implementation of *in situ* treatment technologies (tilth); and others. Knowledge of site-specific engineering characteristics and properties is therefore required for analysis of effectiveness and implementability of remedial alternatives. Engineering characteristics and properties include, but are not limited to:

- Trafficability
- Erodability
- Tilth
- Depth to groundwater
- Thickness of saturated zone
- Depth and total volume of contaminated soil
- Bearing capacity, and others.

## SUMMARY AND CONCLUSIONS

The goal of the CERCLA RI/FS process is to reach a ROD in a timely manner. Soil characterization is critical to this goal. Soil characterization provides data for RI/FS tasks including determination of the nature and extent of contamination, risk assessment, and selection of remedial techniques.

This paper is intended to inform investigators of the data types required for RI/FS tasks, so that data may be collected as quickly, efficiently, and cost effectively as possible. This knowledge should improve the consistency of site evaluations, improve the ability of OSCs and RPMs to communicate data needs to site contractors, and aid in the overall goal of reaching a ROD in a timely manner.

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