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COMBINING INNOVATIVE TECHNOLOGY DEMONSTRATIONS WITH DENSE NONAQUEOUS PHASE LIQUIDS CLEANUP

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ABSTRACT

Radioactively contaminated acidic aqueous wastes and organic liquids were discharged to the soil column at three disposal sites within the 200 West Area of the Hanford Site, Washington (Figure 1). As a result, a portion of the underlying groundwater is contaminated with carbon tetrachloride several orders of magnitude above the maximum contaminant level accepted for a drinking water supply. Treatability testing and cleanup actions have been initiated to remove the contamination from both the unsaturated soils to minimize further groundwater contamination and the groundwater itself. To expedite cleanup, innovative technologies for (1) drilling, (2) site characterization, (3) monitoring, (4) well field development, and (5) contaminant treatment are being demonstrated and subsequently used where possible to improve the rates and cost savings associated with the removal of carbon tetrachloride from the soils and groundwater.

INTRODUCTION

At the Hanford Site, carbon tetrachloride was used primarily in plutonium recovery processes. From 1955 to 1973, radioactively contaminated acidic aqueous wastes and organic liquids from these processes were discharged to the soil column at three adjacent disposal sites (216-Z-1A Tile Field, the 216-Z-18 Crib, and the 216-Z-9 Trench) in the 200 West Area (Figure 2). Between 363,000 and 580,000 L of carbon tetrachloride were discharged to these disposal sites along with 190 kg of plutonium and americium. A substantial amount of carbon tetrachloride remains in the unsaturated soils beneath these disposal sites and continues to contribute to the long-term contamination of the groundwater.

In January 1992, the U.S. Environmental Protection Agency (EPA) and the Washington Department of Ecology (Ecology) authorized the U.S. Department of Energy (DOE) to proceed with the removal of the carbon tetrachloride from the unsaturated soils through an Expedited Response Action (ERA). An ERA is a provision included in the *Comprehensive Environmental Response, Compensation, and Liability Act of 1980* (CERCLA) that allows for accelerated cleanup activities. The goal of the ERA is to halt the spread of the carbon tetrachloride from the disposal sites to the groundwater beneath Hanford's 200 West Area by removing carbon tetrachloride from the unsaturated soils. In addition, a pilot test for the removal of carbon tetrachloride from the groundwater was proposed in early 1993 and is in preparation.

Several innovative technology demonstrations are being conducted in coordination with the cleanup of volatile organics and may eventually be integrated with the cleanup efforts. The demonstration of innovative technologies is being conducted as part of the DOE's Volatile Organic Compounds-Arid Integrated Demonstration (VOC-Arid ID). The VOC-Arid ID was initiated in 1991 by DOE's Office of Technology Development to develop, demonstrate, and deploy the suite of technologies to characterize, remediate, and/or monitor arid or semiarid sites containing VOC (e.g., carbon tetrachloride) with or without associated metal and radionuclide contamination. The program is jointly managed by the Pacific Northwest Laboratory and Westinghouse Hanford Company. The initial focus of the integrated demonstration is the Hanford Site's 200 West Area carbon tetrachloride contaminated area. In the early phases of the VOC-Arid ID, activities are focused primarily on those technologies, characterization and monitoring, drilling, and gas-phase treatment that may immediately improve the performance or support the cleanup of volatile organics.

CONTAMINANT DISTRIBUTION

Carbon tetrachloride and associated contaminants are found in both the groundwater and in the overlying unsaturated soils.

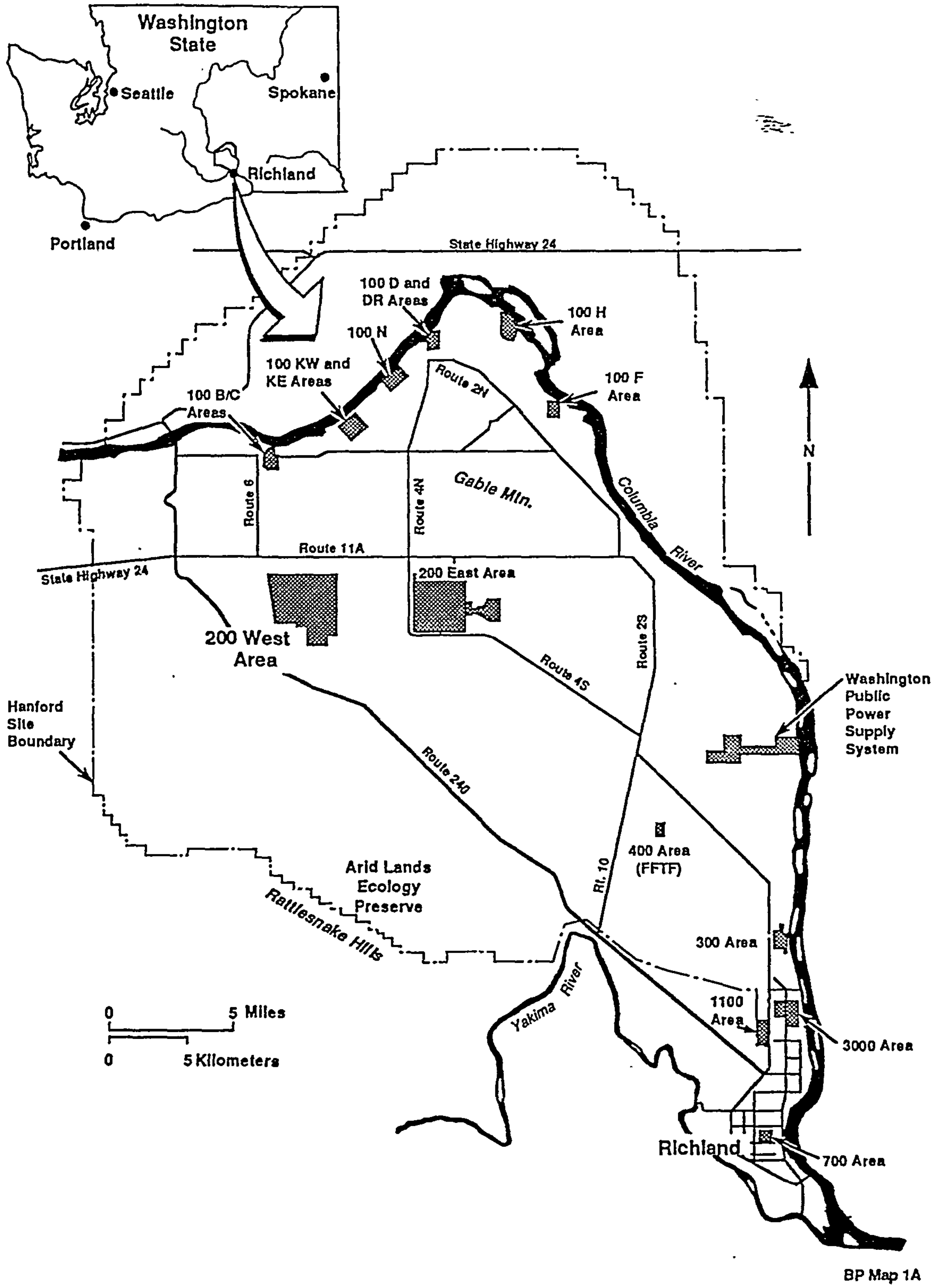

FIGURE 1. HANFORD SITE MAP AND LOCATION OF THE 200 WEST AREA.

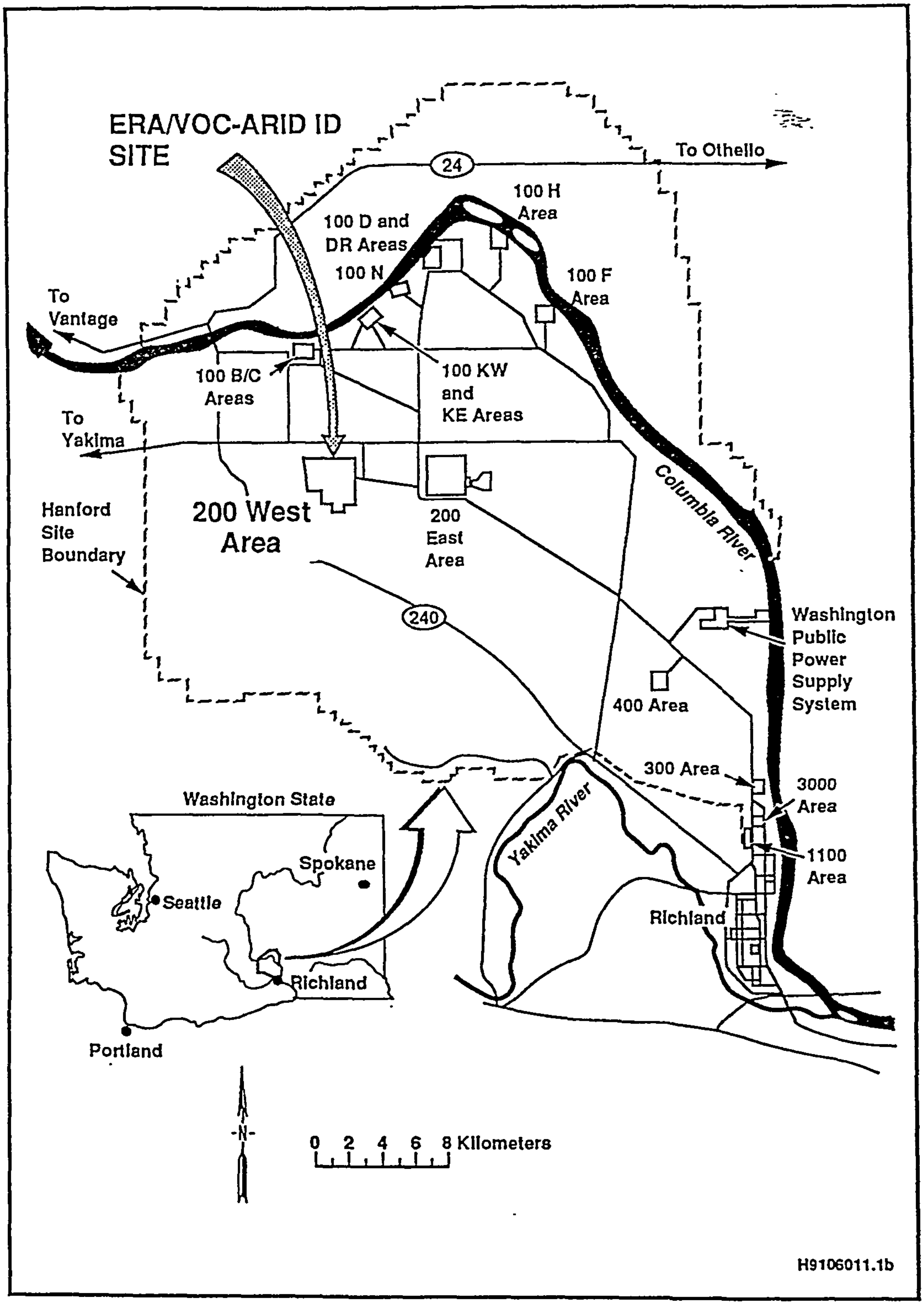

FIGURE 2. SITE MAP OF THE 200 WEST AREA.

Over 95% of the carbon tetrachloride is suspected as remaining within the unsaturated soils and it likely exists in several phases (Rohay et al., 1992; Last and Rohay, 1993). Co-contaminants and/or degradation products in the soils also include chloroform; mono-, di-, and tributylphosphates; dibutylbutylphosphonate; lard oil (a complex mixture of triglycerides); cadmium; nitrates; hydroxides; fluorides; and sulfates. These contaminants coexist with 200 kg of plutonium and americium (Figure 3).

The extent and concentration of dissolved carbon tetrachloride in the groundwater is depicted by the contaminant plume map illustrated in Figure 4, which exhibits three primary centers of mass. The highest concentrations of dissolved carbon tetrachloride approach 8,000 ppb. The total carbon tetrachloride groundwater plume area exceeds 11 km^2. The vertical distribution of carbon tetrachloride in the unconfined aquifer is uncertain because of the limited number of groundwater sample analyses from deeper depths in the aquifer. The mass of carbon tetrachloride in the groundwater is estimated to range from 5,250 to 15,740 kg, assuming a constant concentration to a depth of 10 m in the unconfined aquifer and a porosity ranging from 10% to 20%. This mass represents approximately 2% of the total estimated carbon tetrachloride disposed to the subsurface.

Other volatile organic contaminants found in the groundwater beneath the 200 West Area mixed with the carbon tetrachloride at concentrations greater than their respective drinking water standards include chloroform and trichloroethylene (TCE). Chloroform is intimately associated with carbon tetrachloride and is suspected to be a byproduct of carbon tetrachloride degradation. It was used as a cleaning solvent in various 200 West Area facilities.

In addition to carbon tetrachloride, chloroform, and TCE, several other hazardous and radionuclide contaminants related to 200 West Area liquid waste disposal practices are found comingled in the groundwater beneath the 200 West Area at levels above their respective drinking water standards. These contaminants include arsenic, chromium, cyanide, fluoride, nitrate, undifferentiated alpha and beta particle emitters, tritium, technetium-99, iodine-129, uranium, and plutonium-239/240.

BASELINE REMEDIATION APPROACH

The Environmental Division of Westinghouse Hanford Company, which conducts environmental restoration for the DOE, initiated an ERA using a phased approach to characterize and remediate the residual carbon tetrachloride contamination remaining in the unsaturated soils, where the bulk of the carbon tetrachloride resides. The remediation is phased to accelerate cleanup, constrain costs, and meet the safety requirements for working in a radiologically contaminated area.

Soil vapor extraction from existing and recently installed wells in the vicinity of the disposal sites is currently used to remove the carbon tetrachloride from the unsaturated soils. Soil vapor extraction technology utilizes a vacuum system to induce air flow through the soil, volatilizing carbon tetrachloride from the soil into the air stream. The relatively high volatility of carbon tetrachloride, in conjunction with the relatively high permeability and low moisture content characteristics, makes this technology successful in the vicinity of the disposal sites. In addition, this technology is superior at this site as the plutonium is left behind in the soils.

Currently the extracted vapor is collected aboveground in granular-activated carbon (GAC) canisters. The GAC canisters are sent offsite to a facility for regeneration and the destruction of carbon tetrachloride. High-efficiency particulate air (HEPA) filtration and radiological monitoring (in addition to organic monitoring) are conducted as a precaution against radiological particulate transport.

The current wellfield design incorporates extraction wells for removing soil vapor from the subsurface and monitoring wells to provide an indication of the radial influence of the extraction wells. Within radiologically contaminated soils, the extraction and monitoring wells are selected from existing steel-cased vertical wells and perforated at intervals or deepened below the radiological contaminant and screened. This approach minimizes potential exposure to radiological contaminant, costs, and duration of drilling. Other extraction and monitoring wells are being installed around the perimeter of the disposal sites outside the radiologically contaminated soils. To enhance the rate and removal efficiency of carbon tetrachloride from the soils, further study of the wellfield design will be conducted. This will include modeling and investigations of wellfield enhancement and monitoring technologies, including passive extraction techniques.

An action to remove the volatile organics (i.e., carbon tetrachloride, TCE, and chloroform) from the groundwater is also being investigated at this time. The proposed work includes conducting pilot tests in coordination with the VOC-Arid ID to look at in-well sparging technologies. These technologies are of special interest in that this technique allows the separation of the volatiles from the contaminants remaining in the groundwater (i.e., arsenic, chromium, cyanide, fluoride, nitrate, undifferentiated alpha and beta particle emitters, technetium-99, iodine-129, uranium, and plutonium-239/240).

INNOVATIVE TECHNOLOGY DEMONSTRATIONS

Concurrent with the baseline remediation phase, a detailed search for as well as evaluation of innovative drilling, characterization, extraction, monitoring, and onsite treatment technologies is being conducted.

Drilling

Development and demonstration of innovative drilling techniques for accessing the contaminated soils and groundwater are being conducted to improve upon current baseline drilling methods (i.e., vertical cable tool drilling). Three projects are under way to address drilling technology needs: (1) horizontal drilling, (2) sonic drilling, and (3) cone penetrometer (CPT) system.

<u>Sonic Drilling.</u> The primary method for accessing subsurface soils for characterization is through vertical drilling. At

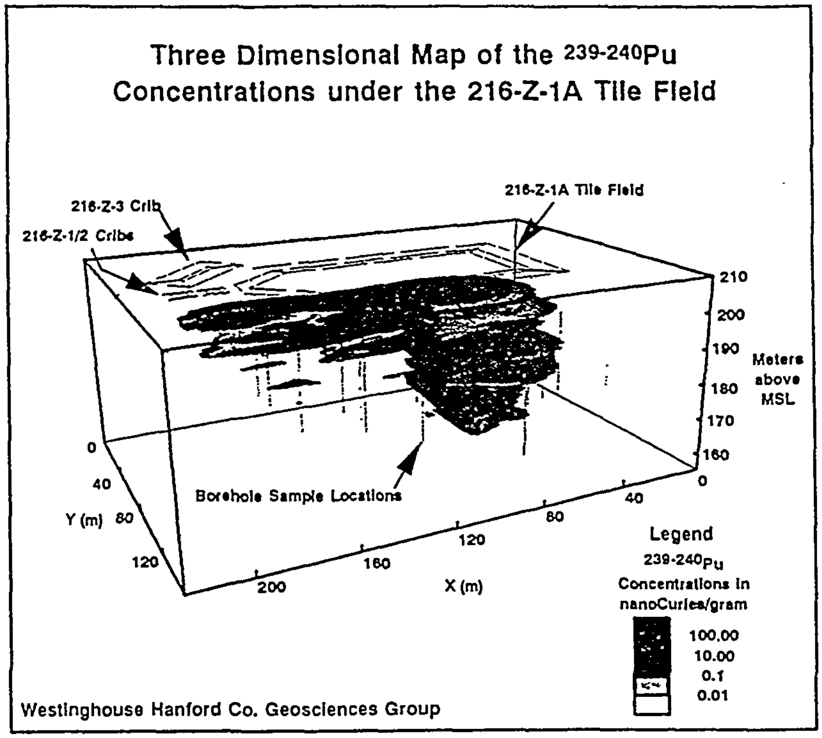

FIGURE 3. DISTRIBUTION OF PLUTONIUM AT THE 216-Z-1A TILE FIELD.

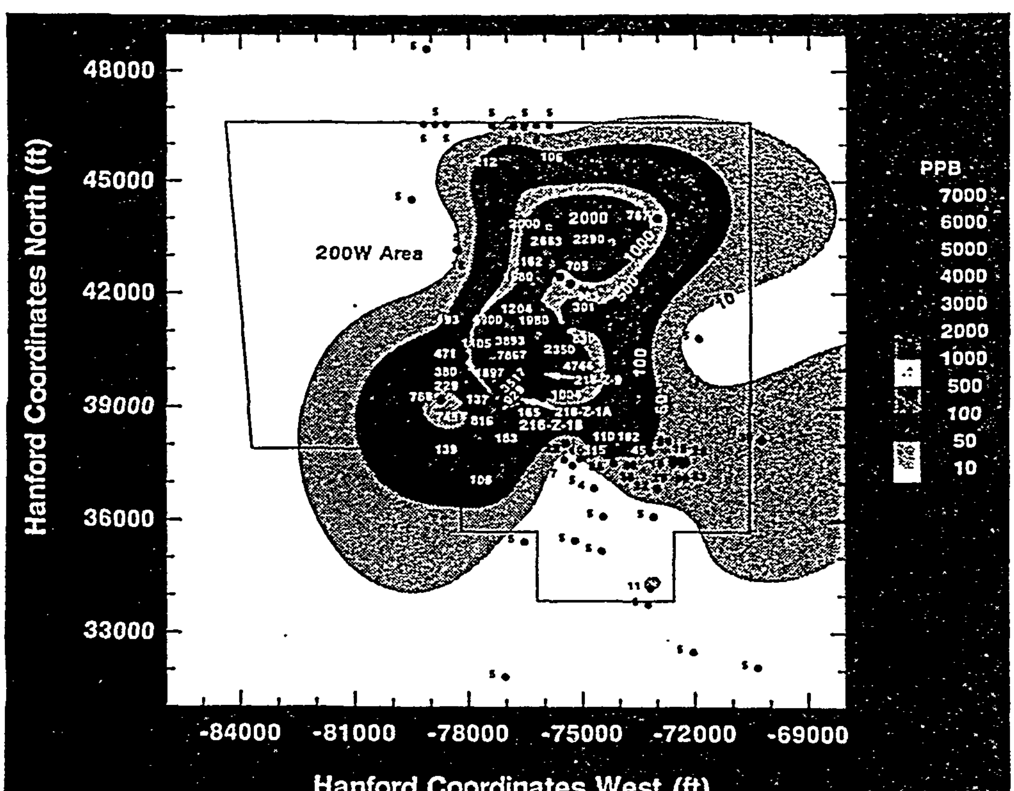

FIGURE 4. CARBON TETRACHLORIDE CONTAMINANT PLUME IN GROUNDWATER.

Hanford, cable-tool drilling techniques have been used because (1) quality soil samples can be taken while drilling through unconsolidated sands, gravels, and cobbles; (2) containment of drill cuttings in radiological or chemical contamination is possible; and (3) there are minimal secondary wastes from drilling fluids. A disadvantage of the cable-tool technique is that it is generally slower than other well drilling techniques.

Sonic drilling has been evaluated as an alternative to the cable-tool technique while still providing the advantages of reliability, containment, and waste minimization. The sonic drilling method's primary component is the sonic drill head. Sonic frequencies range up to 150 Hz with a peak force of 21,800 kg. The hole is advanced through shearing or cutting the formation. Drill cuttings are captured in a core tube and brought to the surface via a wireline winch retrieval system.

The effectiveness of sonic drilling was recently demonstrated at Hanford between September 1991 and May 1992 (Volk, 1992). Eleven wells were drilled using this method. The sonic drilling system was used in the installation of a vapor extraction/monitoring well to a depth in excess of 60 m. In addition, a large-diameter pipe (24.5-cm OD) was used to drill to an unprecedented depth (in a single pass) of 45.72 m. The sonic drill averaged 7.3 m/day) as compared to the average rate of the cable-tool wells of 3.8 m/day (exclusive of "downtime"). Testing of the sonic drilling system demonstrated that the sonic drill system can be used to penetrate Hanford Site soils at a rate double that of the cable-tool rig, while maintaining sampling data objectives. Core samples are obtained using no fluids or air and minimizing waste.

As a result of sonic testing activities during fiscal year 1992, three areas of improvement are needed to increase the productivity of the method. These include drill string integrity, drill bit design, and sonic head reliability. Additional testing around the carbon tetrachloride disposal sites will focus on developing, testing, and evaluating the technology for deeper depths and larger diameter well completions and the impact on samples collected during drilling. In addition, a sonic angle hole test will be conducted to determine whether this technology is feasible for installing holes to support characterization and remediation of cribs, ditches, ponds, and underground tanks. Other outyear activities will include testing system enhancements focused on automating the sonic drilling method.

<u>Cone Penetrometer Testing (CPT).</u> The successful application of cone penetrometer techniques at the Hanford Site has been an area of much speculation because of the coarse gravelly soils typical of much of the site. The cone penetrometer (Figure 5) is an instrumented rod that is hydraulically inserted into the soil. The CPT has been used extensively for soil studies and more recently in environmental investigations in soils more amenable to standard CPT use. In ideal soil conditions, the cone penetrometer can penetrate up to approximately 1 m/minute, a rate significantly greater than standard drilling methods, with little waste generation (no drill cuttings and no drilling fluids) and to depths approaching 60 m. Several soil parameters can be measured in situ with various probe instrumentation. Samples of soil gases and groundwater can also be extracted for analysis. Another recent innovative CPT feature is its grouting capabilities, which allow grouting to seal the boring as the probe is withdrawn from the soils. Cone penetrometer technology holds great promise for in situ characterization without the need for expensive drilling or handling contaminated drill cuttings.

Demonstrations of the standard CPT at the Hanford Site (Cassem, 1993) and resultant difficulties in penetrating the Hanford soils have led to modifying the CPT truck and its operation. These modifications include an increase in truck weight from the commercial standard of 18,200 kg to approximately 31,865 kg, higher hardness cone tips, and improved grouting capabilities. In recent testing, a total of 34 penetration tests were conducted on the Hanford Site. The maximum depth reached was 45 m, and in one case the CPT was used to install a permanent soil-gas monitoring probe near one of the disposal sites. In addition, soil-gas sampling and radiological characterization using the cone penetrometer were successfully conducted during selected tests. All test locations were successfully grouted to seal the boreholes according to regulatory requirements. Another objective accomplished was the testing of various tip geometries to determine the effectiveness in penetration where three different shapes were tested in addition to the standard tip. No significant differences in damage or penetration rates were detected.

Continued work is planned for 1993 to further refine the CPT system. Additional development of the cone penetrometer system will be conducted including (1) decontamination procedures, (2) cone rod and rod connections, (3) soil sampling capabilites, (4) characterization of probe connections, and (5) extraction well installation. In addition, CPT is being developed to support characterization of mixed waste sites, with specific emphasis involving radiologically contaminated soils associated with cribs and underground storage tanks.

<u>Directional Drilling.</u> The ability to construct horizontal wells in contaminated soils will increase the ability to assess the levels of contamination under structures (e.g., buildings, tanks, burial grounds) accurately, perform in situ geophysical monitoring, and apply in situ remediation methods such as barrier walls, microbial injection, and vapor extraction. Directional drilling techniques have been demonstrated at the DOE's Savannah River Site as a method for accessing contaminated zones at depths >30 m for characterization and more effective removal of VOC (Kaback et al., 1989). Shallower applications of directional drilling have been used frequently for river-crossing cable installations and in other near-surface utility applications. In addition, the technology has recently been demonstrated at Sandia National Laboratory and at Tinker Air Force Base for shallow environmental applications. However, application of current technology to Hanford is not likely to be effective because of the geology of the site, the need for containment and minimization of drilling fluids, and the depths of 24 to 75 m required to address the primary contamination zones.

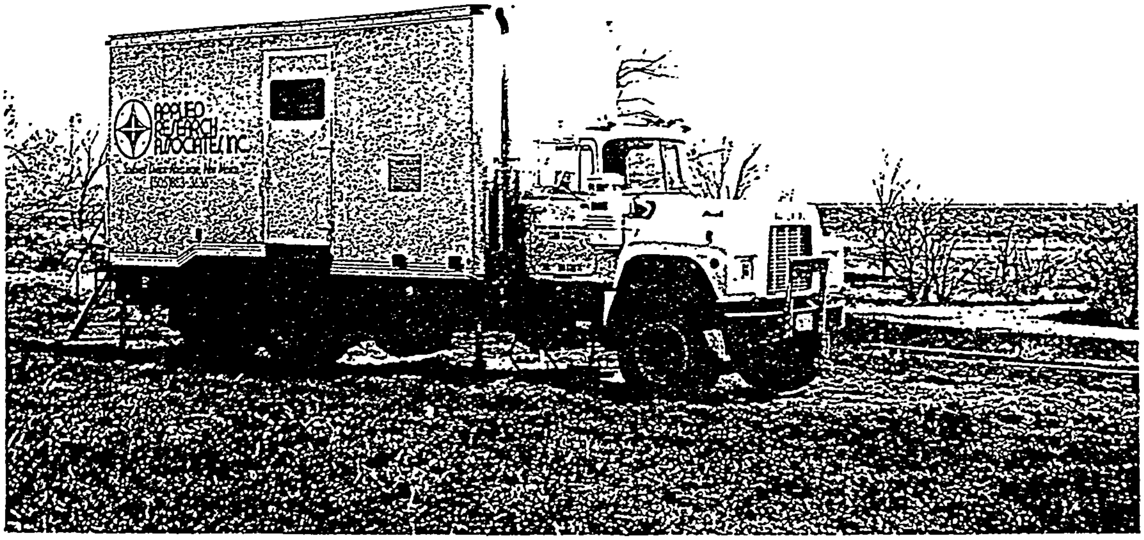

FIGURE 5. CONE PENETROMETER TESTING TRUCK.

To support the shallow horizontal drilling needs at arid sites, the Ditch Witch Directional Drilling System will perform an engineering evaluation test at Hanford during February and March of 1993. Two borings will be advanced in the Hanford formation to evaluate performance and determine whether additional testing of this method is feasible at the Site.

To support the deeper horizontal drilling, the feasibility of horizontal/directional drilling using an air turbine motor in the unconsolidated sands, gravels, and cobbles typical of Hanford Site geology will be tested and evaluated at a "clean" location. Other subsystems to the overall horizontal drilling system will be evaluated and tested as appropriate. These subsystems include a directional control survey system and a circulation and negative air containment system. The long-term focus of the project will be the development of a horizontal/directional drilling system that minimizes secondary waste, maintains total containment of effluents and particulates, provides precision directional control, and obtains samples that meet data quality objectives. Initial tests of horizontal drilling subsystems at clean sites will facilitate timely development of components and minimize the likelihood of personnel and equipment contamination.

Contingent on the success of the clean site test, follow-on work would involve drilling and installing a horizontal vacuum extraction well within the carbon tetrachloride contaminated zone in Hanford's 200 West Area. The primary purpose of this installation is to evaluate vacuum extraction efficiency between vertical and horizontal extraction wells. Additional areas of focus during the horizontal test will include waste minimization techniques to reduce the cost of drilling operations, demonstration of appropriate containment systems to ensure radiological safety during drilling operations, and assessment of a remotely operated directional drilling system for use in highly contaminated sediments.

Site Characterization

Standard site characterization tasks conducted as part of the ERA include soil gas sampling, groundwater sampling, and pipeline integrity testing. Sample analysis is generally conducted with a combination of field screening and laboratory techniques. Because of the costs associated with sampling and analysis, schedules, and safety concerns, several technologies are being investigated including the Science and Engineering Associates Membrane Instrumentation and Sampling Technique (SEAMIST) (a tradename of Science and Engineering Associates, Inc.), EMFLUX (a tradename of Quaddrell Services, Inc.) and PETREX (a tradename of Northwest Research Institute, Inc.), and Unsaturated Flow Apparatus.

SEAMIST. Determining the identity and distribution of VOC in the subsurface is critical to the design and operation of the vapor extraction system (VES). Currently, there is no technology at Hanford for routinely collecting in situ soil-gas samples during borehole drilling. Instead, soil samples that are brought to the surface may be screened at the drill site with a photoionization device or transferred to containers for subsequent laboratory analysis. However, much of the VOC may be easily lost from the sample by disturbance during drilling, sample retrieval, and/or sample handling.

The SEAMIST system (Figure 6) is a borehole instrumenta-

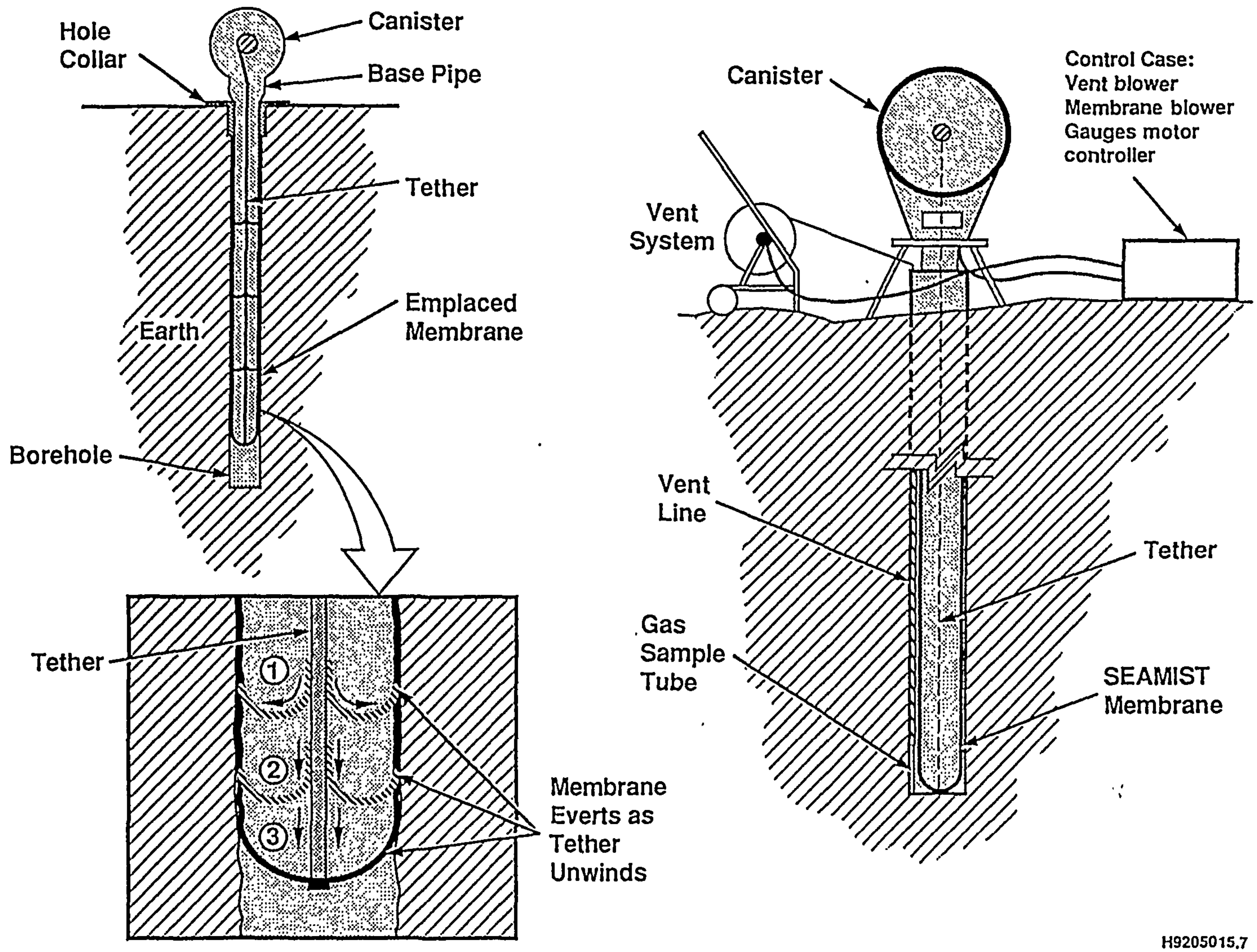

FIGURE 6. SEAMIST System.

tion sampling system for in situ characterization and sampling of the subsurface. The original system was designed by Science and Engineering Associates, Inc. of Santa Fe, New Mexico, to have various sampling devices for liquid and/or vapor built into the membrane for deployment at preselected depths in uncased boreholes. Usually the boreholes at the Hanford Site must be cased to remain open; therefore, the SEAMIST system tested at Hanford was adapted for use in cased boreholes at variable depths. In addition, the system was designed specifically for collecting in situ soil-gas and permeability measurements.

For the testing at Hanford (Rohay and McClellan, 1992), the SEAMIST system was used to collect in situ samples between drilling runs. The sampling technique uses a sample tube lowered into the borehole, followed by an impermeable membrane that is deployed by pressurized air. The membrane is forced out of a canister into the borehole. As the membrane is deployed, it presses against the borehole wall or casing, like a continuous packer. The sample tube is used to collect vapor samples from the soil layer below the bottom of the borehole. A pump is used to pull the vapor to the surface, where it is screened with a field monitoring device until the level of contaminant has reached its maximum concentration, at which point a syringe sample is collected for analysis using gas chromatography. As the gas is pulled to the surface, the flow rate, the pressure at the flowmeter outlet, and the withdrawal zone pressure are measured for use in calculating air permeability.

This SEAMIST system was tested in six 200 West Area boreholes principally to demonstrate its deployment in boreholes of various depths and diameters and to evaluate its capability to collect in situ soil-gas samples and air permeability measurements at specified depths. The SEAMIST system was used 37 times between March and July 1992 to conduct this test. Borehole diameters ranged from 18 to 30 cm; deployment depths ranged from 6 to 60 m. Evaluation of the test results indicate that soil-gas samples were successfully collected in each case using the SEAMIST system and that VOC concentrations collected with the SEAMIST are significantly higher than those analyzed in soil samples from the same depths. Some specific improvements to the system were identified and implemented during the testing. For example, a disposable membrane material was substituted for the original rugged membrane because of difficulties in decontamination. The SEAMIST system subsequently has been used for in situ soil-gas sampling during environmental restoration investigations.

EMFLUX and PETREX. Surface field tests are being conducted to determine the performance of the EMFLUX and PETREX technologies for defining the distribution of volatile organic compounds (VOC) and other contaminants relative to that of conventional soil-gas survey methods.

The EMFLUX soil-gas collection system is a passive, surface-based system, owned and operated by Quaddrell Services Inc. This system employs a variety of sorbent collectors, depending on the nature and number of target contaminants. Once retrieved, the contaminants are thermally desorbed from the sorbent collectors and analyzed using a gas chromatograph/mass spectrometer. The results are used to calculate a flux rate out of the soil for each contaminant. The EMFLUX device is currently being tested at the Hanford Site (Rohay and Last, 1992).

The PETREX Technology is a passive soil-gas sampling technology owned and operated by Northwest Research Institute, Inc., (NERI) of Lakewood, Colorado. The technology is used to collect and detect trace quantities of a broad range of VOC and semivolatile organic compounds near the ground surface. The samplers consist of two ferromagnetic wires coated with an activated carbon adsorbent and placed in a glass tube. Each sampler is typically placed in a shallow hole, backfilled, and left in the ground for several days, depending on the VOC loading rates. Loading rates are determined by a time-sequence PETREX test. Once retrieved, the compounds are analyzed by NERI's Curie-point desorption mass spectrometer. The PETREX device is currently being tested at the Hanford Site (Rohay and Last, 1992).

Unsaturated Flow Apparatus. The Unsaturated Flow Apparatus (UFA) (Figure 7) is being developed to determine transport parameters and other transport information necessary for defensible model predictions of the migration of VOC and water in the subsurface environment and for the development of restoration strategies in the unsaturated zone (Conca and Wright, 1992). This type of information is site specific and traditionally requires lengthy, costly, and difficult experiments to obtain data under unsaturated moisture conditions. Application of the UFA circumvents this problem by allowing rapid achievement of steady-state unsaturated flow conditions in soils/sediments through the use of centrifugal force and precision fluid flow. Acquisition of data requires hours to days rather than months to years.

With this apparatus, soils/sediments are subjected to various controlled fluxes and driving forces and respond by changing their water content. Once the water content is fixed at the target value and the system has achieved hydraulic steady state, transport parameters are determined from associated methods: (1) the electrical conductivity of the sample is measured using a 1 kHz conductivity bridge and the diffusion coefficient calculated from the electrical conductivity using the Nernst-Einstein relationship, (2) hydraulic conductivity is determined from the driving force and flux density, and (3) the effluent is monitored/collected/analyzed for chemical interactions and retardation effects.

Wellfield Development

Several innovative technologies are being investigated to enhance the removal of the carbon tetrachloride in soils and groundwater. These technologies include in situ heating for organics in the vadose zone and in-well sparging for the VOC in groundwater.

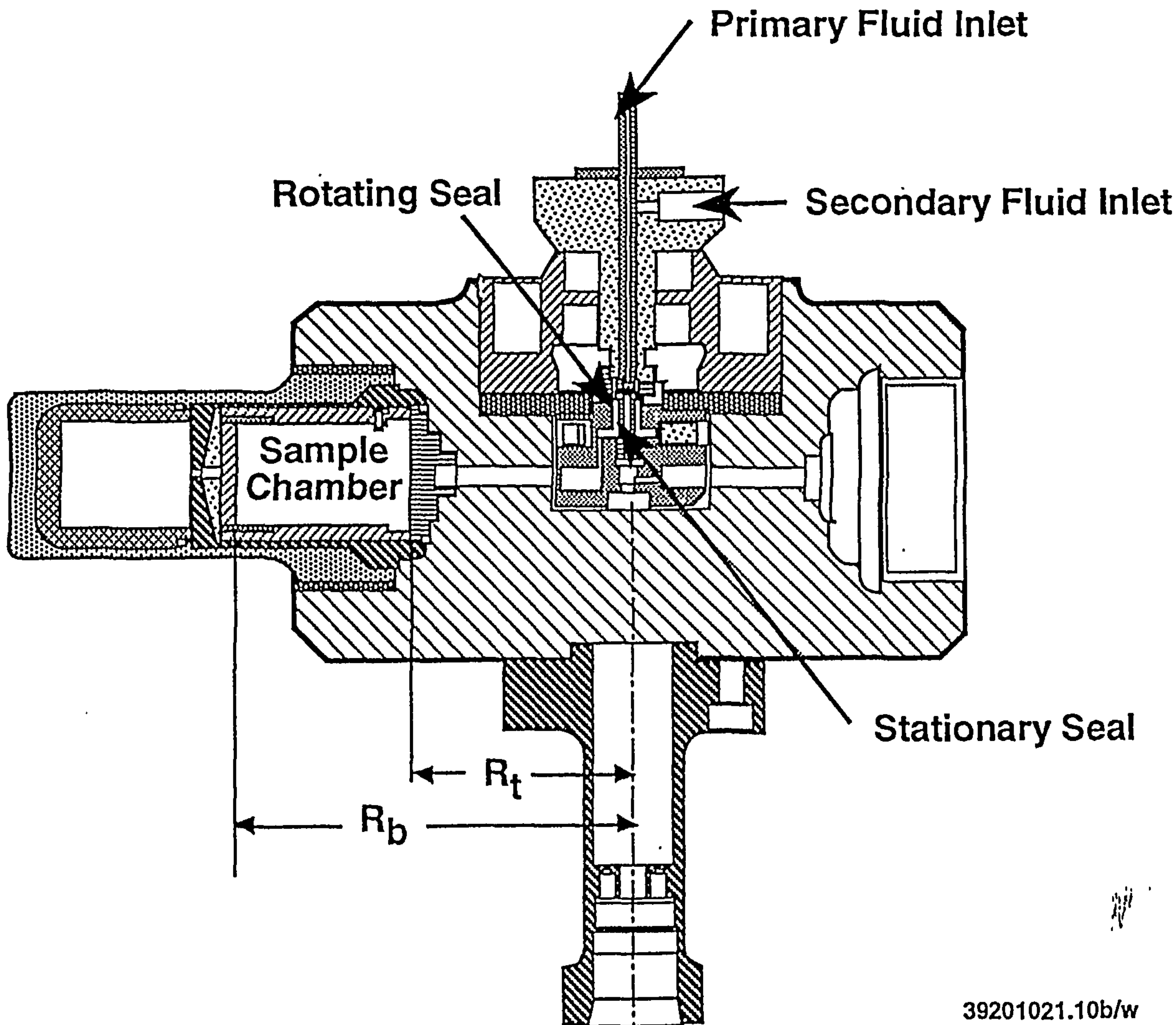

FIGURE 7. UNSATURATED FLOW APPARATUS CENTRIFUGE.

In Situ Heating. A six-phase soil heating technology is being developed by Battelle Pacific Northwest Laboratories to increase subsurface soil temperatures and subsequently increase volatilization and removal of VOC from less permeable soils. In 1991, a 30-kW test facility capable of operating voltages up to 30 kV line-to-line was developed to investigate soil venting along with soil heating. Using this test system, data were obtained on the scale-up characteristics of six-phase electrical fields and the ability of these fields to heat and dry sandy soil at various initial moisture concentrations, simulating different locations within the vadose zone. It was found that extremely uniform heating could be achieved by the six-phase method.

Soil heating tests will be conducted this spring at an uncontaminated outdoor site, and data from a bench-scale laboratory test will help determine the ability to remove trichloroethylene (TCE) and perchloroethylene (PCE) from clays by combined soil heating and soil venting. These activities will culminate in detailed specifications for a full-scale power system for testing at the VOC-Nonarid ID site, which may have applicability to removal of carbon tetrachloride.

In-Well Sparging. The Environmental Restoration (ER) and VOC-Arid Integrated Demonstration programs are combining efforts to test and develop an innovative remediation technology for in-situ treatment of groundwater contaminated with VOCs at the Hanford Site. This technology is referred to as in-well sparging. In-well sparging technology was originally developed by a consortium of German academic and industry groundwater specialists in the late 1980's to treat VOC-contaminated groundwater in Europe (Herrling and Buermann, 1990). More recently, variations on the German design have been developed by Stanford University faculty (Gvirtzman and Gorelick, 1992) for the same purpose in the United States.

The basic concept behind in-well sparging involves drawing groundwater into a well bore where it is sparged with air or some other gas. The sparging action induces an air-stripping effect which causes the VOC contaminants to partition preferentially into the vapor phase as predicted by Henrys Law. The VOC vapors released from the groundwater are subsequently removed from the well bore via vacuum extraction. Treated groundwater is then permitted to flow back into the aquifer.

In-well sparging utilizes a unique groundwater well design that produces a vertical circulation of groundwater in the vicinity of the remediation well during treatment operations. These specialized wells are screened over two intervals in the aquifer. The upper screen is positioned across the water table while the lower screen is placed deeper into the aquifer, typically at the bottom of the contaminant plume. Screens are hydraulically isolated by a packer system within the well bore, although controlled unidirectional groundwater flow is permitted between screened intervals. Contaminated groundwater is extracted from the aquifer through the lower screen, pumped into the upper screened interval, and treated by sparging. Treated groundwater then flows back into the aquifer through the upper screen. The overall hydrologic effect is the development of a groundwater circulation cell around the well. As the in-well sparging system operates, groundwater within the circulation cell becomes sequentially cleaner and cleaner (with respect to VOCs) over time.

Two in-well sparging systems will be assessed in a joint ER/VOC-Arid ID demonstration scheduled to begin in late summer of calendar year 1993. The treatability study will include field-scale pilot tests of the German-developed vacuum vaporizer well and Stanford University in-well sparging systems. Data collected during the treatability study will be used to assess the effectiveness of the technology and to develop and refine engineering design, configuration, and operating conditions for both systems. Ultimately, the results of the treatability study will be used in a focused feasability study to assess in-well sparging technology as a potential alternative for remediation of carbon tetracloride-contaminated groundwater at the Hanford site, and to provide additional development and design criteria for transfer of this innovative technology to private industry in the United States.

Monitoring

Techniques for subsurface and aboveground VOC monitoring are needed to support operations of the VES and improve the efficiency of the cleanup. Improved sensor systems for carbon tetrachloride and other VOC are being developed to meet these needs and also to support development and demonstration of enhanced remediation systems. Several monitoring systems are being evaluated including (1) portable acoustic wave sensor, (2) fiber optic spectrochemical emission sensor, and (3) fiber optic sensor systems based on solvatochromatic dyes.

Portable Acoustic Wave. The portable acoustic wave (PAWS) instrument (a tradename of Sandia National Laboratory) (Frye et al., 1992) was designed to measure both the wave velocity and wave attenuation of a surface acoustic wave (SAW) based on distortions that occur to a chemically sorbed coating. From these measurements, the PAWS instrument can determine the identity of an isolated chemical species as well as its concentration in the vapor phase in the range of 50 ppm to more than 100,000 ppm. The PAWS instrument and associated downhole sensor system represent significant advancements for in situ VOC vapor phase sensing.

This instrument consists of two parts: (1) a downhole sensor and electronic assembly, and (2) a surface signal processing unit with computer interface. The downhole sensor, which is approximately 3 in. in diameter by 30 in. long, can be tethered to a winch assembly for lowering into existing boreholes of 4-in.-diameter or larger to conduct in situ measurements of VOCs (e.g., carbon tetrachloride). The downhole sensor is constructed with two SAW devices that are coated with identically sorptive polymer materials. These two devices are physically separated, allowing one to become a reference device isolated from the environment and the other the sensing device which is challenged by a gaseous phase to detect the desired species. Sensing of contaminants is a result of specific species sorbing into the polymer coating, causing its mass to increase and soften. These physical changes in the polymer result in changes in the wave velocity and wave attenuation, which are detected by the electronics. Prior calibration using known concentrations of the target species and the temperature correction and performance of the reference SAW device allows identification of the target species as well as measurement of its concentration.

At the surface, signal cables from the downhole sensor enter a data acquisition and control system that processes and acquires the relevant sensor data and activates several gas valves in the probe. The gas valves of the PAWS instrument work in parallel with a pump, which purges the borehole at a screened interval with an upper and lower packer in place. The borehole has screened intervals at various depths that allow for soil-gas sampling at these intervals when packers are deployed. Packers consist of inflatable components that are part of the downhole probe and that provide a seal above and below the sensor elements for in situ measurements. A computer provides for data storage, reduction, and analysis using sensor baseline data, calibration data, and real-time measurements. Concentrations are then calculated from these data based on signals from the SAW devices and known performance characteristics of the system.

This technology was developed by Sandia National Laboratory under a DOE program that sought to produce sensors with sufficient sensitivity to monitor the relatively high concentrations of VOC vapor underground. Initial testing was performed at the DOE Savannah River Site, and the technology was used for some borehole investigations during sensor development. Further development led to a 1991 patent on the technology and its incorporation into a dual output device for use in the VOC-Arid-ID. In June 1992, the PAWS instrument was brought to the Hanford Site and demonstrated at the 200 West area in the off-gas stream of a vapor extraction system. The instrument was successfully demonstrated again in July 1992 in the field with the cone penetrometer, a soil probe used to collect soil gas samples. Sandia is currently working with fabrication vendors on the commercialization of the technology and marketing for widespread use.

Fiber Optic Spectrochemical Emission Sensor (HaloSnif). The HaloSnif (a tradename of Pacific Northwest Laboratory) instrument (Anheier et al., 1993) was designed to detect chlorine-containing compounds in a gaseous phase by passing the suspect gas through a plasma chamber where the excited chlorine atom would exhibit optical emissions whose intensity was proportional to concentration. This instrument measures carbon tetrachloride concentrations in off-gas streams in the range of 10 ppm to 10,000 ppm in a continuous real-time monitoring mode. The instrument overcomes the limited range and slow response times of currently available instrumentation.

The HaloSnif instrument uses a radio-frequency power supply to provide a high-power, high-frequency signal to electrodes that surround a ceramic plasma tube chamber. The suspect VOC stream is mixed with helium and fed through the plasma chamber, where the high-energy plasma excites the chlorine atoms. The emission is carried by the fiber optic link to a spectral filter and detector. The technology offers a low detection limit and wide dynamic range, making it suitable for use in off-gas process streams or for real-time monitoring of vapor concentrations from boreholes or other soil sampling probes.

In 1988, a proof-of-concept sensor was developed at Pacific Northwest Laboratory that was specific for measuring the concentration of VOCs containing chlorine. With funding obtained in late 1991, a prototype instrument was constructed for field testing at the Hanford Site VOC-Arid-ID. Additional support for the technology came from the U.S. Air Force at Tinker Air Force Base and from the Savannah River Laboratory. This technology was demonstrated in off-gas and in a vadose zone well stream in September 1992 at the VOC-Arid-ID and is scheduled for further demonstration in 1993. A commercial partner is working with Pacific Northwest Laboratory on the development of the radio frequency power supply and is considering future manufacturing and marketing of the entire instrument.

Fiber Optic Sensor Systems Based on Solvatochromatic Dyes. Solvatochromic dyes have been used with success in silicone polymer matrices for constructing reversible gasoline and methylene chloride sensors (Angel et al., 1991). Nile Red and Reichardts's dyes were used in developing carbon tetrachloride selective reversible fiber-optic-based sensors, and detection limits have been observed in the 100 ppb range. Additional developments included sensors that can detect trichloroethylene with a linear working range of 10 ppb to 1000 ppb. A project currently funded within the IP is currently focused on incorporating these developments into a sensor to measure carbon tetrachloride. This approach serves as an example of an innovative technology going through the IP development process for subsequent field demonstration in the VOC-Arid-ID.

Lawrence Livermore National Laboratory has been a pioneer in the development of fiber-optic chemical sensors (optrodes) and in their application to field measurements of environmental contaminants. Optrodes have been designed for many different types of compounds. Recently Lawrence Livermore developed a successful integrating-type optrode for the Hazardous Waste Remedial Action Program that measures trichloroethylene and chloroform. Funding was approved by the IP for continued development and deployment of this sensor technology in 1992 and 1993 for detection of carbon tetrachloride. The Lawrence Livermore sensor was demonstrated in September 1992 at the Hanford Site in the laboratory as proof of principle in detection of carbon tetrachloride for the VOC-Arid-ID.

Treatment Technologies

Several innovative technologies are being investigated in coordination with the ERA to improve the treatment process of the carbon tetrachloride, either aboveground or in situ. As the existing treatment process is costly and requires the offsite regeneration of the GAC, it is the goal of the ERA to find a technology, or combination of technologies, to treat carbon tetrachloride at the site at less expense and still meet regulatory requirements.

These offgas treatment systems either regenerate GAC canisters or remove the VOC from the offgas stream to minimize the loading of GAC canisters. Technologies are also being developed to destroy the VOC to minimize the need for GAC and eliminate the need for liquid-phase VOC treatment. These technologies include (1) membrane separation process, (2) high-energy electrical discharge (corona) technology being developed at the Pacific Northwest Laboratory, and (3) a tunable hybrid plasma (THP) system being developed at Massachusetts Institute of Technology.

Gas Membrane System. A pilot-scale membrane separation system (Field, 1993) will be demonstrated this year to evaluate its effectiveness for reducing VOC loading of GAC canisters, thereby reducing the ultimate cost of GAC regeneration. Membrane Technology & Research, Inc. will be demonstrating the pilot-scale commercial system in collaboration with Westinghouse Hanford Company. Performance and cost analyses will be conducted as part of the demonstration to fully evaluate the benefits of the membrane separation process for enhancing the existing VES system.

The organic vapor/air separation technology involves the preferential transport of organic vapors through a nonporous, gas-separation membrane (Figure 8). Transport is achieved by the influence of a pressure difference between the feed and permeate sides of the membrane, provided by a vacuum pump on the permeate side or pressure pump on the feed side. Performance of the membrane separation is effected by membrane selectivity and pressure ratio.

Tunable Hybrid Plasma. A system that combines RF or electric heating with low-energy electron beams to destroy VOCs in vapor phase for onsite, in-line offgas treatment has been developed by MaMIT (Bromberg et al., 1993). This low-temperature plasma technology could provide significant advantages for treatment of large throughputs of extracted gas streams containing CCl4 and other VOCs (such as CCl3, TCE, and PCE). The potential advantages include complete (>99.9%) destruction of VOCs using onsite equipment, low cost, versatility, no need for regenerables, and minimal pre- and post-treatment requirements.

Special emphasis is being placed on identification and control of secondary wastes and destruction byproducts from the tunable hybrid plasma prior to field testing.

Six-Phase Soil Heating. Current technology for remediation of VOCs is focused on recovery of the contaminant from the subsurface followed by aboveground destruction (Virden et al., 1992). Methods to destroy the contaminant in place can reduce the cost of treatment, increase the efficiency of treatment, and provide a safer alternative to retrieval. Six-phase soil heating, mentioned earlier in this paper for enhancing vapor extraction can also be used to destroy VOCs insitu. Research efforts are under way to evaluate the feasibility of producing a high energy corona in situ to destroy VOC in place. Development of the six-phase technology is an important preliminary step toward the development of the high energy corona technology for demonstration at Hanford.

Laboratory tests will be accomplished this year to investigate the electrical characteristics of high-energy corona in soils, and a bench-scale test will study the ability to remove carbon tetrachloride from a silty soil. Later, a field test will be completed with the objective to demonstrate removal of volatile and semivolatile organic compounds to acceptable levels and above-surface treatment of soil off gases as they are removed.

Groundwater Bioremediation. An in situ bioremediation process is being developed that uses native microorganisms to anaerobically destroy carbon tetrachloride and nitrates in groundwater (Figure 9). Evidence of carbon tetrachloride degradation by microorganisms native to the Hanford Site was first obtained with a denitrifying consortium from groundwater samples (Skeen et al., 1992). Additional studies conducted at laboratory, bench, and pilot scales confirmed that nitrate and carbon tetrachloride were degraded by these natural microorganisms (Hansen, 1990).

A field test site is being developed in the 200 West Area north of the ERA site to demonstrate and evaluate the effectiveness of in situ bioremediation of carbon tetrachloride in groundwater. The first test site borehole was drilled in 1991 to obtain aquifer samples for biological, chemical, and physical characterization. A second, adjacent borehole is being installed to obtain additional well-to-well field data on the geohydrology, geochemistry and microbiology of the test site. Laboratory- and bench-scale studies using sediment and core samples from the field site are being conducted to obtain kinetic information and design data for field testing. Field data, as well as laboratory- and bench-scale kinetic data, are being incorporated into a three-dimensional transport and reaction model provided by Rice University under a collaborative agreement. Predictive simulations will be conducted to evaluate design options for the field test site and to aid in the evaluation of test data. Critical to the success of the technology, parallel research efforts are under way to assess the potential impacts that bioremediation may have on long-term radionuclide or heavy metal mobility and aquifer permeability, and to improve the understanding of the mechanisms of biodegradation of carbon tetrachloride and chloroform. Field test site development will continue through 1992 and 1993, with initial tests of microbial stimulation scheduled for 1994.

CONCLUSION

By combining actual cleanup actions and technology demonstrations, short- and long-term cost and time savings are expected. Cost savings have already been realized through the

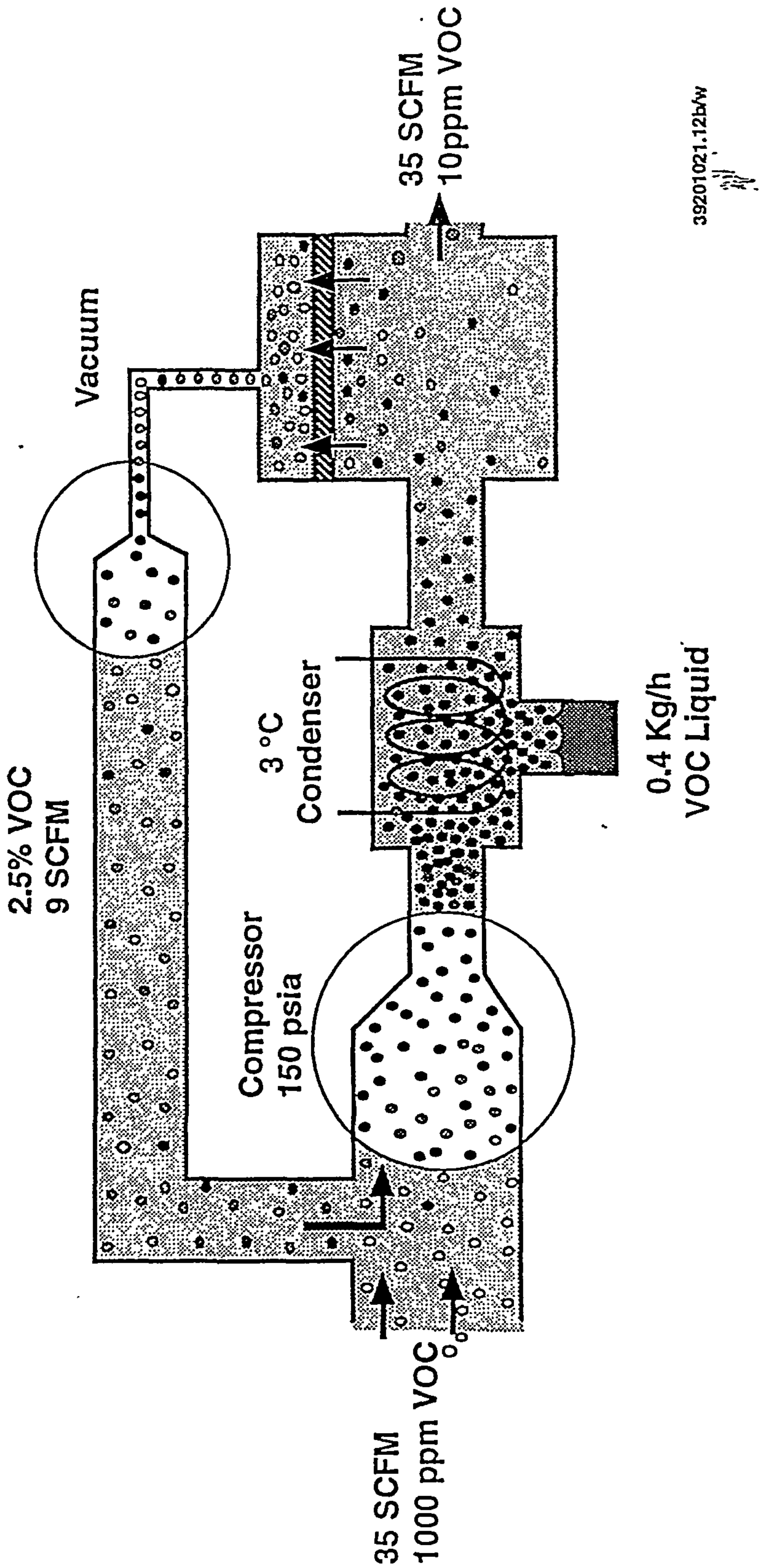

FIGURE 8. SCHEMATIC OF HIGH-PRESSURE GAS MEMBRANE SEPARATION.

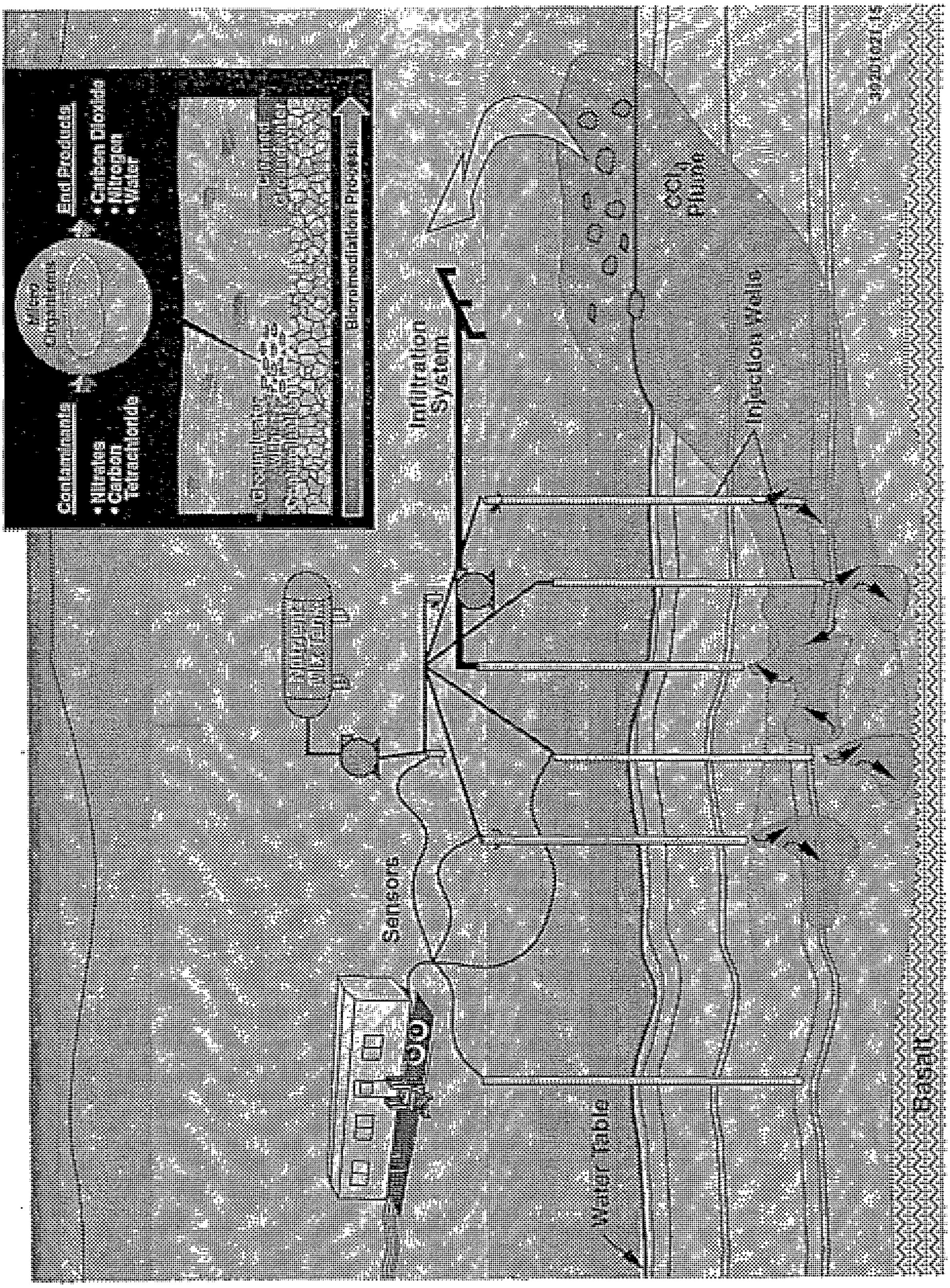

FIGURE 9. BIOLOGICAL TREATMENT SYSTEM.

use of innovative drilling and characterization technologies. Longer term cost savings are expected, especially with the introduction of wellfield enhancement technologies, sensors, and treatment processes.

REFERENCES

Angel, S. M., Kulp, T. J., Myrick, M. L., and Langry, K. C., 1991, "Development and Applications of Fiber Optic Sensors," in *Chemical Sensor Technology*, Vol. 2, N. Yamazoe, Ed., Kodansha Ltd. and Elsevier Science Publishers B. V., Amsterdam.

Anheier, N., Olsen, K. B., Osantowski, R. R., Evans, J. C., and Griffin, J. W., 1993, "Fiber Optic Spectrochemical Emission Sensor: Detection of Volatile chlorinated Compounds in Air and Water Using Ultra-thin Membranes," 183rd Meeting of the Electrochemical Society, Inc. (PNL-SA-21614)

Bromberg, L., Cohn, D. R., Koch, M., Patrick, R. M., and Thomas, P., 1993, "Decomposition of Dilute Concentrations of Carbon Tetrachloride in Air by an Electron-Beam Generated Plasma," *Physics Letters* A 173, 293-299.

Cassem, B. R., 1993, *Demonstration of a Heavyweight Cone Penetrometer at the Hanford Site*, WHC-SD-EN-TRP-003, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Conca, J. L., and Wright, J. V., 1992, "Direct Determinations of Unsaturated Flow and Transport," *Proceedings of the 12th Annual Hydrology Days Conference*, Fort Collins, Colorado, pp 103-1167.

Field, J.G., 1993, *Integrated Test Plan for the Gas Membrane Separation System*, WHC-SD-EN-TP-017, Westinghouse Hanford Company, Richland, Washington.

Frye, G. C., Cemosek, R. W., and Marin, S. J., 1992, "Portable Acoustic Wave Sensors for Volatile Organic Compounds," *Proceedings of the Information Exchange Meetings on Characterization, Sensors, and Monitoring Technologies*, Dallas, Texas.

Hansen, E. J., 1990, "The Transformation of Tetrachloromethane Under Denitrifying Conditions by a Subsurface Bacterial Consortium and Its Isolates," M.S. Thesis, Washington State University, Pullman, Washington.

Herrling, B., and Buermann, W., 1990, "A New Method for In-Situ Remediation of Volatile Contaminants in Groundwater—Numerical Simulation of the Flow Regime." Computational Methods in Subsurface Hydrology—*Proceedings of the Eighth International Conference on Computational Methods in Water Resources*, held in Venice, Italy. Computational Mechanics Publications, Southhampton-Boston. Copublished with Springer-Verlag, Berlin.

Gvirtzman, H., and Gorelick, S. M., 1992, "The Concept of In-Situ Vapor Stripping for Removing VOCs from Groundwater," *Transport in Porous Media*, 8, 71-92.

Kaback, D. S., Looney, B. B., Corey, J. C., Wright III, L. M., and Steele, J., 1989, "Horizontal Wells for In-Situ Remediation of Groundwater and Soils," paper presented at the National Water Well Association Outdoor Action Conference, Orlando, Florida.

Last, G. V., and Rohay, V. J., 1993, *Refined Conceptual Model for the Volatile Organic Compounds-Arid Integrated Demonstration and 200 West Area Carbon Tetrachloride Expedited Response Action*, PNL-8597, Pacific Northwest Laboratory, Richland, Washington.

Rohay, V. J., Last, G. V., King, V. L., and Doremus, L. A., 1992, *FY 92 Site Characterization Status Report and Data Package for the Carbon Tetrachloride Site*, WHC-SD-EN-TI-063, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Rohay, V. J., and McLellan, G. W., 1992, *Integrated Test Plan for Demonstration of a Sonic Drilling System and the SEAMIST System*, WHC-SD-EN-AP-075, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Rohay, V. J., and Last, G. V., 1992, *Integrated Test Plan for Demonstration of EMFLUX and PETREX Passive Soil-Gas Sampling Technologies*, WHC-SD-EN-AP-103, Rev. 0., Westinghouse Hanford Company, Richland, Washington.

Skeen, R. S., Roberson, K. R., Brouns, T. M., Petersen, J. M., Shouche, M., 1992, "In-Situ Bioremediation of Hanford Groundwater," *Proceedings of the First Federal Environmental Restoration Conference*, Vienna, Virginia.

Virden, J. W., Heath, W. O., Goheen, S. C., Miller, M. C., Mong, G. M., and Richardson, R. L., 1992, "High-Energy Corona for Destruction of Volatile Organic Contaminants in Process Off-Gases," Vol. 1: *Nuclear and Hazardous Waste Management*, Spectrum '92.

Volk, B. W., 1992, *Results of Testing the Sonic Drilling System at the Hanford Site*, WHC-SD-EN-TRP-002, Rev. 0, Westinghouse Hanford Company, Richland, Washington.