

TECHNOLOGY EVALUATION REPORT

PEROX-PURE<sup>TM</sup> CHEMICAL OXIDATION TECHNOLOGY

RISK REDUCTION ENGINEERING LABORATORY  
OFFICE OF RESEARCH AND DEVELOPMENT  
U.S. ENVIRONMENTAL PROTECTION AGENCY  
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16. ABSTRACT This report evaluates the perox-pure chemical oxidation technology's ability to remove volatile organic compounds (VOC) and other organic contaminants present in liquid wastes. This report also presents economic data from the Superfund Innovative Technology Evaluation (SITE) demonstration and three case studies. The perox-pure chemical oxidation technology was developed by Peroxidation Systems Inc. (PSI), to destroy dissolved organic contaminants in water. The technology uses ultraviolet (UV) radiation and hydrogen peroxide to oxidize organic compounds present in water at parts per million levels or less. This treatment technology produces no air emissions and generates no sludge or spent media that require further processing, handling, or disposal. Ideally, the end products are water, carbon dioxide, halides (for example, chloride), and in some cases, organic acids. The technology uses medium-pressure, mercury-vapor lamps to generate UV radiation. The principal oxidants in the system, hydroxyl radicals, are produced by direct photolysis of hydrogen peroxide at UV wavelengths. The perox-pure chemical oxidation technology was demonstrated under the SITE Program at Lawrence Livermore National Laboratory Site 300 in Tracy, CA. Over a 3-week period in September 1992, about 40,000 gallons of VOC contaminated ground water was treated in the perox-pure system. For the SITE demonstration, the perox-pure system achieved trichloroethene (TCE) and tetrachloroethene (PCE) removal efficiencies of about 99.7 & 97.1 percent, respectively.		
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## Foreword

The Superfund Innovative Technology Evaluation (SITE) program was authorized in the 1986 Superfund Amendments and Reauthorization Act (SARA). The program is a joint effort between EPA's Office of Research and Development (ORD) and Office of Solid Waste and Emergency Response (OSWER). The purpose of the program is to assist the development of innovative hazardous waste treatment technologies, especially those that offer permanent remedies for contamination commonly found at Superfund and other hazardous waste sites. The SITE program evaluates new treatment methods through technology demonstrations designed to provide engineering and cost data for selected technologies.

A field demonstration was conducted under the SITE program to evaluate the perox-pure™ chemical oxidation technology's ability to treat groundwater contaminated with volatile organic compounds. The technology demonstration took place at the Lawrence Livermore National Laboratory in Tracy, California. The purpose of the demonstration was to obtain information on the performance and cost of the technology and to assess its use at this and other uncontrolled hazardous waste sites. Documentation consists of two reports: (1) this Technology Evaluation Report, which describes field activities and laboratory results, and (2) an Applications Analysis Report, which interprets the data and discusses the potential applicability of the technology.

Copies of this report can be purchased from the National Technical Information Service, Ravensworth Building, Springfield, Virginia 22161, (703) 487-4600. Reference copies will be available at EPA libraries in the Hazardous Waste Collection.

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Risk Reduction Engineering Laboratory

## Abstract

This report evaluates the perox-pure™ chemical oxidation technology's ability to remove primarily volatile organic compounds (VOC) from groundwater at the Lawrence Livermore National Laboratory (LLNL), Site 300 in Tracy, California. The perox-pure™ chemical oxidation technology was developed by Peroxidation Systems, Inc., to destroy dissolved organic contaminants in water. The technology uses ultraviolet (UV) radiation and hydrogen peroxide to oxidize organic compounds present in water at parts per million levels or less. This treatment technology produces no air emissions and generates no sludge or spent media that require further processing, handling, or disposal. Ideally, the end products are water, carbon dioxide, halides (for example, chloride), and, in some cases, organic acids. The technology uses medium-pressure, mercury-vapor lamps to generate UV radiation. The principal oxidants in the system, hydroxyl radicals, are produced by direct photolysis of hydrogen peroxide at UV wavelengths.

The perox-pure™ chemical oxidation technology was demonstrated under the Superfund Innovative Technology Evaluation (SITE) program at LLNL Site 300 in Tracy, California. Over a 3-week period in September 1992, about 40,000 gallons of VOC-contaminated groundwater was treated in the perox-pure™ system. The technology demonstration had the following primary objectives: (1) determine the ability of the perox-pure™ system to remove VOCs from groundwater at the LLNL site under different operating conditions, (2) determine whether treated groundwater met applicable disposal requirements at the 95 percent confidence level, and (3) gather information necessary to estimate treatment costs, including process chemical dosages and utility requirements. The secondary objective for the technology demonstration was to obtain information on the presence and types of by-products formed during the treatment.

For the SITE demonstration, the perox-pure™ system achieved trichloroethene (TCE) and tetrachloroethene (PCE) removal efficiencies of about 99.7 and 97.1 percent, respectively. The system also achieved chloroform, 1,1-dichloroethane (DCA); and 1,1,1-trichloroethane (TCA) removal efficiencies of 93.1, 98.3, and 81.8 percent, respectively. In general, the perox-pure™ system produced an effluent that contained (1) TCE, PCE, and DCA below detection limits, and (2) chloroform and TCA slightly above detection limits. The treatment system effluent met California drinking water action levels and federal drinking water maximum contaminant levels for TCE, PCE, chloroform, DCA, and TCA at the 95 percent confidence level.

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## Abbreviations, Acronyms, and Symbols

AAR	Applications Analysis Report
AOX	Adsorbable organic halide
ARAR	Applicable or relevant and appropriate requirement
°C	Degree Celsius
CaCO <sub>3</sub>	Calcium carbonate
CDEP	Department of Environmental Protection, State of Connecticut
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFR	Code of Federal Regulations
COC	Chain of custody
DCA	1,1-dichloroethane
1,1-DCE	1,1-dichloroethene
1,2-DCE	1,2-dichloroethene
EPA	U.S. Environmental Protection Agency
ESBL	Engineering-Science Berkeley Laboratory
FS	Feasibility study
°F	Degree Fahrenheit
GC	Gas chromatography
gpd	Gallons per day
gpm	Gallons per minute
GSA	General Services Area
GTC	General Testing Corporation
H <sub>2</sub> O <sub>2</sub>	Hydrogen peroxide
hν	Ultraviolet radiation
ICP	Inductively coupled plasma
kW	Kilowatt
kWh	Kilowatt-hour
L	Liquid
LLNL	Lawrence Livermore National Laboratory
Lpm	Liters per minute
MCL	Maximum contaminant level
μg/L	Micrograms per liter
mg/L	Milligrams per liter
mL	Milliliter
mL/min	Milliliters per minute
μmho/cm	Micromhos per centimeter
MS/MSD	Matrix spike/matrix spike duplicate
N	Normal (equivalents/liter) solution
NA	Not applicable
ND	Not detected
NTU	Nephelometric Turbidity Unit
OH·	Hydroxyl radical
ORD	Office of Research and Development
OSWER	Office of Solid Waste and Emergency Response
P	Polyethylene
%	Percent
PCE	Tetrachloroethene
POC	Purgeable organic carbon
ppm	Parts per million

## Abbreviations, Acronyms, and Symbols (Continued)

PRC	PRC Environmental Management, Inc.
PSI	Peroxidation Systems, Inc.
QAPP	Quality Assurance Project Plan
QA/QC	Quality assurance/quality control
RI	Remedial investigation
RCRA	Resource Conservation and Recovery Act
RPD	Relative percent difference
RREL	Risk Reduction Engineering Laboratory
SARA	Superfund Amendments and Reauthorization Act
S/SD	Sample/sample duplicate
SDWA	Safe Drinking Water Act
SITE	Superfund Innovative Technology Evaluation
SVOC	Semivolatile organic compound
TC	Total carbon
TCA	1,1,1-trichloroethane
TCE	Trichloroethene
TER	Technology Evaluation Report
TIC	Tentatively identified compound
TOC	Total organic carbon
TOX	Total organic halide
TRL	Target reporting limit
TSR	Technical systems review
UCL	Upper confidence limit
UV	Ultraviolet
VOA	Volatile organic analysis
VOC	Volatile organic compound

## Conversion Factors

	<i>To Convert From</i>	<i>To</i>	<i>Multiply By</i>
<b>Length:</b>	inch	centimeter	2.54
	foot	meter	0.305
	mile	kilometer	1.61
<b>Area:</b>	square foot	square meter	0.0929
	acre	square meter	4,047
<b>Volume:</b>	gallon	liter	3.78
	cubic foot	cubic meter	0.0283
<b>Mass:</b>	pound	kilogram	0.454
<b>Energy:</b>	kilowatt-hour	megajoule	3.60
<b>Power:</b>	kilowatt	horsepower	1.34
<b>Temperature:</b>	(°Fahrenheit - 32)	°Celsius	0.556

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## **SECTION 1**

### **EXECUTIVE SUMMARY**

#### **INTRODUCTION**

The perox-pure™ chemical oxidation technology, developed by Peroxidation Systems, Inc. (PSI), was evaluated under the U.S. Environmental Protection Agency (EPA) Superfund Innovative Technology Evaluation (SITE) program. The perox-pure™ technology demonstration was conducted at Lawrence Livermore National Laboratory (LLNL), Site 300 in Tracy, California, over a 3-week period in September 1992.

The perox-pure™ chemical oxidation technology is designed to destroy dissolved organic contaminants in water. The technology uses ultraviolet (UV) radiation and hydrogen peroxide to oxidize organic compounds present in water at parts per million (ppm) levels or less. This treatment technology produces no air emissions and generates no sludge or spent media that require further processing, handling, or disposal. Ideally, end products are water, carbon dioxide, halides (for example, chloride), and in some cases, organic acids. The technology uses medium-pressure, mercury-vapor lamps to generate UV radiation. The principal oxidants in the system, hydroxyl radicals, are produced by direct photolysis of hydrogen peroxide at UV wavelengths.

The perox-pure™ chemical oxidation treatment system (Model SSB-30) used for the SITE technology demonstration was assembled from the following portable, skid-mounted components: a chemical oxidation unit, a hydrogen peroxide feed module, an acid feed module, a base feed module, a UV lamp drive, and a control panel. The oxidation unit consists of six reactors in series with one 5-kilowatt (kW) UV lamp in each reactor; the unit has a total volume of 15 gallons. The UV lamp is mounted inside a UV-transmissive quartz tube in the center of each reactor so that water flows through the space between the reactor walls and the quartz tube. Circular wipers mounted on the quartz tubes periodically remove any solids that have accumulated on the tubes.

The perox-pure™ system requires little attention during operation and can be operated and monitored remotely, if needed. Remotely monitored systems can be connected to devices that automatically dial a telephone to notify responsible parties at remote locations of alarm conditions. Remotely operated and monitored systems are hard-wired into centrally located control panels or computers through programmable logic controllers.

The technology demonstration had the following primary objectives: (1) determine the ability of the perox-pure™ system to remove volatile organic compounds (VOC) from groundwater at the LLNL site under different operating conditions, (2) determine whether treated groundwater met applicable disposal requirements at the 95 percent confidence level, and (3) gather information necessary to estimate treatment costs, including process chemical dosages and utility requirements. The secondary objective for the technology demonstration was to obtain information on the presence and types of by-products formed during treatment.

This report presents information from the SITE demonstration that will be useful for implementing the perox-pure™ chemical oxidation technology at Superfund and Resource Conservation and Recovery Act hazardous waste sites. Section 2 presents an overview of the SITE program; discusses the perox-pure™ technology and demonstration site selection; and presents the demonstration objectives, the evaluation criteria and regulatory considerations, the project organization, and technical operations. Section 3 describes the perox-pure™ system, discusses the factors affecting the perox-pure™ system's performance, and outlines the support equipment and facilities and utility requirements. Section 4 describes the site selected for the technology demonstration. Section 5 describes the demonstration procedures, which include the testing program, field activities, sampling procedures and field measurements, analytical procedures, deviations from the demonstration plan, technical systems review, and community relations and technology transfer. Section 6 discusses the critical and noncritical parameters for the technology demonstration, summarizes the analytical data for those parameters, evaluates the perox-pure™ system's performance, and describes field operational and equipment problems. Section 7 presents EPA's and the developer's costs for the technology demonstration. Section 8 presents conclusions and recommendations. References are provided at the end of this report.

## **OVERVIEW OF THE SITE DEMONSTRATION**

Groundwater from a shallow aquifer at the LLNL site was selected as the waste stream for evaluating the perox-pure™ chemical oxidation system. About 40,000 gallons of groundwater contaminated with VOCs was treated during the demonstration. The principal groundwater contaminants were trichloroethene (TCE) and tetrachloroethene (PCE), which were present at concentrations of about 1,000 and 100 micrograms per liter ( $\mu\text{g/L}$ ), respectively. Groundwater was pumped from two wells into a 7,500-gallon bladder tank to minimize any variability in influent characteristics. In addition, cartridge filters were used to remove suspended solids



greater than 3 micrometers in size from the groundwater before it entered the tank. Treated groundwater was stored in two 20,000-gallon steel tanks before being discharged.

The technology demonstration was conducted in three phases. Phase 1 consisted of eight runs of raw groundwater, Phase 2 consisted of four runs of spiked groundwater, and Phase 3 consisted of two runs of spiked groundwater to evaluate the effectiveness of quartz tube cleaning. These phases are described below.

During Phase 1, the principal operating parameters for the perox-pure™ system, hydrogen peroxide dose, influent pH, and flow rate (which determines the hydraulic retention time), were varied to observe treatment system performance under different operating conditions. Preferred operating conditions, those under which the concentrations of effluent VOCs would be reduced to below target levels for spiked groundwater used in Phases 2 and 3, were then determined for the system.

Phase 2 involved spiked groundwater and reproducibility tests. Groundwater was spiked with about 200 to 300 µg/L each of chloroform; 1,1-dichloroethane (DCA); and 1,1,1-trichloroethane (TCA). These compounds were chosen because they are difficult to oxidize and because they were not present in the groundwater at high concentrations. This phase was also designed to evaluate the reproducibility of treatment system performance at the preferred operating conditions determined in Phase 1.

During Phase 3, the effectiveness of the quartz tube wipers was evaluated during two runs using scaled and clean quartz tubes.

During the demonstration, samples were collected at several locations, including the treatment system influent; effluent from Reactors 1, 2, and 3; and the treatment system effluent. Samples were analyzed for VOCs, semivolatile organic compounds, total organic carbon (TOC), total carbon (TC), purgeable organic carbon (POC), total organic halides (TOX), adsorbable organic halides (AOX), metals, pH, alkalinity, turbidity, temperature, specific conductance, hydrogen peroxide residual, and hardness. In addition, samples of influent to Reactor 1 and treatment system effluent were collected and analyzed for acute toxicity to freshwater organisms. The hydrogen peroxide, acid, and base solutions were also sampled and analyzed to verify concentrations.

Strict quality assurance and quality control procedures were followed to produce well documented sampling and analytical data of known quality. To accomplish this goal, a detailed and comprehensive quality assurance project plan (QAPP) was developed before the demonstration. During the demonstration, field sampling and measurement activities, field laboratory analytical activities, and off-site laboratory analytical activities for critical parameters were audited. In general, all sampling and analytical activities conformed with the procedures described in the QAPP. Only one minor issue was noted during the audits. The issue was regarding nonavailability of calibration data for a factory calibrated wattmeter. The SITE team resolved this issue by recalibrating the wattmeter at the end of demonstration and providing the calibration data to EPA's quality assurance manager.

## **RESULTS FROM THE SITE DEMONSTRATION**

For the spiked groundwater, PSI determined the following preferred operating conditions: (1) influent hydrogen peroxide level of 40 milligrams per liter (mg/L); (2) hydrogen peroxide level of 25 mg/L in the influent to Reactors 2 through 6; (3) an influent pH of 5.0; and (4) a flow rate of 10 gallons per minute (gpm). At these conditions, the effluent TCE, PCE, and DCA levels were generally below detection limit (5 µg/L) and effluent chloroform and TCA levels ranged from 15 to 30 µg/L. The average removal efficiencies for TCE, PCE, chloroform, DCA, and TCA were about 99.7, 97.1, 93.1, 98.3, and 81.8 percent, respectively.

For the unspiked groundwater, the effluent TCE and PCE levels were generally below detection limit (1 µg/L) with corresponding removal efficiencies of about 99.9 and 99.7 percent. The effluent TCA levels ranged from 1.4 to 6.7 µg/L with corresponding removal efficiencies ranging from 35 to 84 percent.

The perox-pure™ system effluent met California drinking water action levels and federal drinking water maximum contaminant levels (MCL) for TCE, PCE, chloroform, DCA, and TCA at the 95 percent confidence level.

The quartz tube wipers were effective in keeping the tubes clean and appeared to reduce the adverse effect scaling has on contaminant removal efficiencies.

Bioassay tests showed that the perox-pure™ system effluent was acutely toxic to freshwater organisms, although the influent was not toxic. Comparison of effluent toxicity data with that of

hydrogen peroxide residual in the effluent (10.5 mg/L) indicated that the effluent toxicity may be due to hydrogen peroxide residual rather than perox-pure™ treatment by-products. Additional studies are needed to draw any conclusion on the effluent toxicity.

TOX removal efficiencies ranged from 93 to 99 percent. AOX removal efficiencies ranged from 95 to 99 percent.

For spiked groundwater, during reproducibility runs, the system achieved average removal efficiencies of 38 percent and about 93 percent for TOC and POC, respectively.

The temperature of groundwater increased at a rate of 12 °F per minute of UV exposure in the perox-pure™ system. Since the oxidation unit is exposed to the surrounding environment, the temperature increase may vary depending upon the ambient temperature or other atmospheric conditions.

## **SECTION 2**

### **INTRODUCTION**

This section provides information about SITE program; discusses the perox-pure™ technology; summarizes the technology and demonstration site selection; and describes the demonstration objectives, evaluation criteria and regulatory considerations, project organization, and technical operations.

#### **OVERVIEW OF THE SITE PROGRAM**

The Superfund Amendments and Reauthorization Act of 1986 (SARA) (Section 209(b)) amends Title III of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) of 1980 by adding Section 311. Section 311 directs the U.S. Environmental Protection Agency (EPA) to establish an "Alternative or Innovative Treatment Technology Research and Demonstration Program." In response to the SARA directive, EPA established a formal program to accelerate the development, demonstration, and use of new or innovative treatment technologies. This program is called the SITE program.

The overall goal of the SITE program is to "carry out a program of research, evaluation, testing, development, and demonstration of alternative or innovative treatment technologies... which may be utilized in response actions to achieve more permanent protection of human health and welfare and the environment." Specifically, the program's goal is to maximize the use of alternatives to land disposal in cleaning up Superfund sites by encouraging the development and demonstration of new, innovative treatment and monitoring technologies. The SITE program categorizes alternative technologies by their development status, as follows:

- Available alternative technologies that have been fully proven and are available for commercial or private use
- Innovative alternative technologies that have been fully developed but lack complete cost or performance information
- Emerging alternative technologies that are in an early stage of development involving laboratory or pilot testing

One of the most important components of the SITE program is the Demonstration program, through which EPA evaluates field- or pilot-scale technologies that can be scaled up for

commercial use. The Demonstration program is the primary focus of the SITE program because the innovative alternative technologies evaluated are close to being available for remediation of Superfund sites. The main objective of the Demonstration program is to develop performance, engineering, and cost information for innovative technologies. With this information, potential users can make informed decisions on whether to use these technologies to remediate hazardous waste sites. Specifically, potential users can use this information to compare the technology's effectiveness and cost to other alternatives and make sound judgments regarding the technology's applicability to a specific site.

The results of the demonstration identify possible limitations of the technology, the potential need for pre- and post-processing of wastes, the types of wastes and media to which the process can be applied, the potential operating problems, and the approximate capital and operating costs. The demonstrations also permit evaluation of long-term risks. Demonstrations usually occur at Superfund sites or under conditions that duplicate or closely simulate actual wastes and conditions found at Superfund sites to ensure the reliability of the information collected and acceptability of the data by users.

Developers are responsible for demonstrating their innovative systems at selected sites and are expected to pay the costs to transport equipment to the site, operate the equipment on site during the demonstration, and remove the equipment from the site. EPA is responsible for project planning, sampling and analysis, data quality assurance and quality control, report preparation, and information dissemination.

Two important elements of the Demonstration program include (1) technology selection and (2) site selection. These two elements are discussed below.

### **Technology Selection**

Technologies are accepted into the program through an annual solicitation published in the Commerce Business Daily and trade journals. In response to the solicitations, technology developers submit proposals to EPA addressing the following selection criteria:

- Technology Factors. Description of the technology and its history; identification of effective operating range; materials handling capabilities; application to hazardous waste site cleanup; mobility of equipment; capital and operating costs; advantages over existing comparable technologies;

previous performance data; and identification of health, safety, and environmental problems.

- Capability of the Developer. Development of other technologies; completion of field tests; experience, credentials, and availability of key personnel; and capability to commercialize and market the technology.
- Approach to Testing. Operations plan; materials and equipment; range of testing; health and safety plan; monitoring plan; quality assurance plan; assignment of responsibilities; backup treatment system plan; and regulatory compliance plan.

## **Site Selection**

Once EPA has evaluated the technology proposals and notified the developers of their acceptance into the SITE program, the demonstration site selection process begins. Potential SITE demonstration locations include federal and state Superfund removal and remedial sites, sites from other federal agencies, and developers' facilities. The criteria used to screen and select candidate demonstration sites include the following:

- Compatibility of waste with the technology
- Volume of waste
- Variability of waste
- Availability of data characterizing the waste
- Accessibility of waste
- Applicability of the technology to site cleanup goals
- Availability of required utilities (such as power sources, water sources, and sewers)
- Support of community, state and local governments, and potentially responsible parties

The staff of EPA's Office of Research and Development (ORD) and Office of Solid Waste and Emergency Response (OSWER) evaluate the technology proposals and, with the assistance of EPA regional offices, match the technologies to appropriate sites. OSWER and ORD establish the criteria for the selection of each demonstration site. Candidate demonstration sites are selected

cooperatively by OSWER, ORD, EPA regional offices, and the states. The final demonstration site is selected in close cooperation with the technology developer.

Each site is evaluated based on considerations and preferences provided by the developer and on four principal program goals. These goals are as follows:

- Production of the most useful information on each technology's capabilities
- Expeditious implementation
- Production of information relevant to the specific site cleanup goals
- Involvement of EPA regions and states in the SITE program

## **TECHNOLOGY AND DEMONSTRATION SITE SELECTION**

In April 1991, EPA learned that PSI was contracted by LLNL to perform pilot-scale studies as part of remediation activities at the LLNL site. At that time, EPA and PSI discussed the possibility of PSI participating in the SITE program to demonstrate how the perox-pure™ chemical oxidation technology could be used to treat contaminated groundwater at Site 300 of LLNL in Tracy, California. EPA subsequently accepted the perox-pure™ technology into the SITE Demonstration program. Through a cooperative effort between EPA ORD, EPA Region IX, LLNL, and PSI, the perox-pure™ technology was demonstrated at LLNL Site 300 under the SITE program. The demonstration took place over a 3-week period in September 1992. During the demonstration, about 40,000 gallons of groundwater contaminated with VOCs was treated in the perox-pure™ system.

The perox-pure™ technology can be applied at Superfund and other hazardous waste sites where groundwater or other liquid wastes are contaminated with organic compounds. The technology has been used to treat landfill leachate, groundwater, and industrial wastewater, all containing a variety of organic contaminants, including chlorinated solvents, pesticides, polynuclear aromatic hydrocarbons, and petroleum hydrocarbons. In some applications, where the contaminant concentration was higher than about 500 mg/L for the perox pure™ system to handle alone, the system was combined with other treatment technologies.

## **DEMONSTRATION OBJECTIVES**

In addition to meeting the general objectives of the SITE program, the perox-pure™ technology demonstration had three primary objectives and one secondary objective. The primary objectives of the technology demonstration were as follows:

- Assess the technology's ability to destroy VOCs from groundwater at the LLNL site under different operating conditions
- Determine whether the treated water meets applicable disposal requirements at the 95 percent confidence level
- Obtain information required to estimate the operating costs for the treatment system, such as electrical power consumption and chemical doses

The secondary objective for the technology demonstration was to obtain preliminary information on the presence and types of by-products formed during treatment.

## **EVALUATION CRITERIA AND REGULATORY CONSIDERATIONS**

EPA used the following technical criteria to evaluate the effectiveness of the perox-pure™ technology in treating groundwater containing VOCs.

- Removal efficiencies achieved for VOCs present in groundwater at the LLNL site and those that were added to the groundwater
- Compliance of the treated groundwater with federal drinking water MCLs and California state drinking water action levels at the 95 percent confident level

The groundwater at the LLNL site contained primarily TCE and PCE which can be oxidized easily. To enhance the applicability of SITE demonstration data, the groundwater was spiked in line with three VOCs that are difficult to oxidize (chloroform, DCA, and TCA).

For purposes of SITE demonstrations, EPA follows procedures regarding on- and off-site remedial actions taken under CERCLA. According to OSWER, application for and receipt of permits is not required for on-site response actions performed under CERCLA authority. Although the normal permitting processes are not required for demonstrations, CERCLA removal and remedial activities must comply with applicable or relevant and appropriate requirements



(ARAR) of federal and state environmental and public health laws. Table 1 summarizes the ARARs identified for this project.

## **PROJECT ORGANIZATION**

Participants in the SITE demonstration included the EPA Risk Reduction Engineering Laboratory (RREL), PSI, EPA Region IX, LLNL, the German Federal Ministry of Research and Technology, and the PRC Environmental Management, Inc. (PRC), SITE team.

To demonstrate the perox-pure™ chemical oxidation technology at the LLNL site, a cooperative agreement was signed between the EPA RREL and PSI. PSI was responsible for the treatment system delivery, setup, operation, and demobilization.

The EPA SITE project manager had the overall responsibility for overseeing, reviewing, and approving the project quality assurance activities during the demonstration. The PRC SITE team, including Engineering-Science, Inc., Versar, Inc., General Testing Corporation, Sound Analytical Services, and James Reed & Associates, provided sampling, analytical, and other technical support to EPA RREL. PRC was responsible for the overall direction of the PRC SITE team, including the activities of the subcontractors and coordination with the EPA RREL, EPA Region IX, LLNL, PSI, and the German Federal Ministry of Research and Technology.

EPA Region IX and LLNL assisted the SITE program by providing access to the demonstration site, coordinating community relations activities, ensuring all applicable state and local regulations were met, and coordinating with RREL for the disposal of waste generated during the demonstration.

Under a U.S.-German bilateral program, the German Federal Ministry of Research and Technology reviewed the demonstration plan and requested additional analyses. The EPA SITE project manager arranged for the additional analyses and supported the U.S.-German bilateral program activities.

**TABLE 1**  
**LIST OF FEDERAL AND STATE ARARS FOR THE perox-pure™**  
**CHEMICAL OXIDATION DEMONSTRATION AT THE LLNL SITE**

Demonstration Program Activity	ARAR	Description	Basis	Response
Waste extraction	RCRA 40 CFR Part 262 or State equivalent	Standards that apply to generators of hazardous waste	The groundwater is extracted for treatment	Provide appropriate containment for all waste storage tanks as advised by EPA Region IX.
Storage prior to processing	RCRA 40 CFR Part 264 or State equivalent	Standards that apply to the storage or treatment of hazardous wastes in tanks	The waste is stored in a tank prior to processing	Tank integrity will be monitored and maintained to prevent leakage or failure; the tank will be decontaminated when processing is complete.
Waste processing	RCRA 40 CFR Part 264 or State equivalent	Standards that apply to the storage or treatment of hazardous wastes in tanks	The treatment process occurs in a tank	Tank integrity will be monitored and maintained to prevent leakage or failure; the tank will be decontaminated when processing is complete.
Waste characterization	RCRA 40 CFR Part 261	Standards that apply to waste characteristics	Need to determine if treated material is RCRA hazardous waste	Testing will be performed prior to disposal.
Storage after processing	RCRA 40 CFR Part 264 or State equivalent	Standards that apply to the storage of hazardous wastes in containers	The treated waste will be placed in tanks prior to a decision on their final dispositions	The containers will be maintained in good condition; the container storage area will be constructed to control runoff and runoff of precipitation.
Transportation for off-site disposal	RCRA 40 CFR Part 262	Manifest requirements and packaging and labeling requirements prior to transporting	If found hazardous, wastes generated during the demonstration must be manifested and managed as a hazardous waste	If found hazardous, obtain an ID number from EPA.
	40 CFR Part 263	Transportation standards	If found hazardous, wastes generated during the demonstration must be transported as a hazardous waste	If found hazardous, use a transporter that is licensed by EPA to transport the wastes off-site for disposal.
Off-Site disposal	40 CFR Part 264 and Part 268, or state equivalent	Requirements for the off-site disposal of hazardous wastes	If found hazardous, wastes generated during the demonstration must be disposed of as hazardous wastes. If disposed of in land-based units, the waste must comply with land disposal restrictions.	If found hazardous, dispose of the wastes at a RCRA-permitted hazardous waste facility.

## **TECHNICAL OPERATIONS**

Initially, background information on the technology was obtained from the developer and from literature. Subsequently, a demonstration plan was prepared that discussed the perox-pure™ chemical oxidation technology and the planned demonstration procedures. The demonstration procedures included preparing a schedule for the project; obtaining information on the site and its contamination; characterizing the groundwater at the site; mobilizing equipment and materials to the site, collecting groundwater for demonstration; developing a matrix of test runs to evaluate the technology; and identifying the appropriate sampling and analytical procedures to be followed during the demonstration (PRC, 1992).

## SECTION 3

### DESCRIPTION OF TECHNOLOGY

This section provides an overview of the perox-pure™ chemical oxidation technology, perox-pure™ treatment system equipment, and factors affecting the technology and briefly describes the treatment system support equipment and utility requirements. Detailed information on applications of this technology is presented in the Applications Analysis Report for the perox-pure™ technology, prepared under the SITE program (EPA, 1993).

#### PROCESS DESCRIPTION

The perox-pure™ chemical oxidation technology was developed by PSI to destroy dissolved organic contaminants in water. The technology uses UV radiation and hydrogen peroxide to oxidize organic compounds present in water at ppm levels or less. In broad terms, oxidation is a chemical change in which electrons are lost by an atom or a group of atoms. Oxidation is always accompanied by reduction, a chemical change in which electrons are gained by an atom or group of atoms. The atom or group of atoms that has lost electrons has been oxidized, and the atom or group of atoms that has gained electrons has been reduced. The reduced atom or group of atoms is called an oxidant. Oxidation and reduction always occur simultaneously; the total number of electrons lost in the oxidation must equal the number of electrons gained in the reduction. In the perox-pure™ technology, organic contaminants in water are oxidized by hydroxyl radicals, powerful oxidants produced by UV radiation and hydrogen peroxide. Subsequently, the organic contaminants are broken down into carbon dioxide, water, halides, and in some cases, organic acids.

A variety of organic contaminants can be effectively oxidized by the combined use of (1) UV radiation and hydrogen peroxide, (2) UV radiation and ozone, or (3) ozone and hydrogen peroxide. The principal oxidants in the perox-pure™ system, hydroxyl radicals, are produced by direct UV photolysis of the hydrogen peroxide added to contaminated water. The perox-pure™ system generates UV radiation by using medium-pressure, mercury-vapor lamps.

In principle, the most direct way to generate hydroxyl radicals ( $\text{OH}\cdot$ ) is to cleave hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) through photolysis. The photolysis of hydrogen peroxide occurs when UV radiation ( $h\nu$ ) is applied, as shown in the following reaction:



Thus, photolysis of hydrogen peroxide results in a quantum yield of two hydroxyl radicals formed per quantum of radiation absorbed. This ratio of hydroxyl radicals generated from the photolysis of hydrogen peroxide is high. Unfortunately, at 253.7 nanometers, the dominant emission wavelength of low-pressure UV lamps, the absorptivity (or molar extinction coefficient) of hydrogen peroxide is only 19.6 liters per mole-centimeter. This absorptivity is relatively low for a primary absorber in a photochemical process. Because of the low absorptivity value for hydrogen peroxide, a high concentration of residual hydrogen peroxide must be present in the treatment medium to generate a sufficient concentration of hydroxyl radicals. According to PSI, the perox-pure™ system overcomes this limitation by using medium-pressure UV lamps.

The hydroxyl radicals formed by photolysis react rapidly with organic compounds, with rate constants on the order of  $10^8$  to  $10^{10}$  liters per mole-second; they also have a relatively low selectivity in their reactions (Glaze and others, 1987). However, naturally occurring water components, such as carbonate ion, bicarbonate ion, and some oxidizable species, act as free radical scavengers that consume hydroxyl radicals. Free radical scavengers are compounds that consume any species possessing at least one unpaired electron. In addition to naturally occurring scavengers, excess hydrogen peroxide can itself act as a free radical scavenger, decreasing the hydroxyl radical concentration. Reactions with hydroxyl radicals are not the only removal pathway possible in the perox-pure™ system; direct photolysis by UV radiation of organic compounds also provides a removal pathway for contaminants. With these factors affecting the reaction, the proportion of oxidants required for optimum removal is difficult to predetermine. Instead, the proportion for optimum removal must be determined experimentally for each waste.

## TREATMENT SYSTEM EQUIPMENT

The perox-pure™ chemical oxidation systems typically consist of the following portable, skid-mounted components: a chemical oxidation unit, a hydrogen peroxide feed module, a UV lamp drive, and a control panel unit. In addition to these main system components, other equipment is used to address site-specific conditions or requirements, including contaminated water characteristics and effluent discharge limits. For example, Figure 1 presents a schematic diagram of the main and ancillary components of the perox-pure™ chemical oxidation system used for the SITE demonstration (Model SSB-30).

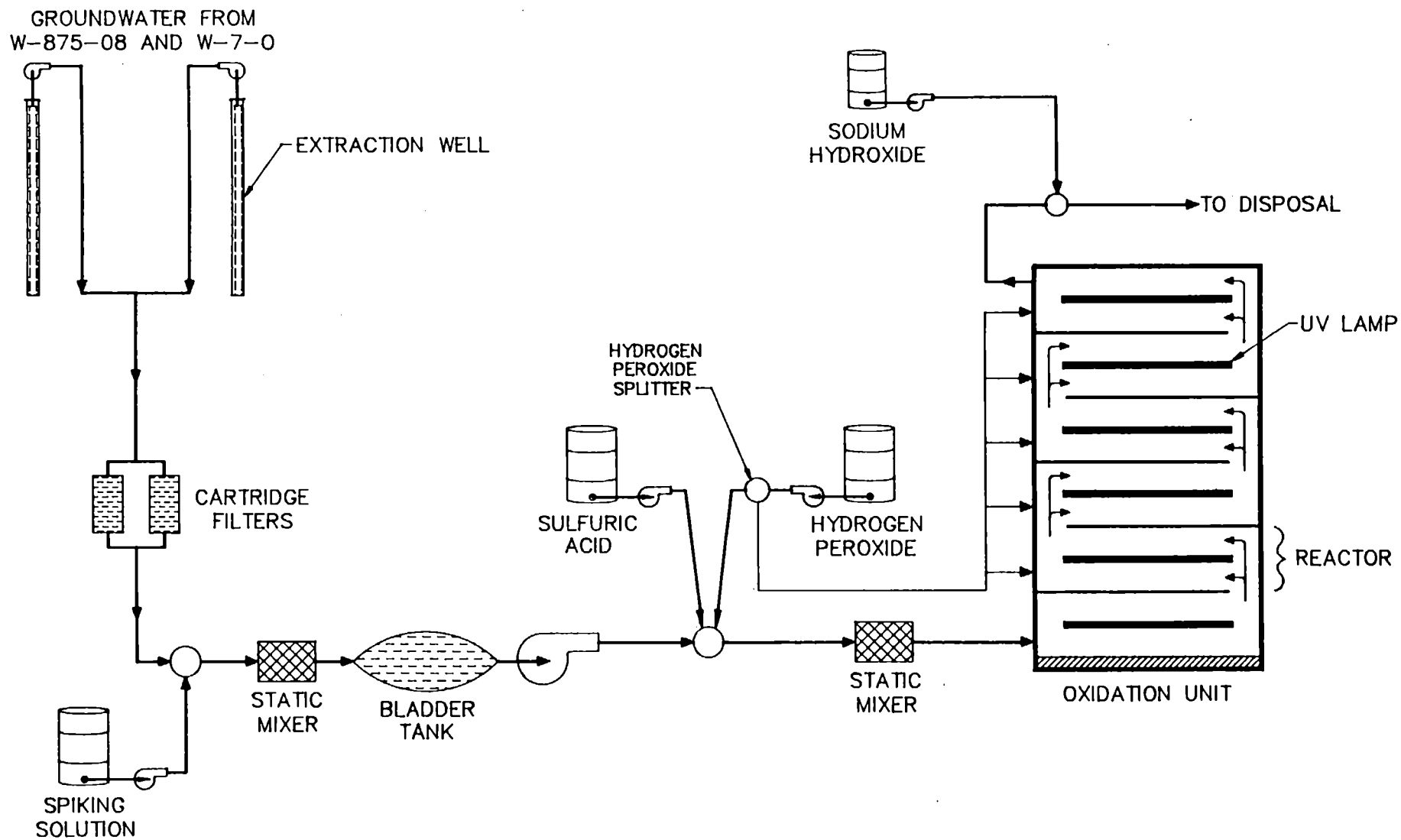


Figure 1. perox-pure<sup>™</sup> Chemical Oxidation Treatment System

For the SITE demonstration, skid-mounted acid feed module and base feed module were used to adjust the pH of the influent and effluent, respectively. PSI provided the acid (sulfuric acid) and base (sodium hydroxide) solutions in drums. Two cartridge filters arranged in parallel, capable of screening suspended silt larger than 3 micrometers, were used to remove particles from the groundwater, which was primarily contaminated with VOCs including TCE and PCE. A spiking solution feed module was used to spike effluent from cartridge filters with chloroform, DCA, and TCA for certain demonstration runs. A 7,500-gallon bladder tank was used (1) as an equalization tank and (2) as a holding tank to perform a few demonstration runs at flow rates greater than the groundwater well yield. The bladder tank was useful in minimizing the volatilization of contaminants. To ensure a relatively homogeneous process water, static mixers were used after chemicals were added at upstream locations in the treatment system.

The SSB-30 model consists of six reaction chambers, or reactors, with one UV lamp in each reactor. Each UV lamp has a power rating of 5 kW, for a total system rating of 30 kW. The UV lamps are mounted inside UV-transmissive quartz tubes at the center of the reactors, so that water flows through the space between the reactor wall and the quartz tube. Circular wipers are mounted on the quartz tubes housing the UV lamps. The wipers periodically remove any suspended particles that have coated the quartz tubes. In a coating environment, coating diminishes the effectiveness of the system by blocking some of the UV radiation.

Contaminated water is pumped to the treatment system and enters the oxidation unit through a section of pipe containing a temperature gauge, a flow meter, an influent sampling port, and hydrogen peroxide and sulfuric acid addition points. Hydrogen peroxide is added to the contaminated water before it enters the first reactor; however, a splitter can be used to add hydrogen peroxide at the inlet of each lamp section to allow for different doses into each reactor. Inside the oxidation unit, the contaminated water follows a serpentine path that parallels each of the six UV lamps. The water passes each lamp individually, allowing lamps to be turned on or off as needed. Sample ports are located after each reactor. Inside the oxidation unit, photolysis of hydrogen peroxide by UV radiation results in the formation of hydroxyl radicals; these free radicals react rapidly with oxidizable compounds, such as organic contaminants.

Treated water exits the oxidation unit through an effluent pipe equipped with a temperature gauge and sample port. The hydrogen peroxide dose is usually set so that the concentration of the residual hydrogen peroxide in the treated water is less than 5 mg/L. Sodium

hydroxide is then added to adjust the treated groundwater pH so that the effluent meets the pH discharge requirement.

The control panel on the perox-pure™ system monitors water flow rate, total flow through the system, UV lamp current in each reactor, and alarm conditions for the perox-pure™ equipment. Hydrogen peroxide and acid injection are activated by switches on the control panel and are monitored with flow meters.

## **FACTORS AFFECTING THE perox-pure™ TECHNOLOGY**

Several factors influence the effectiveness of the perox-pure™ chemical oxidation technology. These factors can be grouped into three categories: (1) influent characteristics, (2) operating parameters, and (3) maintenance requirements. Each of these is discussed below.

### **Influent Characteristics**

The perox-pure™ chemical oxidation technology is capable of treating water containing a variety of organic contaminants, including VOCs, semivolatile organic compounds (SVOC), pesticides, polynuclear aromatic hydrocarbons, polychlorinated biphenyls, and petroleum hydrocarbons. Under a given set of operating conditions, contaminant removal efficiencies depend on the chemical structure of the contaminants. Removal efficiencies are high for organic contaminants with double bonds (such as TCE, PCE, and vinyl chloride) and aromatic compounds (such as phenol, toluene, benzene, and xylene), because these compounds are easy to oxidize. Organic contaminants without double bonds (such as TCA and chloroform) are not easily oxidized and are more difficult to remove.

Contaminant concentration also affects treatment system effectiveness. The perox-pure™ system is most effective in treating water with contaminant concentrations less than about 500 mg/L. If contaminant concentrations are greater than 500 mg/L, the perox-pure™ system may be used in combination with other treatment technologies, such as air stripping. For highly contaminated water, the perox-pure™ system can also be operated in a "flow-through with recycle" mode, in which part of the effluent is recycled through the oxidation unit to improve overall removal efficiency.



The perox-pure™ system uses a chemical oxidation process to destroy organic contaminants; therefore, other species in the influent that consume oxidants present an additional load for the system. These species are called scavengers. A scavenger may be described as any species in water other than the target contaminants that consumes oxidants. Common scavengers include anions such as bicarbonate, carbonate, sulfide, nitrite, bromide, and cyanide. Metals present in reduced states, such as trivalent chromium, ferrous iron, manganous ion, and several others, are also likely to be oxidized. In addition to acting as scavengers, these reduced metals can cause additional concerns under alkaline pH conditions. For example, trivalent chromium can be oxidized to hexavalent chromium, which is more toxic. Ferrous iron and manganous ion are converted to less soluble forms, which precipitate in the reactor, creating suspended solids that can build up on the quartz tubes housing the UV lamps. Natural organic compounds, such as humic acid (often measured as TOC), are also potential scavengers in this treatment technology.

Other influent characteristics of concern include suspended solids, oil, and grease. These constituents can build up on the quartz tubes housing the UV lamps, resulting in reduced UV transmission and decreased treatment efficiency.

### **Operating Parameters**

Operating parameters are those parameters that can be varied during the treatment process to achieve desired removal efficiencies. The principal operating parameters for the perox-pure™ system are hydrogen peroxide dose, influent pH, and flow rate.

Hydrogen peroxide dose is selected based on treatment unit configuration, contaminated water chemistry, and contaminant oxidation rates. Under ideal conditions, hydrogen peroxide is photolyzed to hydroxyl radicals, which are the principal oxidants in the system. Direct photolysis of each hydrogen peroxide molecule yields two hydroxyl radicals. The molar extinction coefficient of hydrogen peroxide at 253.7 nanometers, the dominant emission wavelength of low-pressure UV lamps, is only 19.6 liters per mole-centimeter, which is low for a primary absorber in a photochemical process (Glaze and others, 1987). Therefore, although the yield of hydroxyl radicals from hydrogen peroxide photolysis is relatively high, the low molar extinction coefficient requires that a relatively high concentration of hydrogen peroxide exist in the water. However, because excess hydrogen peroxide is also a hydroxyl radical scavenger, hydrogen peroxide levels that are too high could decrease treatment efficiency. According to PSI, the perox-pure™ system overcomes these limitations by using medium pressure UV lamps.

The perox-pure™ system is equipped with a hydrogen peroxide splitter that allows the operator to inject hydrogen peroxide to the oxidation unit influent and directly at an individual reactor. The distribution of the total hydrogen peroxide dose is an important operating parameter, because the hydroxyl radical has a short lifetime. If the total hydrogen peroxide dose is delivered to the influent, depending on other operating conditions, the resulting hydroxyl radical concentration in the last reactor may be zero. Consequently, removal efficiency in the last reactor would decrease significantly. Distributing part of the hydrogen peroxide dose directly to the reactors guarantees that hydroxyl radicals are present throughout the oxidation unit.

Influent pH controls the equilibrium among carbonic acid, bicarbonate, and carbonate. This equilibrium is important to treatment efficiency because carbonate and bicarbonate ions are hydroxyl radical scavengers. If the influent carbonate and bicarbonate concentration is greater than about 400 mg/L as calcium carbonate, the pH should be lowered to between 4 and 6 to improve the treatment efficiency. At low pH, the carbonate equilibrium is shifted to carbonic acid, which is not a scavenger.

Flow rate through the treatment system determines the hydraulic retention time. In general, increasing the hydraulic retention time improves treatment efficiency by increasing the time available for contaminant destruction. Theoretically, at a certain point, the reaction proceeds toward equilibrium, and increasing the hydraulic retention time no longer significantly increases removal efficiency. PSI notes that it did not observe such a phenomenon in the range of hydraulic retention times provided by the perox-pure™ system.

### **Maintenance Requirements**

The maintenance requirements for the perox-pure™ system summarized below are based on discussions with PSI, during and after the SITE demonstration. Regular maintenance by trained personnel is essential for the successful operation of the perox-pure™ system.

The only major system component that requires regular maintenance is the UV lamp assembly. Regular UV lamp assembly maintenance includes periodically cleaning the quartz tubes housing the UV lamps. Eventually, the lamps may need to be replaced. The frequency at which the quartz tubes should be cleaned depends on the type and concentration of suspended solids present in the influent or formed during treatment. Cleaning frequency may range from once every month to once every 3 months. UV lamp assemblies can be removed from the oxidation

unit to provide access to the quartz tubes, which can then be cleaned manually. The quartz tubes can also be cleaned automatically during operation with wipers. Automatic tube cleaning is a standard feature on most PSI treatment units. The quartz tube wipers require replacement once every 3 to 6 months depending upon the cleaning cycle frequency.

Maintenance requirements for the medium-pressure, mercury-vapor, broad-band UV lamps used in the perox-pure™ system are similar to those for conventional, low-pressure UV lamps. The life of low-pressure UV lamps normally cited by most manufacturers is 7,500 hours, based on a use cycle of 8 hours. The use cycle represents the length of time the UV lamp is operated between shutdowns. Decreasing the use cycle or increasing the frequency at which a UV lamp is turned on and off can lead to early lamp failure.

A number of factors contribute to UV lamp aging. These factors include plating of mercury to the interior lamp walls, a process called blackening, and solarization of the lamp enclosure material, which reduces its transmissibility. These factors cause steady deterioration in lamp output at the effective wavelength (253.7 nanometers) and decrease output at the end of a lamp's life by 40 to 60 percent. This reduction in lamp output requires more frequent replacement of the UV lamps. According to PSI, no significant decline in UV lamp output occurs until after about 3,000 hours of operation. Therefore, PSI recommends replacing the UV lamps after 3,000 hours. PSI guarantees the UV lamps in the perox-pure™ unit for 3,000 hours when they are turned on and off no more than two or three times a day.

The only other part of the UV lamp assembly requiring periodic maintenance is the gasket between the UV lamp and the reactor. This gasket, which is used to maintain a water-tight seal on each reactor, is generally replaced once a year.

Other components of the perox-pure™ system, such as valves, flow meters, piping, hydrogen peroxide feed module, acid feed module, and base feed module, should be checked for leaks once a month. In addition, the influent, hydrogen peroxide, acid, and base feed pumps should be checked once a month for proper operation and maintenance. Feed pump heads are usually replaced annually. PSI offers a full-service program to its customers that covers all regular maintenance and replacement parts for the system.

## **TREATMENT SYSTEM SUPPORT EQUIPMENT AND FACILITIES**

Typically, support equipment and facilities are needed depending on the site logistics, required operating procedures, and equipment limitations. The major support equipment and facilities used during the SITE demonstration of the perox-pure™ system included a cartridge filtration system to remove suspended solids from groundwater, storage tanks for untreated and treated groundwater, an acid feed module for untreated groundwater, a base feed module for treated groundwater, an office and laboratory trailer, and pumps.

A more detailed discussion of the specific support equipment and facilities used during the field demonstration is given in Section 5.

## **UTILITY REQUIREMENTS**

Utilities required for the perox-pure™ chemical oxidation technology demonstration included water, electricity, and telephone service. LLNL provided most of the support required to arrange utilities for the demonstration.

Water was required for equipment and personnel decontamination, for field laboratory use, and for drinking. During operation of the demonstration unit, personnel and equipment decontamination required about 10 gallons per day (gpd) of potable water. About 5 gpd of distilled, deionized water was needed for field laboratory use, and about 5 to 10 gpd were needed for drinking water.

Electricity was needed for the perox-pure™ system, the office trailer, and the laboratory equipment. The perox-pure™ system required 480-volt, 3-phase electrical service. Additional electrical power (110-volt, single-phase) was needed for operating the pumps, the mixing device in the spiking solution feed system, the office trailer lights, and the on-site laboratory and office equipment.

Telephone service was required for ordering equipment, parts, reagents, and other chemical supplies; scheduling deliveries; and making emergency communications.

## **SECTION 4**

### **DESCRIPTION OF DEMONSTRATION SITE**

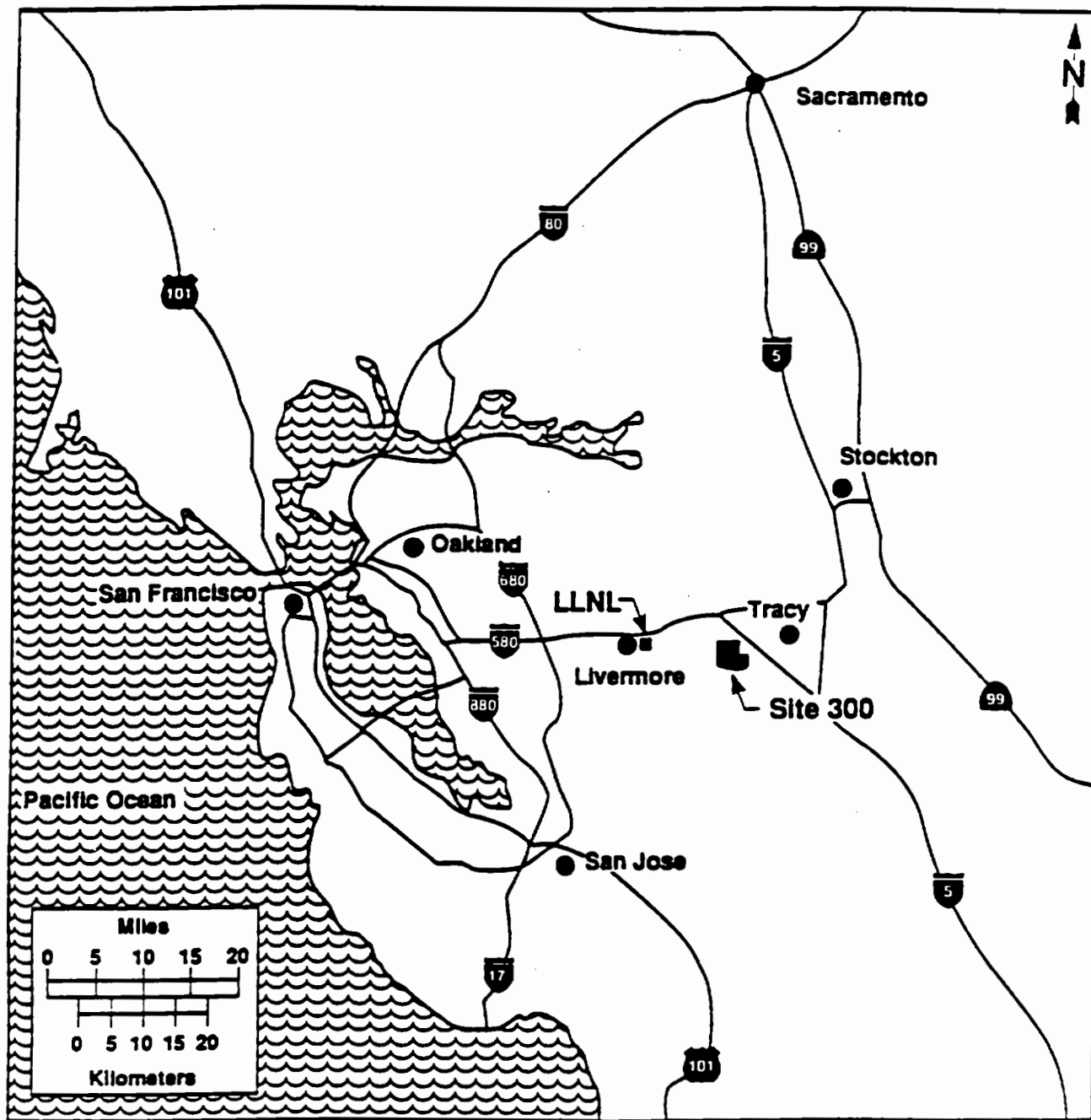
The perox-pure™ technology demonstration was conducted at the LLNL Site 300 in Tracy, California. This section describes the LLNL site characteristics and summarizes the site contamination results.

#### **SITE CHARACTERISTICS**

LLNL is a 640-acre research facility about 45 miles east of San Francisco and 3 miles east of Livermore, California (see Figure 2). Development of the site began in 1942, when it was used as a U.S. Navy aviation training base. Subsequent activities at LLNL varied considerably under the management of several government agencies, including the Atomic Energy Commission, the Energy Research and Development Agency, and the U.S. Department of Energy, which is the present owner. Various hazardous materials, including VOCs, metals, and tritium were used and released at the site.

The demonstration was conducted at Site 300, which is operated by LLNL but is separate from the LLNL main campus (see Figure 2). Site 300 occupies 11 square miles in the Altamont Hills about 15 miles southeast of Livermore and 8.5 miles southwest of Tracy, California. LLNL established Site 300 as a high-explosives test area in 1955. Site 300 operations include (1) hydrodynamic testing; (2) charged particle-beam research; (3) physical, environmental, and dynamic testing; and (4) high-explosive formulation and fabrication.

EPA chose a specific area of Site 300 for the technology demonstration. This area is called the General Services Area (GSA). The GSA occupies about 80 acres in the southeastern corner of Site 300. Various administrative, medical, engineering, and maintenance operations are conducted in buildings located in the GSA. Before 1982, several GSA facilities used dry wells to dispose of waste rinse, process, and wash waters. Wastes from these facilities might have included photolaboratory rinse water; water- and oil-based paint waste; automotive shop waste containing degreasing solvents; and acid dip rinse water. Between 1983 and 1984, the dry wells were investigated and closed. After the dry well closure, wastewater from these activities was shipped off site for treatment and disposal. Other wastes are currently stored on site in a permitted



**Figure 2. LLNL Site Location**

Source: LLNL, 1990

hazardous waste storage area. The suspected sources of groundwater contamination in the GSA are the dry wells, accidental releases and leaks during facility operations, and leaking underground fuel storage tanks.

LLNL's Environmental Restoration Division submitted a remedial investigation (RI) report and a feasibility study (FS) report to EPA Region IX in May and December 1990, respectively. The FS report outlined a treatment system for contaminated groundwater from the central GSA. The system will be designed to treat both vapor and groundwater obtained from extraction wells in the area. Groundwater will be collected both on and off site for remediation. Currently, several treatment alternatives are being evaluated at the site.

## **SITE CONTAMINATION**

Dry wells, accidental releases and leaks during facility operations, and leaking underground fuel storage tanks are suspected sources of groundwater contamination in the central GSA. Based on the RI report (LLNL, 1990), the shallow aquifer at the site was selected as the candidate waste stream for the technology demonstration.

In May 1992, LLNL performed an 8-hour drawdown pump test using existing groundwater extraction wells. The groundwater was sampled throughout the test and analyzed for VOCs, SVOCs, metals, and a variety of other parameters, such as pH and alkalinity. Samples for VOC and SVOC analyses were collected after approximately 1, 3, 6, and 8 hours elapsed pumping time. These analyses showed that (1) only five VOCs were present above detection limits, (2) SVOCs were not present above detection limits, and (3) all five VOCs detected showed gradual decreases in concentration over the 8-hour test duration. At the end of 8 hours, TCE; PCE; 1,1-dichloroethene (1,1-DCE); 1,2-dichloroethene (1,2-DCE); and TCA were present at 1,200 µg/L; 95 µg/L; 7.1 µg/L; 8.7 µg/L; and 7.5 µg/L, respectively.

The following parameters were also measured in the groundwater samples collected after 6 hours of pumping: (1) pH was 7.8; (2) alkalinity was 300 mg/L as calcium carbonate; (3) the concentration of total dissolved solids was 930 mg/L; (4) the concentration of iron was 10 µg/L, and (5) the concentration of manganese was 20 µg/L.

## **SECTION 5**

### **DEMONSTRATION PROCEDURES**

Procedures for the perox-pure™ chemical oxidation system demonstration were developed to evaluate the system's effectiveness in treating groundwater contaminated with VOCs from Site 300 at LLNL. A demonstration plan was prepared that detailed the proposed sampling, analytical, quality assurance, quality control, and health and safety procedures for the demonstration (PRC, 1992). This section summarizes the actual demonstration procedures, including the testing program, field activities, sampling procedures and field measurements, analytical procedures, deviations from the demonstration plan, technical systems review, and community relations and technology transfer activities.

#### **TESTING PROGRAM**

The demonstration was conducted in the GSA at Site 300 in Tracy, California, over a 3-week period in September 1992. The demonstration was divided into three stages: (1) site preparation; (2) technology demonstration; and (3) site demobilization. During the demonstration, the perox-pure™ system (Model SSB-30) treated about 40,000 gallons of groundwater contaminated with VOCs. Principal groundwater contaminants included TCE and PCE, which were present at concentrations of about 1,000 and 100 µg/L, respectively. Other VOCs, such as chloroform, 1,1-DCA, 1,1-DCE, 1,2-DCE, and TCA, were present at average concentrations below 15 µg/L. Groundwater was pumped from two wells into a 7,500-gallon bladder tank to minimize any variability in influent characteristics. In addition, cartridge filters were used to remove suspended solids greater than 3 micrometers in size from the groundwater before it entered the bladder tank. Treated groundwater was stored in two 20,000-gallon steel tanks before being discharged.

Both primary and secondary objectives were identified for the technology demonstration. Primary objectives were critical for the technology evaluation, while secondary objectives provided useful, but noncritical information. The primary objectives for the demonstration were as follows:

- Determine the VOC removal efficiencies in the treatment system under different operating conditions



- Determine whether the treated groundwater met the applicable discharge standards at the 95 percent confidence level
- Gather the information necessary to estimate treatment costs, including chemical doses and utility requirements

The first objective was met by calculating the percent contaminant removal efficiencies using Equation 2:

$$CRE = \frac{MCI - MCE}{MCI} \times 100 \quad (2)$$

where

CRE = percent contaminant removal efficiency  
MCI = mean contaminant concentration in the influent  
MCE = mean contaminant concentration in the effluent

To determine whether the concentration of selected contaminants in the treated water met the applicable target levels (see Table 2), PRC performed a one-tailed Student's t-test, assuming that the data were normally distributed. The upper confidence limit (UCL) for the mean contaminant concentration in the treated water was calculated at the 95 percent confidence level using Equation 3:

$$UCL = \bar{x} + \frac{ts}{\sqrt{n}} \quad (3)$$

where

x = sample mean contaminant concentration  
t = Student's t-test statistic value at a specified confidence level  
s = sample standard deviation  
n = sample size (number of replicates)

Information such as chemical doses and power consumption was recorded during the demonstration to estimate costs. Additional information, such as operating and maintenance costs for the technology, was provided by the developer and operating facilities.

**TABLE 2**  
**TARGET LEVELS FOR VOCs IN EFFLUENT SAMPLES**

<i>VOC</i>	<i>Target Level (µg/L)</i>
Chloroform	100
DCA	5
1,1-DCE	6
1,2-DCE	6
TCA	200
TCE	5
PCE	5

The secondary objective for the demonstration was to obtain information on the presence and types of by-products formed during treatment. This objective was accomplished by analyzing the treated water for VOCs and SVOCs using gas chromatography and mass spectrometry (GC/MS) methods and by performing bioassays to evaluate whether the treated groundwater contained by-products harmful to fresh water organisms.

The technology demonstration was conducted in three phases (see Table 3). Phase 1 consisted of eight runs using raw groundwater, Phase 2 consisted of four runs using spiked groundwater, and Phase 3 consisted of two runs using spiked groundwater to test the effect of quartz tube cleaning. These phases are described below.

The principal operating parameters for the perox-pure™ system include hydrogen peroxide dose, influent pH, and flow rate, which determines the hydraulic retention time. These parameters were varied during Phase 1 to observe treatment system performance under different operating conditions. For Phase 1 runs, the initial operating conditions were based on groundwater characterization performed by LLNL in May 1992 (see Section 4) and PSI's professional judgment and experience. In Runs 1, 2, and 3 the influent pH was varied while the other parameters were held constant to determine preferred operating conditions. The preferred operating conditions were those under which the concentration of effluent VOCs would be reduced to below target levels (see Table 2) during Phase 2 spiked groundwater runs. After the preferred value for pH was determined, that value was held constant, while the other parameters were varied. Preferred operating conditions for each parameter were determined based on quick turnaround analytical data for three selected indicator VOCs: TCE, PCE, and TCA. Even though TCE and PCE are easily oxidized, they were chosen because they were present in relatively high concentrations. TCA was chosen because it is relatively difficult to oxidize, although it was present at a low concentration. Based on quick turnaround analytical data, PSI selected Run 3 operating conditions as the preferred operating conditions for spiked groundwater.

Phase 2 involved spiked groundwater and reproducibility tests. Groundwater was spiked with sufficient chloroform, DCA, and TCA so that the spiked groundwater contained about 200 µg/L of each of these VOCs. These compounds were chosen because they are relatively difficult to oxidize and because they were not initially present in the groundwater at high concentrations. Phase 2 increased the applicability of the demonstration data to other sites that may be contaminated with VOCs that are difficult to oxidize. Phase 2 was also designed to evaluate the reproducibility of the perox-pure™ system's performance at the preferred operating

**TABLE 3**  
**EXPERIMENTAL MATRIX FOR perox-pure™ SYSTEM**

<i>Run Number</i>	<i>Influent pH</i>	<i>Hydrogen Peroxide at Influent to Reactor 1 (mg/L)</i>	<i>Hydrogen Peroxide at Influent to Reactors 2 to 6 (mg/L)</i>	<i>Flow Rate (gpm)</i>
<b>Phase 1 (Raw Groundwater Runs)</b>				
1	8.0	40	25	10
2	6.5	40	25	10
3	5.0	40	25	10
4	5.0	70	50	10
5	5.0	30	15	10
6	5.0	240	Hydrogen Peroxide was added at Influent to Reactor 1 only	10
7	5.0	240		40
8	5.0	60		40
<b>Phase 2 (Spiked Groundwater and Reproducibility Runs)</b>				
9	5.0	70	50	10
10	5.0	40	25	10
11	5.0	40	25	10
12	5.0	40	25	10
<b>Phase 3 (Quartz Tube Cleaner Runs)</b>				
13	5.0	40	25	10
14	5.0	40	25	10

Notes:

mg/L = milligrams per liter  
gpm = gallons per minute

conditions determined in Phase 1. Specifically, Runs 10, 11, and 12 were performed at Run 3 conditions to evaluate the reproducibility of the perox-pure™ system's performance.

During Phase 3, the effectiveness of the quartz tube wipers was evaluated by performing two runs using spiked groundwater at the preferred operating conditions. The quartz tubes used in Phase 3 were obtained from a hazardous waste site where the water hardness and iron content caused scaling on the tubes. PSI obtained two sets of quartz tubes for Phase 3. One set of quartz tubes was relatively clean, because the wipers were routinely used to minimize scaling. The other set of tubes had significant scaling because wipers were not used. Because PSI was able to obtain only two tubes of each type (scaled and clean), only two reactors were used during Phase 3. Specifically, Run 13 was performed using scaled quartz tubes, while Run 14 was performed using clean quartz tubes. In both runs, only two UV lamps were operating.

## **FIELD ACTIVITIES**

After the GSA location was selected, support services, facilities, and equipment were procured and installed. EPA arranged utility connections, ordered and rented equipment, and supervised and directed subcontractors. Field activities associated with site preparation and mobilization, and site demobilization and waste disposal are described below.

### **Site Preparation and Mobilization**

Approximately 10,000 square feet of the site was used for the perox-pure™ chemical oxidation system and support equipment and facilities. This equipment included treated and untreated water storage tanks, nonhazardous and potentially hazardous waste storage containers, an office and field laboratory trailer, and a parking area. A temporary canopy covering approximately one-fourth of the demonstration area was erected to provide shelter for the perox-pure™ system and personnel during the technology demonstration. Site preparation and mobilization included setting up major support equipment, on-site support services, and utilities. These activities are discussed below.

### **Major Support Equipment**

Support equipment for the perox-pure™ system demonstration included a cartridge filtration system to remove suspended solids from groundwater, storage tanks for untreated and

treated groundwater, an acid feed module for untreated groundwater, a base feed module for treated groundwater, a spiking solution feed system, a static mixer, two 55-gallon drums for collecting equipment wash down and decontamination rinse water, a dumpster, a forklift with operator, pumps, sampling equipment, health and safety equipment, and vehicles. Specific items included the following:

- One cartridge filtration system containing two filters upstream of the treatment unit; the filters were capable of removing suspended solids greater than 3 micrometers in size from groundwater
- One 55-gallon closed-top, polyethylene drum containing spiking solution equipped with a floating lid and a mixing device; during the demonstration, a spiking solution containing chloroform, DCA, and TCA was added in line to the groundwater to evaluate the perox-pure™ system's ability to treat compounds that are difficult to oxidize
- One static mixer to mix the spiking solution and groundwater before the mixture entered the untreated groundwater storage tank
- One 7,500-gallon bladder tank used to store untreated groundwater and minimize VOC losses during storage and as an equalization and storage tank during the technology demonstration
- One pump for transferring contaminated water from the bladder tank to the perox-pure™ system and one pump for adding spiking solution in line to the groundwater
- One sulfuric acid feed module to adjust the pH of the influent to the perox-pure™ system; PSI provided the module, which consisted of a 55-gallon acid feed drum, two pumps, and flow measuring devices
- One sodium hydroxide feed module provided by PSI consisting of a 55-gallon base feed drum, two pumps, and flow measuring devices to adjust the pH of the effluent from the perox-pure™ system
- Several large garbage cans to store nonhazardous wastes before disposal
- A number of 55-gallon drums to contain used disposable field sampling and analytical equipment, used disposable health and safety gear, and field laboratory wastes before disposal
- A forklift with operator for setting up equipment and for moving drummed wastes
- Sampling equipment for aqueous media and process chemical solutions
- Analytical equipment for measuring field parameters at the demonstration site

- Two 20,000-gallon steel tanks to store treated groundwater before analysis and disposal
- Health and safety related equipment, such as a first-aid kit, protective coveralls, latex or similar gloves, nitrile gloves, steel-toe boots and disposable overboots, safety glasses, and a hard hat
- Vehicles to transport personnel and supplies to and from the site

### On-Site Support Services

One portion of the field trailer (12 by 44 feet) was used for on-site laboratory analyses, the rest of the trailer served as an office for field personnel and provided shelter and storage for small equipment and supplies. Two toilets were available near the demonstration area.

### Utilities

Utilities required for the demonstration included water, electricity, and telephone service. LLNL provided most of the support required to arrange utilities for the demonstration. Water was required for equipment and personnel decontamination, for field laboratory use, and for drinking. During operation of the demonstration unit, personnel and equipment decontamination required about 10 gpd of potable water. About 5 gpd of distilled, deionized water was needed for field laboratory use, and about 5 to 10 gpd were needed for drinking water.

Electricity was needed for the perox-pure™ system, the office trailer, and the laboratory equipment. The perox-pure™ system required 480-volt, 3-phase electrical service. Additional electrical power (110-volt, single-phase) was needed for operating the pumps, the mixing device in the spiking solution feed system, the office trailer lights, and the on-site laboratory and office equipment.

Telephone service was required mainly for ordering equipment, parts, reagents, and other chemical supplies; scheduling deliveries; and making emergency communications.

### **Site Demobilization and Waste Disposal**

After the demonstration was completed and on-site equipment was disassembled and decontaminated, equipment and site demobilization activities began. Equipment demobilization

included loading the skid-mounted units on a flat-bed trailer and transporting them off site, returning rented support equipment, and disconnecting utilities.

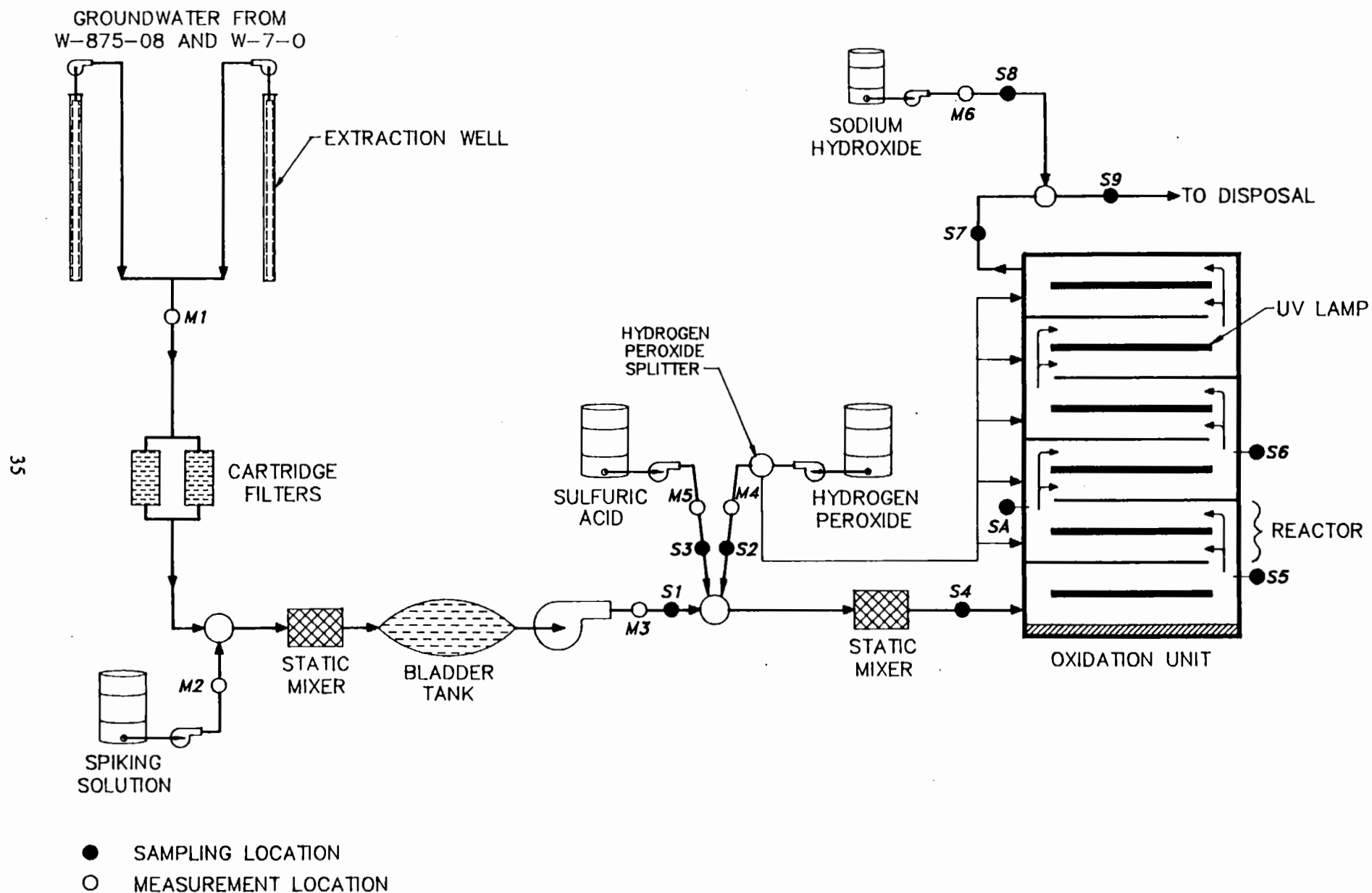
Decontamination was necessary for the perox-pure™ unit, the storage tanks, and field sampling and analytical equipment. Demonstration equipment was either cleaned with potable water or steam, as required. LLNL tested and disposed of the treated water collected during the demonstration in accordance with applicable discharge permits. LLNL also handled all hazardous wastes through their Hazardous Waste Management Program. Regular garbage service at LLNL collected all nonhazardous wastes generated during the demonstration.

## **SAMPLING PROCEDURES AND FIELD MEASUREMENTS**

Samples were collected and measurements were taken during the demonstration to evaluate the effectiveness of the perox-pure™ chemical oxidation system. Figure 3 shows sampling and measurements locations and Table 4 outlines the sample collection and field measurement program for the technology demonstration. Tables 5 and 6 give quality assurance (QA) objectives for critical and noncritical parameters, respectively. During the demonstration, TOX and AOX were added to the analyte list as requested by the German Federal Ministry of Research and Technology, under a U.S.-German bilateral technology transfer program. Additionally, GC/MS analyses for VOCs and SVOCs were done in all test runs instead of only in Runs 10, 11, and 12, as requested by the German Federal Ministry of Research and Technology.

The following parameters were considered critical for evaluating the perox-pure™ technology: (1) VOCs, hydrogen peroxide, base, and acid concentrations; and (2) flow rate and pH. VOCs were measured by both GC and GC/MS methods. Only GC measurement of VOCs listed in Table 2 was considered critical, because GC data was planned for quantitative use (for example, to evaluate the primary objectives) while GC/MS data was planned for qualitative use (for example, to evaluate the secondary objective). This section describes liquid sampling procedures, field measurements, and associated QA procedures as implemented during the demonstration. Deviations from the demonstration plan are discussed later in this section.





**Figure 3. perox-pure™ Chemical Oxidation Treatment System Sampling and Measurement Locations**

**TABLE 4**  
**OUTLINE OF SAMPLE COLLECTION AND FIELD MEASUREMENT PROGRAM**

Location <sup>a</sup>	Run No.	Analytical Parameter	Number of Field and Field QC Samples/Measurements					Field Generated Lab QC Samples		Total No. of Samples <sup>d</sup> (Measurements <sup>e</sup> )
			Number of Samples (Measurements) per run	Total Number of Field Samples (Measurements)	Field QC		Total No. of Field + Field QC Samples <sup>b</sup>	No. of MS/MSD Sample Sets <sup>c</sup>	No. of S/SD Sample Sets <sup>e</sup>	
					No. of Field Blanks <sup>b</sup>	No. of Trip Blanks <sup>b</sup>				
Feed Line to Equalization Tank (M1)	9-14	Flow Rate	(3)	(18)	NA	NA	(18)	NA	NA	(18)
Spike Solution Feed Tank (M2)	9-14	Flow Rate	(3)	(18)	NA	NA	(18)	NA	NA	(18)
Feed Line from the Equalization Tank (S1, M3)	1-14	VOCs (GC Analysis)	4	56	0	0	56	3	0	62
		VOCs (GC/MS Analysis)	1	14	0	0	14	1	0	16
		SVOCs	1	14	0	0	14	1	0	16
		pH	2	28	NA	NA	28	NA	2	32
		Alkalinity	2	28	NA	NA	28	2	0	32
		Hardness	2	28	NA	NA	28	2	0	32
		Flow Rate	(3)	(42)	NA	NA	(42)	NA	NA	(42)
		Temperature	1	14	NA	NA	14	NA	1	16
		TOX	1	14	0	0	14	1	0	16
	4, 7, 9, and 13	AOX	1	4	0	0	4	1	0	6
	10-12	TC	1	3	0	0	3	1	0	5
		TOC	1	3	0	0	3	1	0	5
		POC	1	3	0	0	3	1	0	5
		Metals	1	3	0	0	3	1	0	5
Hydrogen Peroxide Feed Tank (S2, M4)	1-14	Hydrogen Peroxide	1	14	NA	NA	14	NA	1	16
		Flow Rate	(3)	(42)	NA	NA	(42)	NA	NA	(42)

**TABLE 4**  
**OUTLINE OF SAMPLE COLLECTION AND FIELD MEASUREMENT PROGRAM (Continued)**

Location <sup>a</sup>	Run No.	Analytical Parameter	Number of Field and Field QC Samples/Measurements					Field Generated Lab QC Samples		Total No. of Samples <sup>d</sup> (Measurements <sup>e</sup> )
			Number of Samples (Measurements) per run	Total Number of Field Samples (Measurements)	Field QC		Total No. of Field + Field QC Samples <sup>b</sup>	No. of MS/MSD Sample Sets <sup>c</sup>	No. of S/SD Sample Sets <sup>c</sup>	
					No. of Field Blanks <sup>b</sup>	No. of Trip Blanks <sup>b</sup>				
Sulfuric Acid Feed Tank (S3, M5)	1-14	Acid	1	14	NA	NA	14	NA	1	16
		Flow Rate	(3)	(42)	NA	NA	(42)	NA	NA	(42)
Influent Line to Reactor 1 (S4)	1-14	pH	2	28	NA	NA	28	NA	2	32
		Alkalinity	2	28	NA	NA	28	2	0	32
		Hardness	2	28	NA	NA	28	2	0	32
	10-12	Specific Conductance	1	3	NA	NA	3	0	1	5
		Turbidity	1	3	NA	NA	3	0	1	5
		Bioassay: C. dubia	1	3	NA	NA	3	NA	NA	3
		Bioassay: P. promelas	1	3	NA	NA	3	NA	NA	3
Effluent from Reactor 1 (S5)	1-14	VOCs (GC Analysis)	4	56	0	0	56	3	0	62
Effluent from Reactor 2 (SA)	12-14	VOCs (GC Analysis)	4	12	1	1	14	1	0	16
		VOCs (GS/MS Analysis)	1	3	0	0	3	0	0	3
		SVOCs	1	3	0	0	3	0	0	3
		Hydrogen Peroxide	1	3	NA	NA	3	NA	1	5
		pH	2	6	NA	NA	6	NA	1	8
		Temperature	1	3	NA	NA	3	NA	1	5
		Alkalinity	2	6	NA	NA	6	1	0	8
		Hardness	2	6	NA	NA	6	1	0	8
		TOX	1	3	2	0	5	1	0	7
	13	AOX	1	1	1	0	1	0	0	2

**TABLE 4**  
**OUTLINE OF SAMPLE COLLECTION AND FIELD MEASUREMENT PROGRAM (Continued)**

Location <sup>a</sup>	Run No.	Analytical Parameter	Number of Field and Field QC Samples/Measurements					Field Generated Lab QC Samples		Total No. of Samples <sup>d</sup> (Measurements <sup>a</sup> )
			Number of Samples (Measurements) per run	Total Number of Field Samples (Measurements)	Field QC		Total No. of Field + Field QC Samples <sup>b</sup>	No. of MS/MSD Sample Sets <sup>c</sup>	No. of S/SD Sample Sets <sup>c</sup>	
					No. of Field Blanks <sup>b</sup>	No. of Trip Blanks <sup>b</sup>				
Effluent from Reactor 3 (S6)	1-12	VOCs (GC Analysis)	4	48	0	0	48	3	0	54
Effluent from the Treatment System (S7)	1-12	VOCs (GC Analysis)	4	48	12	8	68	4	0	76
		VOCs (GC/MS Analysis)	1	12	12	3	27	2	0	31
		SVOCs	1	12	12	0	24	2	0	28
		Hydrogen Peroxide	1	12	NA	NA	12	NA	1	14
		pH	2	24	NA	NA	24	NA	2	28
		TOX	1	12	12	2	26	2	0	30
	4, 7, and 9	AOX	1	3	3	2	8	1	0	10
	10-12	TC	1	3	0	0	3	1	0	5
		TOC	1	3	0	0	3	1	0	5
		POC	1	3	0	0	3	1	0	5
		Metals	1	3	0	0	3	1	0	5
		Specific Conductance	1	3	NA	NA	3	0	1	5
		Turbidity	1	3	NA	NA	3	0	1	5
		Bioassay: <i>C. dubia</i>	1	3	NA	NA	3	NA	NA	3
		Bioassay: <i>P. promelas</i>	1	3	NA	NA	3	NA	NA	3
Sodium Hydroxide Feed Tank (S8, M6)	1-14	Base	1	14	NA	NA	14	NA	1	16
		Flow Rate	(3)	(42)	NA	NA	(42)	NA	NA	(42)
Discharge Line (S9)	1-14	pH	2	28	NA	NA	28	NA	2	32
Watt Hour Meter	1-14	Electricity Consumption	(1)	(14)	NA	NA	(14)	NA	NA	(14)

**TABLE 4**  
**OUTLINE OF SAMPLE COLLECTION AND FIELD MEASUREMENT PROGRAM (Continued)**

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**Notes:**

MS/MSD	Matrix spike/matrix spike duplicate
NA	Not applicable
QC	Quality control
S/SD	Sample/sample duplicate

- <sup>a</sup> The numbers in the parentheses refer to sample or measurement locations identified in Figure 3.
  - <sup>b</sup> Field blanks were collected once every run. Trip blanks were collected once every day (shipment).
  - <sup>c</sup> MS/MSD and S/SD samples were obtained through the collection of a triple volume/container of sample. MS/MSD and S/SD samples were counted as two when calculating the total number of samples.
  - <sup>d</sup> The total number of samples includes samples collected for analysis (1) at the laboratory and (2) in the field.
  - <sup>e</sup> No samples were collected for measurements. The measurements were made directly at the sampling location.
-

**TABLE 5**  
**ANALYTICAL METHODS AND QA OBJECTIVES FOR CRITICAL PARAMETERS**

Parameter	Method Ref. <sup>a</sup>	Unit	TRL <sup>b</sup>	Precision <sup>c</sup>	Accuracy <sup>d</sup>
VOCs					
Chloroform	SW-846 8010	µg/L	1.0	± 30%	50 - 150%
DCA	SW-846 8010	µg/L	1.0	± 30%	50 - 150%
1,1-DCE	SW-846 8010	µg/L	1.0	± 30%	50 - 150%
1,2-DCE	SW-846 8010	µg/L	1.0	± 30%	50 - 150%
TCA	SW-846 8010	µg/L	1.0	± 30%	50 - 150%
TCE	SW-846 8010	µg/L	1.0	± 30%	50 - 150%
PCE	SW-846 8010	µg/L	1.0	± 30%	50 - 150%
pH	MCAWW 150.1	pH unit	NA	± 0.2 <sup>e</sup>	± 0.04 <sup>f</sup>
Acid	Note g	N	0.01	± 10%	± 10% <sup>h</sup>
Hydrogen Peroxide	Boltz and Howell, 1979	mg/L	1	± 10%	± 10% <sup>h</sup>
Base	Note i	N	0.01	± 10%	± 10%
Flow Rate	Note j	Lpm	0.1	± 10%	NA

Notes:

NA = Not applicable  
N = Normal (equivalents/liter) solution  
Lpm = Liters per minute

<sup>a</sup> SW-846: EPA (1986); MCAWW: EPA (1983)

<sup>b</sup> Target Reporting Limits (TRL) for effluent (treated) samples. Influent samples with elevated concentrations of VOCs will have higher detection limits

<sup>c</sup> Precision as RPD unless stated otherwise

<sup>d</sup> Accuracy as percent recovery unless stated otherwise

<sup>e</sup> For pH, precision is expressed in pH units as range

<sup>f</sup> For pH, accuracy is expressed in pH units as bias

<sup>g</sup> Titration with a standardized base solution (for example, 0.1 N NaOH)

<sup>h</sup> For acid, base, and hydrogen peroxide measurements, accuracy is expressed as percent bias from true value of a QC check standard

<sup>i</sup> Titration with a standardized acid solution (for example, 0.1 N H<sub>2</sub>SO<sub>4</sub>)

<sup>j</sup> Flow rate was measured using the equipment available on the treatment system. The equipment was calibrated manually with a graduated container and a stop watch

**TABLE 6**  
**ANALYTICAL METHODS AND QA OBJECTIVES FOR NONCRITICAL PARAMETERS**

Parameter	Method Ref. <sup>a</sup>	Unit	TRL <sup>b</sup>	Precision <sup>c</sup>	Accuracy <sup>d</sup>
VOCs (GC, noncritical)	SW-846 8010	µg/L	≤ 10	± 30%	50 - 150%
VOCs (GC/MS)	SW-846 8240	µg/L	≤ 50	See Table 8	See Table 8
SVOCs <sup>e</sup> (GC/MS)	SW-846 8270	µg/L	≤ 25	See Table 8	See Table 8
Metals <sup>f</sup>	SW-846 6010	µg/L	100	± 25%	75 - 125%
TC and TOC	SM 5310C	µg/L	100	± 25%	75 - 125%
POC	SM 5310B	µg/L	100	± 25%	75 - 125%
Bioassay	EPA/600/4/85-013	% Sample	NA	NA	NA
Turbidity	MCAWW 180.1	NTU	0.1	± 20%	± 10%
Alkalinity	MCAWW 310.1	mg/L as CaCO <sub>3</sub>	10	± 10%	± 10%
Hardness	MCAWW 130.2	mg/L as CaCO <sub>3</sub>	10	± 25%	75 - 125%
Temperature	MCAWW 170.1	°C	5	± 0.5	± 1
TOX	SW-846 9020	µg/L	≤ 5	± 30%	50 - 135%
AOX	DIN 38409 H14 <sup>g</sup>	µg/L	≤ 10	± 30%	50 - 135%
Specific Conductance	SW-846 9050	µmho/cm	10	± 10%	± 10%
Electricity Consumption	None <sup>h</sup>	kilowatt hour	0.1	NA	NA

Notes:

µmho/cm = Micromhos per centimeter  
 NA = Not applicable  
 NTU = Nephelometric Turbidity Unit

<sup>a</sup> SW-846: EPA (1986); SM: APHA et al. (1989); MCAWW: EPA (1983)

<sup>b</sup> TRL for effluent (treated) samples. Influent samples with elevated concentrations of VOCs will have higher detection limits

<sup>c</sup> Precision estimated as relative percent difference for all applicable parameters except for temperature; for temperature precision is estimated as range

<sup>d</sup> Accuracy estimated as percent recovery for all applicable parameters except for turbidity, specific conductance, and temperature; for turbidity and specific conductance accuracy expressed as percent error; for temperature, accuracy expressed as bias

<sup>e</sup> SVOCs: bases, neutrals, and acids

<sup>f</sup> Iron and manganese

<sup>g</sup> Kai Steffens (1993)

<sup>h</sup> Electricity consumption was measured as described in the watt hour meter manual

## **Liquid Sampling Procedures**

Samples of untreated and treated groundwater were collected at locations S1, S4, S5, SA, S6, S7, and S9 from sample taps located in the process flow (see Figure 3). Sample ports were opened briefly prior to collecting samples to allow any stagnant water in the line to clear. Samples of process chemicals (sampling locations S2, S3, and S8 in Figure 3) were collected from storage containers through a sample port on the container, or from a pipet used to draw a sample from the container. The time interval between collecting the first and last replicate sample sets during runs varied from 45 to 180 minutes.

Because VOC samples were preserved by adding ascorbic acid (reducing agent added to stop the oxidation of VOCs) and hydrochloric acid, samples were first collected into a 250-milliliter (mL) bottle containing ascorbic acid in a manner to minimize or eliminate head space. Starch iodide paper was used in the field to determine the amount of reducing agent needed. The sample was gently shaken, allowed to sit for 5 minutes, and then transferred to a 40-mL volatile organic analysis (VOA) vial containing hydrochloric acid. Samples were transferred to the VOA vials without introducing any air bubbles. TC, TOC, and POC samples were collected in the same manner as VOC samples using sulfuric acid instead of hydrochloric acid for preservation. TOX and AOX samples were preserved using ascorbic acid and sulfuric acid. SVOC samples were preserved using sodium thiosulfate (reducing agent).

For metals, SVOCs, turbidity, and hardness samples, about 10 percent of the container was left unfilled to prevent breakage in case the sample was accidentally frozen before analysis. Minimal headspace was left in alkalinity, TOX, AOX, and bioassay sample containers.

Acid, base, hydrogen peroxide, pH, specific conductance, and temperature samples were collected into a plastic beaker and analyzed on site immediately. The plastic beakers were rinsed with distilled water prior to the collection of each sample.

## **Field Measurements**

Parameters measured in the field included groundwater flow rate to and from the equalization tank, flow rates of the spiking solution, hydrogen peroxide, sulfuric acid, and sodium hydroxide, and electrical power consumption. Groundwater flow rates were measured using factory calibrated and field confirmed in-flow paddle wheel meters. Process chemical and spiking



solution flow rates were measured using pulse pumps with variable speed and piston volume settings. All flow meters were calibrated by direct measurement of diverted flow into graduated containers. Electrical power was measured with a factory calibrated watt meter wired into the site electrical supply.

### **Field Sampling Quality Assurance Procedures**

This section describes procedures followed during the technology demonstration to maintain sample integrity and quality, including procedures related to sample containerization, preservation and holding times, chain of custody (COC), trip blanks, and field blanks.

#### **Sample Containerization, Preservation, and Holding Times**

Sample containerization, preservation, and holding times followed are given in Table 7. All samples for critical parameters arrived at the appropriate laboratory intact, properly cooled, and appropriately preserved. GC analysis of four VOC samples (a replicate from location S6 during Run 8, a replicate from location S1 and a trip blank during Run 10, and a replicate from location S7 during Run 12) was performed 1 day after the designated holding time. Data for the investigative samples was within 20 percent of the corresponding replicates. The trip blank analyzed after the holding time had characteristics similar to other trip blanks collected during the demonstration. All reported detections or reporting limits for these samples were qualified as estimated. Three influent samples (Location S4 in Runs 10, 11, and 12) and one effluent sample (Location S7 in Run 10) for bioassay exceeded the holding time by 36 hours due to delay caused by overnight shipping service (Federal Express). Based on the groundwater characteristics, this delay should not have significant impact on data quality.

One influent sample each from Runs 12 and 13 collected for SVOC analysis, arrived at the off-site laboratory in broken containers and therefore, were not analyzed. Because SVOCs are noncritical parameters for this demonstration, only one sample was collected at each location and no additional samples were available. Because Runs 9 through 14 should have the same influent characteristics, average influent characteristics from Runs 9 through 11 and Run 14 were used to substitute for missing data. Reanalysis of four matrix spike/matrix spike duplicate (MS/MSD) samples due to low surrogate recovery in SVOC samples occurred after the holding time expired;

**TABLE 7**  
**SAMPLE CONTAINERIZATION, PRESERVATION, AND HOLDING TIMES**

Parameter	Media	Minimum Sample Volume <sup>1,2</sup> (mL)	Container	Preservative	Holding Time
Bioassay: C. dubia, P. promelas	L	4,000	P	Cool, 4°C	36 hours
Metals (ICP)	L	1,000	P,G	HNO <sub>3</sub> to pH<2, Cool 4°C	6 months
SVOCs (GC/MS Analysis)	L	2 @ 1,000	G	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , Cool 4°C	7 days to extraction, 40 days to analysis
TC, TOC, and POC	L	3 @ 40	VOA	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , Cool 4°C, H <sub>2</sub> SO <sub>4</sub> to pH<2	14 days
Turbidity	L	250	P,G	Cool, 4°C	48 hours
VOCs (GC Analysis)	L	3 @ 40	VOA	Ascorbic Acid, Cool 4°C HCl to pH<2	14 days
VOCs (GC/MS Analysis)	L	3 @ 40	VOA	Ascorbic Acid, Cool 4°C HCl to pH<2	14 days
Acid	L	250	P,G	None	Analyzed Immediately in Field
Alkalinity	L	500	P,G	Cool 4°C	14 days
Base	L	250	P,G	None	Analyzed Immediately in Field
Hardness	L	250	P,G	HNO <sub>3</sub> to pH<2	6 months
Hydrogen Peroxide	L	40	G	None	Analyzed Immediately in Field
pH	L	100	P,G	None	Analyzed Immediately in Field
Specific Conductance	L	100	P,G	None	Analyzed Immediately in Field
Temperature	L	100	P,G	None	Analyzed Immediately in Field
AOX	L	250	G	Ascorbic Acid, Cool 4°C H <sub>2</sub> SO <sub>4</sub> to pH<2	7 days
TOX	L	250	G	Ascorbic Acid, Cool 4°C H <sub>2</sub> SO <sub>4</sub> to pH<2	7 days

Notes:

- <sup>1</sup> Minimum sample volume applies to all samples, including field QC samples.  
<sup>2</sup> For samples selected for MS/MSD or S/SD analyses, triple containers/volume were required. With the exception of VOC samples, MS/MSD and duplicate samples were taken from the same container, whenever practical.
- G = Amber glass and Teflon™-lined cap  
ICP = Inductively coupled plasma  
L = Liquid  
P = Polyethylene

nevertheless, QA objectives for precision and accuracy for these samples were met during reanalysis.

#### Chain-of-Custody

Each sample container was labeled with a unique sample identification number. The label identified the sampling location, date, time of collection, and analyses to be performed. Samples that were analyzed on site were delivered to the field laboratory trailer immediately. Project number, project name, sampler's name, station number, date, time, sampling location, number of containers, and analytical parameters were included on all COC forms. Samples were placed in ice chests, packed with ice, and shipped to the various off-site laboratories. COC forms were packaged inside each ice chest, and a custody seal was affixed across the openings of each ice chest to prevent sample tampering. Except for one field blank, all samples arrived at the appropriate laboratory with complete documentation, in the proper container, and with custody seals intact. The field blank for VOCs by GC analysis in Run 6 was not analyzed due to an error in the COC form. This error appeared to have little impact on data quality because no problems were noted with VOC samples collected during Run 6.

#### Field Blanks

Field blanks were collected to assess the potential for contamination of the sample during sample collection from dust or other sources at the demonstration site. Field blanks were collected for VOC, SVOC, TOX, and AOX analyses. A sample bottle was filled with organic-free water and left open near the treatment system during the sample collection period. When sampling was complete, the sample bottle was closed and shipped to the laboratory with the rest of the samples. A separate bottle was set up for each analysis. Field blanks were collected at a frequency of one per run.

During Runs 7 and 9, there was trace level contamination of field blanks with critical VOCs and as a result, data from Run 7 (at locations S5 and S6 for chloroform), and Run 9 (at location S7 for TCA) were qualified as nondetected due to probable field contamination.

### Trip Blanks

Trip blanks were prepared for VOCs, TOX, and AOX to determine whether contamination was introduced through sampling containers or as a result of exposure during shipment. The PRC SITE team used thoroughly cleaned sample containers prepared and certified by vendors to be free of contamination. Engineering-Science Berkeley Laboratory (ESBL) prepared trip blanks in the laboratory by filling sample containers with analyte-free water. The trip blanks were shipped with sampling equipment and bottles and were handled in the same way as regular samples. Trip blanks were collected and analyzed at a frequency of one per cooler of VOC samples per shipment. No trip blanks were found to be contaminated.

### **ANALYTICAL PROCEDURES**

This section describes the analytical methods and procedures used for data reduction, validation, and reporting during the technology demonstration. In addition, analytical QA is discussed. Generally, the samples were successfully analyzed as required by the QAPP. Except for the aromatic VOC results for one replicate sample in Run 9 at Location S5, no data were qualified as unusable during the validation process [for this demonstration, aromatic VOCs are noncritical analytes]. Some samples required dilution due to matrix interferences or levels of target analytes above the calibration range. The target reporting limits (TRL) for samples affected were adjusted to reflect the dilutions. Unless specifically noted, samples collected for the U.S.-German bilateral technology transfer program met QA objectives.

Other data quality issues discussed below include laboratory blank contamination and calibration outliers. At least one laboratory blank in each run except Runs 13 and 14 contained noncritical VOCs. All reported detections of these noncritical VOCs in these blanks were qualified as not detected due to probable laboratory contamination, and results were raised to the reporting limit. Also, for all runs some calibration outliers were reported for calibration runs associated with noncritical VOCs. All reported detections or reporting limits for the affected analytes were qualified as estimated. Both of these conditions are considered minor and neither had significantly affected the data quality.

## **Analytical Methods**

Tables 5 and 6 include the analytical and measurement methods used for the technology demonstration. In selecting the appropriate analytical methods for the demonstration, the PRC SITE team evaluated the specific analytes of interest, the sample matrix, and the minimum detection limits required all within the context of the demonstration objectives. All parameters were analyzed according to the methods described in the demonstration plan, with the exception of some samples collected in the reproducibility runs. During the GC analysis of VOC samples, one of three GCs at ESBL needed repair. Because ESBL was uncertain about the time required for repairing the GC, to avoid holding time violations, all influent samples (Location S1) in Runs 9 through 12 and one replicate sample at Location S5 in Run 9 were analyzed for VOCs using GC/MS instead of GC as described in the demonstration plan. Accuracy and precision data for samples analyzed by GC/MS were better than for those analyzed by GC. A comparison of average influent VOC concentrations in Runs 9 through 12 with those in Runs 13 and 14 showed no trend to conclude that use of GC/MS instead of GC affected data quality. A similar observation was made when Run 9, Location S5 data for replicate samples were compared.

The AOX sample analysis did not strictly follow the German Method DIN 38409 H14. The method requires pyrolysis temperature to be set at 950 °C. However, General Testing Corporation (GTC) performed this analysis at 800 °C, the recommended temperature for TOX analysis by SW 846 Method 9020. During an EPA audit of GTC's analytical procedures, the auditor recommended that some samples be analyzed at both 800 °C and 950 °C to evaluate the temperature impact on data quality. However, operation of the instrument at 950 °C caused undue stress on the pyrolysis tube and damaged the tube only after a few firings. For this reason, GTC could successfully analyze only one sample at both temperatures. AOX levels at 950 °C and 800 °C were 0.60 and 0.71 mg/L, respectively. Based on this limited data, no conclusion could be drawn on the impact of lower temperature on data quality.

## **Data Reduction, Validation, and Reporting**

Laboratory data reduction, validation, and reporting procedures used in this technology demonstration are described in the demonstration plan. Equations presented in the demonstration plan for calculating compound or parameter concentrations were followed. Data validation and reporting procedures for QA data did not deviate from those proposed in the demonstration plan.

As recommended by the EPA RREL QA manager, a discussion of QA data is included in this section instead of raw QA data. A summary of data for investigative samples collected during the preferred operating condition runs (Runs 10, 11, and 12) is included in Appendix A.

### **Analytical Quality Assurance**

Analytical QA is the process of ensuring and confirming data reliability. This process includes establishing data quality objectives for the project and developing data quality indicators (quantitative or qualitative measures of precision, accuracy, completeness, representativeness, and comparability) that can be used to determine whether the data met the project's QA objectives.

#### **Precision and Accuracy**

Precision and accuracy goals depend on the types of samples and analyses performed for critical parameters and on the ultimate use of analytical data. Precision and accuracy objectives for critical and noncritical parameters are given in Tables 5 and 6, respectively. Additional surrogate and MS/MSD spiking compound acceptance criteria are given in Table 8. Precision and accuracy QA objectives stated in the demonstration plan were met for all critical parameters analyzed or measured in the field.

Precision for critical VOCs was estimated as the relative percent difference (RPD) between the analytical results of the MS and MSD samples. The spiking solution contained all critical VOCs and vinyl chloride, as requested by the German Federal Ministry of Research and Technology. The RPD between the spiked analyte levels measured in the MS sample and MSD sample was calculated using Equation 4:

$$RPD = \frac{|MS - MSD|}{0.5 (MS + MSD)} \times 100 \quad (4)$$

For measurements of acid, base, and hydrogen peroxide concentrations, precision was estimated as RPD between a sample/sample duplicate (S/SD) pair. An analogous equation to Equation 4 was used for S/SD, where S replaces MS and SD replaces MSD.

**TABLE 8**  
**SURROGATE AND MS/MSD SPIKING COMPOUNDS ACCEPTANCE CRITERIA**

Method	Surrogate Compound	Percent Recovery
8270-BN	Nitrobenzene-d5	35-114
	2-Fluorobiphenyl	43-116
	p-Terphenyl-d14	33-141
8270-A	Phenol-d5	10-110
	2-Fluorophenol	21-110
	2,4,6-Tribromophenol	10-123
8240	Toluene-d8	88-110
	4-Bromofluorobenzene	86-115
	1,2-Dichloroethane-d4	76-150
8010	Bromochloromethane	50-150
	Chlorofluorobenzene	50-150

Method	Matrix Spike Compound	Percent Recovery	RPD
8270-BN	1,2,4-Trichlorobenzene	39-98	28
	Acenaphthene	46-118	31
	2,4-Dinitrotoluene	24-96	38
	Pyrene	26-127	31
	n-Nitroso-di-n-propylamine	41-116	38
	1,4-Dichlorobenzene	36-97	28
8270-A	Pentachlorophenol	9-103	50
	Phenol	12-110	42
	2-Chlorophenol	27-123	40
	4-Chloro-3-methylphenol	23-97	42
	4-Nitrophenol	10-80	50
8240	1,1-Dichloroethene	61-145	14
	Trichloroethene	71-120	14
	Chlorobenzene	75-130	13
	Toluene	76-125	13
	Benzene	76-125	11
	Vinyl chloride	50-150	25
8010	1,2-Dichloroethane	See Table 5	See Table 5
	1,1-Dichloroethene		
	1,2-Dichloroethene		
	1,1,1-Trichloroethane		
	Trichloroethene		
	Tetrachloroethene		
	Chloroform		

Precision for pH was estimated as a range by analyzing duplicate aliquots -- an S/SD pair.

$$D(pH) = |pH_1 - pH_2| \quad (5)$$

where

$D(pH)$  = range for pH

$pH_1$  and  $pH_2$  = observed values for duplicate aliquots of a sample

Precision was estimated as RPD at each flow rate required during the demonstration by performing duplicate measurements.

RPD results for GC analysis of VOCs ranged from 0 to 29 percent compared to the QA objective of less than or equal to 30 percent. RPD results for GC/MS analysis of VOCs ranged from 0 to 9 percent (the QA objective was less than or equal to 11 to 25 percent depending on the spike compound). RPD values for both TOX and AOX analyses was determined using MS and MSD data. The RPD was determined to be 28 percent (the QA objective was less than or equal to 30 percent).

The range of RPD for the process chemical concentrations were as follows: 0 to 2.3 percent for acid analyses (the QA objective was less than or equal to 10 percent), 0 to 6 percent for base analyses (the QA objective was less than or equal to 10 percent), and 0.8 to 8.5 percent for hydrogen peroxide analyses (the QA objective was less than or equal to 10 percent).

The range of RPD for precision for pH analysis was 0.01 to 0.012 compared to the QA objective of less than or equal to 0.2. The QA objective of less than or equal to 10 percent for precision for flow rates was easily met.

Accuracy for VOCs was estimated from MS samples by calculating the percent recovery of laboratory MS samples using Equation 6:



$$\%R = \frac{(C_j - C_o)}{C_i} \times 100 \quad (6)$$

where

%R = percent recovery  
 $C_j$  = measured concentration in spiked sample aliquot  
 $C_o$  = measured concentration in unspiked sample aliquot  
 $C_i$  = actual concentration of spike added

For pH, accuracy was estimated as bias, reported in pH units, from the true value using Equation 7:

$$B = pH_m - pH_t \quad (7)$$

where

B = bias  
 $pH_m$  = measured pH of standard reference material  
 $pH_t$  = actual pH of standard reference material

Similarly, accuracy for acid, base, and hydrogen peroxide concentration measurements was estimated as percent bias using QC check samples prepared by ESBL.

Percent recovery results for GC analysis of VOCs ranged from 54 to 143 percent compared to the QA objective of 50 to 150 percent. Percent recovery results for GC/MS analysis of VOCs ranged from 75 to 99 percent, which met the QA objective listed in Table 8.

The percent bias for the pH analyses ranged from 0.00 to 0.04 compared to the QA objective of 0.04. Percent bias for process chemical concentrations was as follows: 100 to 104 percent for acid analyses (the QA objective was 90 to 110 percent); 98 to 102 percent for base analyses (the QA objective was 90 to 110 percent); and 92 to 104 percent for hydrogen peroxide analyses (the QA objective was 90 to 110 percent).

Accuracy for TOX and AOX analyses was measured as percent recovery in the MS sample. The percent recovery for the samples ranged from 82 to 106 percent (the QA objective was 50 to 135 percent).

#### Completeness

Completeness is an assessment of the amount of valid data obtained from a measurement system compared to the amount of data expected to achieve a particular statistical level of confidence. The percent completeness is calculated by dividing the number of samples with acceptable data by the total number of samples planned to be collected. The result is then multiplied by 100. Greater than 95 percent of completeness was achieved for the demonstration samples. The QA objective for degree of completeness was 90 percent and was met during the demonstration.

For all parameters, critical or noncritical, analyzed either in the field or at an off-site laboratory, all but one sample had usable results. Only results for analysis of aromatic VOCs, a noncritical parameter, on a replicate taken from location S5 (effluent from Reactor 1) during Run 9 were unusable due to poor surrogate recovery. Two samples collected for SVOC analysis, a noncritical parameter, were not analyzed because they arrived at the laboratory in broken containers.

Assuming that the lower temperature for AOX analysis had little impact on data quality, all results from samples analyzed for TOX and for AOX under the U.S.-German bilateral technology transfer program are considered usable.

#### Representativeness

For this project, representativeness involves sample size, sample volume, sampling times, and sampling locations. The QA goal was to obtain a statistically adequate number of samples that represented the various waste streams at the time samples were collected. The volume of sample collected depends on the analytical method chosen, allowing for QC sample analyses and reanalysis, if needed. A sufficient number of samples were collected to analyze all of the parameters required; therefore, the QA objective for representativeness was met.

## Comparability

All parameters were measured using standard methods listed in Tables 5 and 6. Therefore, the demonstration data are considered comparable to any other perox-pure™ system's performance data generated using standard methods.

## Target Reporting Limits

The TRLs for critical and noncritical parameters are provided in Tables 5 and 6, respectively. TRLs were set based on the project requirements and the analytical laboratory's experience in analyzing groundwater samples and effluents similar to those of the perox-pure™ system. Except for those cases noted below, TRL QA objectives for all parameters were met.

As expected, most influent samples required dilution to quantitate levels of critical VOCs above the calibration range or due to matrix interference. In addition, some effluent samples from Runs 9 through 14 required dilution because spiking compound levels were above the calibration range. Any TRLs affected were adjusted to reflect these dilutions. TRLs for all undiluted sample analyses met the QA objectives.

## **DEVIATIONS FROM THE DEMONSTRATION PLAN**

Due to unforeseen site conditions or necessary procedural changes, the PRC SITE team deviated from procedures described in the demonstration plan in a few cases. The PRC SITE team discussed these deviations with the EPA project manager and implemented the resolutions after the EPA project manager approved them. These deviations can be classified as follows: system operation, sample collection, field measurement, and analytical procedures. This section describes all deviations of each type that occurred during the technology demonstration, any related effect, and corrective actions taken.

### **System Operation**

The following system operation deviations occurred during the technology demonstration:

- Based on the 8-hour drawdown test performed in May 1992, LLNL estimated that during the demonstration, contaminated groundwater could

be extracted from Wells W-7-O and W-875-08 at approximately 9 gpm and 3 gpm, respectively. The demonstration tests were designed assuming that the combined stream would be the influent to the perox-pure™ system. However, based on observations made in early September 1992, LLNL informed the PRC SITE team that the wells might not provide the estimated yield throughout the demonstration. The PRC SITE team resolved this issue by reducing the extraction rates from both wells in the same proportion, so that the influent characteristics would be approximately the same as those estimated before the demonstration. The SITE team extracted groundwater from Wells W-7-O and W-875-08 at 6 gpm and 2 gpm, respectively. This approach did not affect the demonstration schedule or the technology evaluation.

- Flow rates through the perox-pure™ system for Runs 7 and 8 were planned to be 50 gpm. Because PSI's acid feed pump could not transfer enough acid to the process flow to maintain influent pH at approximately 5, the system flow rate was reduced to 40 gpm. This deviation did not alter the selection of preferred conditions from Phase 1 of the technology evaluation despite the increased hydraulic retention time resulting from the change in flow rate because only Runs 1 through 6 were evaluated to select the preferred operating conditions, as stated in the demonstration plan.
- PSI requested that one of its operating facilities ship three scaled (coated) and three clean (uncoated) quartz tubes to perform Phase 3 test runs. However, of the six quartz tubes, one tube was broken in transit. PSI did not have enough time to replace the broken tube. Therefore, Phase 3 tests (Runs 13 and 14) were performed using only two instead of three UV lamps. As a result, perox-pure™ system's performance with coated tubes and uncoated tubes was compared based on the removals achieved in two reactors, instead of those achieved in three reactors.
- The approach for calibrating the meter measuring the system flow rate at location SI was changed. Instead of calibrating the flow meter only at the beginning and end of the demonstration at three flow rates covering the expected flow rates, calibrations were performed before each run at the specified flow rate for that run. This approach provided continuous check on the flow rate measurement during the demonstration.
- The demonstration plan called for emptying all but 10 to 50 gallons of contaminated water from the bladder tank between Phases 1 and 2. The tank was emptied to the extent possible, but contained approximately 250 gallons after the completion of Phase 1. The PRC SITE team compensated for this by allowing for this dilution in the spiking solution flow rate. Based on the influent concentrations of the spiking compounds, this deviation had no effect on the technology evaluation.

## **Sample Collection**

- Samples for TOX and AOX analyses were added to the analyte list as requested by German Federal Ministry of Research and Technology, under a U.S.-German bilateral technology transfer program.

## **Field Measurement**

- In addition to the measurement parameters listed in the demonstration plan, the PRC SITE Team also monitored the flow rates of the supply wells, W-7-O and W-875-0, to confirm that the proportional contribution of the wells remained constant.
- Because the solubility of the spiking compounds in water was less than anticipated, the spiking solution was prepared in two batches instead of one batch as stated in the demonstration plan. This deviation resulted in a slight dilution of the spiking solution and was compensated for by increasing the spiking solution flow rate. This deviation had no effect on the technology evaluation.

## **Analytical Procedures**

- Because of capacity limitations, GC/MS analyses of VOCs and SVOCs were performed by Versar laboratory instead of ESBL. This change in analytical laboratory had no effect on the technology evaluation.
- To avoid holding time violations, ESBL analyzed some influent samples by GC/MS instead of GC as described in the demonstration plan. Accuracy and precision data for samples analyzed by GC/MS were better than for those analyzed by GC.
- GC/MS analyses of VOCs and SVOCs was originally planned only for reproducibility runs. Based on the request of the German Federal Ministry of Research and Technology, one sample each from the influent and effluent matrices was analyzed for VOCs and SVOCs by GC/MS in all runs.

## **TECHNICAL SYSTEMS REVIEW**

During the demonstration, EPA directed that two technical systems reviews (TSR) be conducted to audit the sampling and analytical procedures. One TSR focused on field sampling and analytical activities, and the other focused on the off-site laboratory analyses.

The TSR for field-related activities was conducted on September 17, 1992. The TSR covered project organization and QA management, process measurements, sampling procedures, and on-site laboratory measurements. Overall, all aspects of the technology evaluation were considered well organized and competently implemented. EPA noted one minor issue regarding the calibration data for the wattmeter used to measure power consumption of the perox-pure™ system. While not considered a critical parameter, power consumption was considered important since this measurement was required to address utility costs incurred during the treatment process. The wattmeter was factory calibrated by General Electric Corporation before shipment to LLNL site. However, because of the cost associated with receiving the data (\$950), the EPA project manager and PRC SITE team did not request the data. Based on the TSR recommendation, the wattmeter was recalibrated after the demonstration and the data were sent to the EPA project manager. The data showed that the QA objectives specified in the demonstration plan were met.

A TSR for VOC analysis by GC at ESBL was conducted on September 24, 1992. No concerns were noted for any portion of the laboratory operation including QA management and analytical methods. One suggestion given by the auditor was that ESBL establish retention time windows as soon as possible, instead of after the completion of quick turnaround analyses. ESBL immediately established the retention time windows as suggested by the auditor.

## **COMMUNITY RELATIONS AND TECHNOLOGY TRANSFER**

The public had several opportunities to participate in the SITE demonstration activities. The technology demonstration was first announced in a fact sheet distributed in July 1992 to community members and government officials identified in the LLNL's Community Relations Plan for Site 300. The fact sheet discussed the SITE program, the technology, the proposed demonstration location, and the objectives of the demonstration. A 30-day comment period for questions or concerns about the demonstration was offered to the public. The public comment period was held from July 8 to August 7, 1992. EPA did not receive any responses during the public comment period.

Invitations to a formal Visitors' Day were distributed to approximately 150 individuals, including federal, state, and local officials and agencies; environmental and business professionals; nearby universities with environmental engineering departments; media representatives; interested community groups; and nearby residents. The Visitors' Day was conducted on September 23, 1992. All Visitors' Day participants received information about the SITE program, the

perox-pure™ chemical oxidation technology, LLNL Site 300, and the criteria and approach used to evaluate the technology.

A total of 17 people attended the Visitors' Day. The session included presentations by an LLNL representative, the EPA SITE project manager, the technology developer, and the EPA support contractor for the demonstration. Following the presentations, the group went to the demonstration area to view the perox-pure™ system while it was in operation. Of the 17 attendees, seven were federal, state, or local officials; five were environmental professionals or businessmen; four were media representatives; and one was a local resident.

The field demonstration and Visitors' Day program were videotaped to produce a comprehensive videotape of all major field activities.

## SECTION 6

### PERFORMANCE DATA AND EVALUATION

The perox-pure™ chemical oxidation technology demonstration had the following objectives: (1) assess the technology's abilities to destroy VOC in groundwater at the LLNL site under different operating conditions; (2) determine whether the treated water met applicable disposal requirements; and (3) obtain information required to estimate the operating costs for the treatment system, such as electrical power consumption and chemical doses. A secondary objective of the demonstration was to obtain preliminary information on the presence and types of by-products formed during treatment.

The technology demonstration was conducted in three phases as described in detail in Section 5. Phase 1 consisted of eight runs, Phase 2 consisted of four runs, and Phase 3 consisted of two runs. Unaltered groundwater was used during Phase 1, and spiked groundwater was used during Phases 2 and 3. The principal operating parameters for the perox-pure™ system, hydrogen peroxide dose, influent pH, and flow rate, were varied during Phase 1 test runs to observe the system's performance under different operating conditions. Phase 2 consisted of reproducibility test runs using groundwater spiked with known concentrations of contaminants. Phase 3 evaluated the effectiveness of the quartz tube wipers by performing two runs using scaled and clean quartz tubes.

In each test run, various critical and noncritical parameters were measured at specific sampling or measurement locations (as described in Section 5) to evaluate the system's performance. This section presents and discusses the performance data collected during the perox-pure™ SITE demonstration. In addition, field operational problems encountered during the demonstration are discussed.

#### CRITICAL PARAMETERS

The critical parameters for this technology demonstration include specific VOC concentrations, acid, base, and hydrogen peroxide concentrations, pH, and flow rate. Table 5 in Section 5 identifies the critical parameters and presents the QA objectives for each parameter. VOCs were measured by both GC and GC/MS methods. GC measurement of VOCs was used to determine the removal efficiencies of critical VOCs and to verify compliance with disposal requirements. The hydrogen peroxide concentration and the pH and flow rate measurements were



considered critical since they are principal parameters for the perox-pure™ technology and are required to establish the operating conditions in each test run. Acid and base concentrations were also considered critical because the cost of these chemical additives will be included in the treatment costs.

## **NONCRITICAL PARAMETERS**

Table 6 in Section 5 lists the noncritical parameters for this technology demonstration and presents the QA objectives for each parameter. Noncritical parameters include noncritical VOCs and SVOCs, metals, TC, TOC, POC, bioassay, turbidity, alkalinity, hardness, temperature, specific conductance, TOX, AOX, and electricity consumption.

## **SUMMARY OF RESULTS**

This section summarizes the results of both critical and noncritical parameters for the perox-pure™ chemical oxidation system demonstration, as well as the technology's effectiveness in treating groundwater contaminated with VOCs. Data are presented in graphic or tabular form. For samples with analyte concentrations at nondetectable levels, one-half the detection limit was used as the estimated concentration. However, if more than one replicable sample had concentrations at nondetectable levels, using one-half the detection limit as the estimated concentration for all replicable samples with nondetectable levels of contaminants will significantly reduce the standard deviation of the mean and will affect the statistical inferences made. For this reason, 0.5, 0.4, 0.6, and 0.4 times the detection limit were used as estimated concentrations for the first, second, third, and fourth replicate samples, respectively. Throughout this section, the terms "Reactor 6 effluent," "perox-pure™ system effluent," and "effluent" are used synonymously.

### **Summary of the Results for Critical Parameters**

Results for the critical parameters are presented below for each phase of the demonstration.

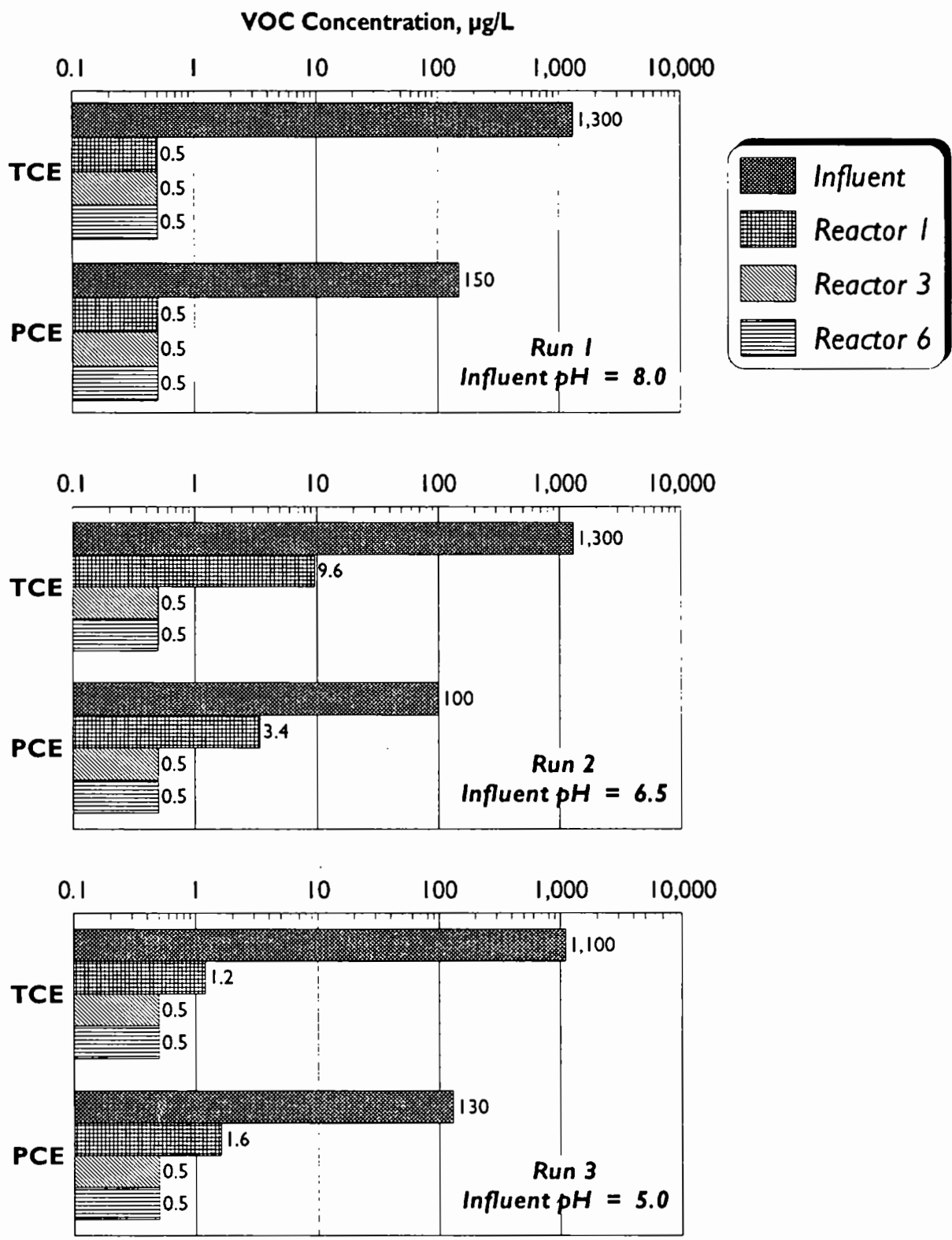
## Phase 1 Results

In Phase 1 (Runs 1 through 8), only three VOCs were detected in the influent to and effluent from the perox-pure™ system. In general, TCE and PCE were detected only in the influent. TCA could not be measured in the influent because it was present at concentrations two orders of magnitude lower than the average TCE concentration and was diluted out during the analysis. However, TCA concentration could be measured in effluent samples because no dilution was required. In general, TCA was detected in the effluent from the perox-pure™ system.

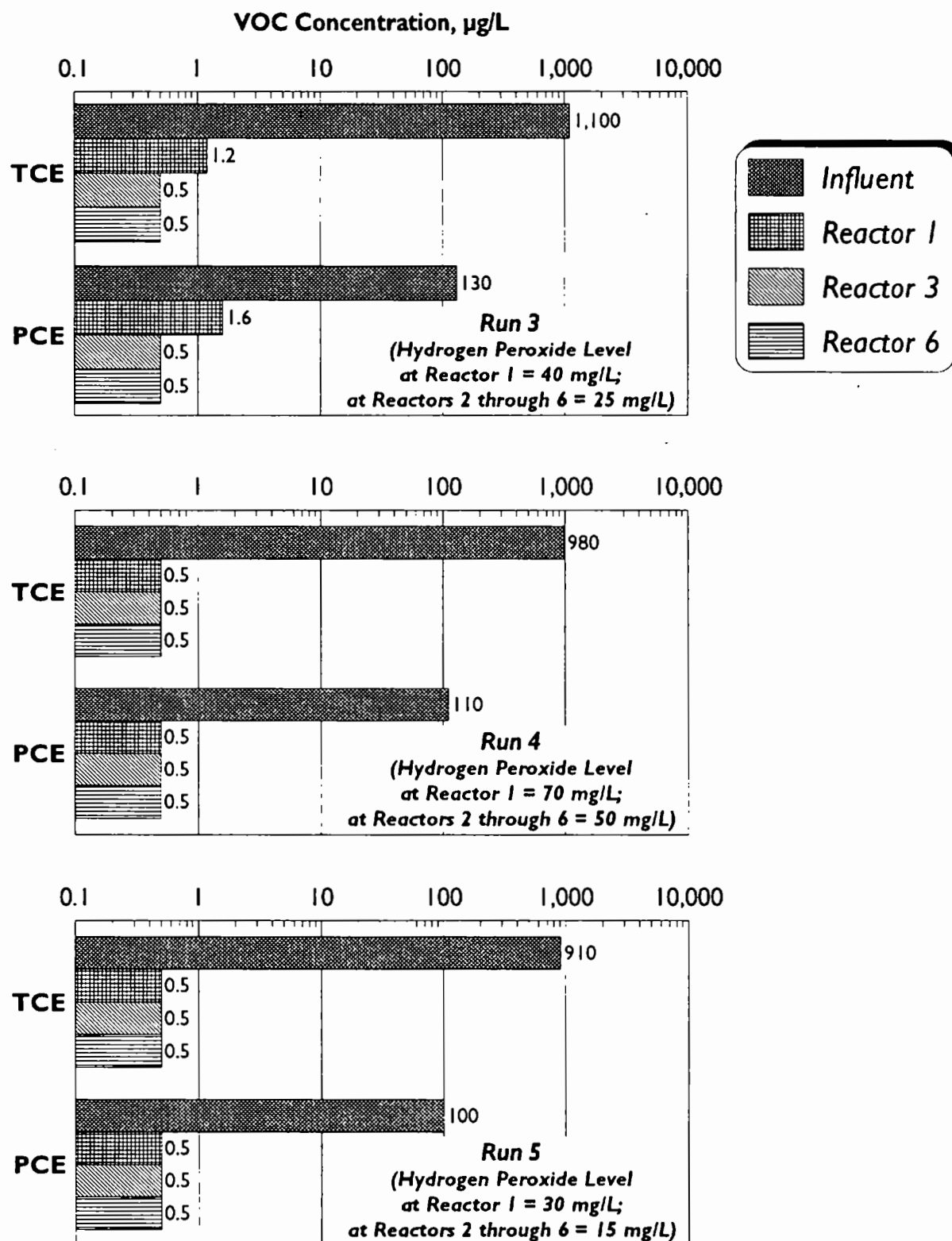
Figures 4 through 6 present Phase 1 VOC concentration data for TCE and PCE. TCA concentrations are not shown in these figures because TCA concentrations in the influent could not be measured.

Figure 4 presents TCE and PCE concentrations in the influent to the treatment system and effluent from Reactors 1, 3, and 6 for Runs 1, 2, and 3. Concentrations are expressed as a function of influent pH. In all three runs, the effluent TCE and PCE concentrations were well below the target concentration of 5 µg/L and below the detection limit of 1 µg/L. Figure 4 shows that the perox-pure™ system performed best in Run 1, when the influent pH was 8 (the unadjusted pH of the groundwater). In this run, the Reactor 1 effluent had lower concentrations of TCE and PCE than in Runs 2 and 3, and it had the same concentrations of TCE and PCE as the Reactor 6 effluent in Runs 2 and 3. However, Reactor 6 effluent TCA concentration was lowest in Run 3 at 1.4 µg/L (Reactor 6 effluent TCA concentrations in Runs 1 and 2 were 6.7 and 3.1 µg/L, respectively). Because TCA is difficult to oxidize, PSI selected Run 3 as the preferred operating condition, with an influent pH of 5.0.

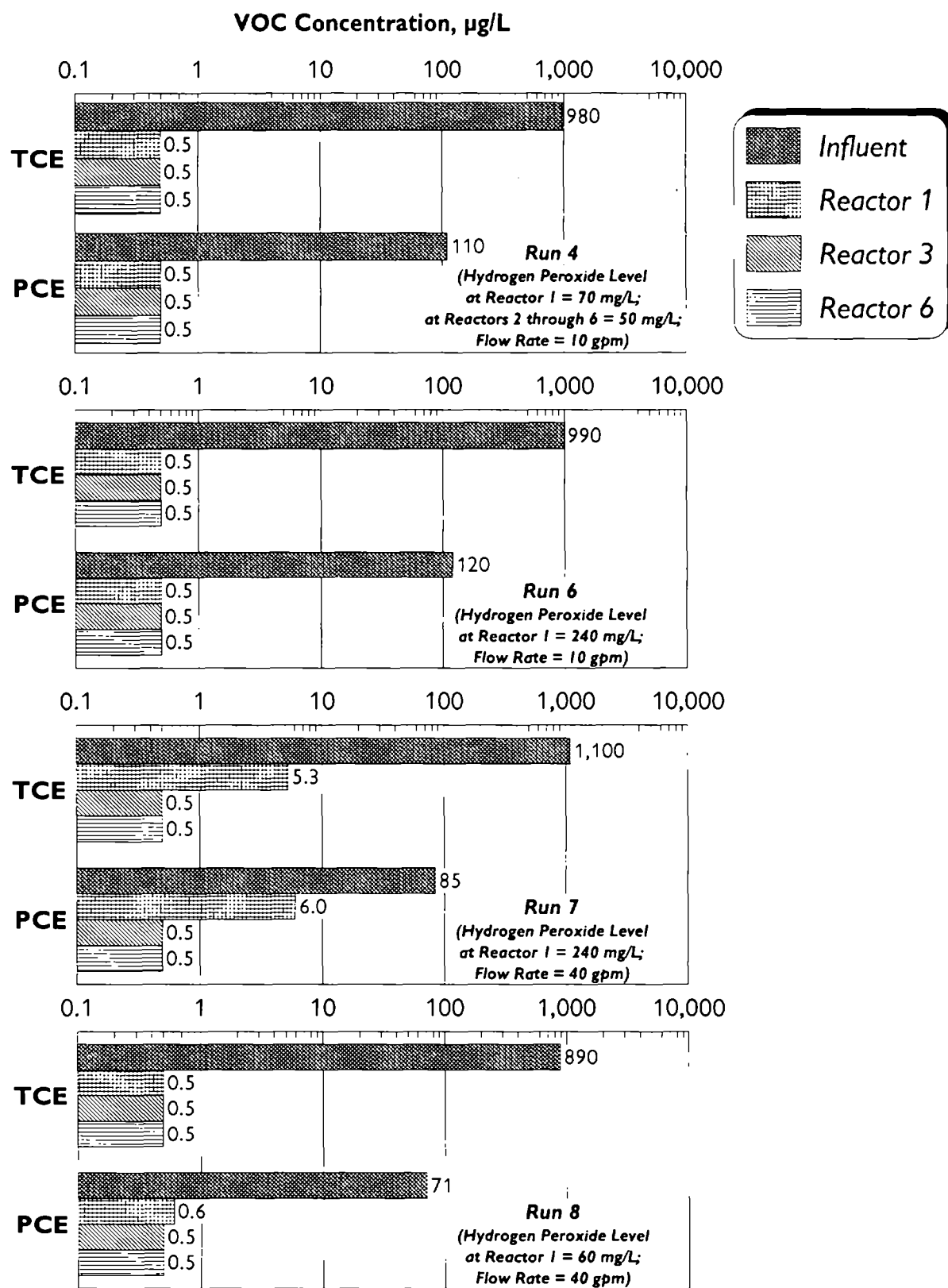
Figure 5 presents a comparison of VOC concentrations in Runs 3, 4, and 5 as a function of hydrogen peroxide levels. Although the effluent TCE and PCE concentrations were the same in all runs, the data also show that Reactor 1 effluent TCE and PCE concentrations were the lowest in Run 4 (the highest hydrogen peroxide level) and in Run 5 (the lowest hydrogen peroxide level). Reasons for higher concentrations of TCE and PCE in the Reactor 1 effluent at intermediate hydrogen peroxide levels cannot be determined from this data. The Reactor 6 effluent TCA concentrations in Runs 3, 4, and 5 were 1.4, 1.8, and 2.1 µg/L, respectively. No definite trend can be identified based on TCE, PCE, and TCA data in Runs 3, 4, and 5.



**Figure 4. Comparison of VOC Concentrations at Different Influent pH Levels**  
 (Hydrogen Peroxide Level at Reactor 1 = 40 mg/L; Hydrogen Peroxide Level at Reactors 2 through 6 = 25 mg/L; Flow Rate = 10 gpm)



**Figure 5. Comparison of VOC Concentrations at Different Hydrogen Peroxide Levels** (Influent pH = 5.0; Flow Rate = 10 gpm)



**Figure 6. Comparison of VOC Concentrations at Different Flow Rates and Hydrogen Peroxide Levels (Influent pH = 5.0)**

Figure 6 presents TCE and PCE concentrations at different flow rates and hydrogen peroxide levels. Runs 4 and 6 were performed at a flow rate of 10 gpm. Runs 7 and 8 were performed at a flow rate of 40 gpm. In Runs 4 and 6, identical total amounts of hydrogen peroxide were added to the contaminated groundwater. However, in Run 4, hydrogen peroxide was added at multiple points in the system using the splitter, while in Run 6, all hydrogen peroxide was added at the influent to the system. Based on a comparison of TCE and PCE concentrations in Runs 4 and 6, the effect of adding hydrogen peroxide at multiple points in the perox-pure™ system cannot be evaluated, because in both runs, TCE and PCE concentrations in the effluent were below the detection limit of 1.0 µg/L. However, effluent TCA concentrations in Runs 4 and 6 were 1.8 and 3.0 µg/L, respectively. Based on the decreased concentrations of the less easily oxidized TCA with splitter use, adding hydrogen peroxide at multiple points in the perox-pure™ system appears to enhance the system's performance.

A comparison of Runs 6 and 7 shows that both TCE and PCE concentrations in Reactor 1 effluent were higher in Run 7 than in Run 6. Similarly, the effluent TCA concentration in Run 7 (3.9 µg/L) was higher than in Run 6 (3.0 µg/L). These observations are consistent with the operating conditions, because contaminated groundwater had a much longer UV exposure time in Run 6 than in Run 7. UV exposure times were 1.5 and 0.4 minutes in Runs 6 and 7, respectively.

A comparison of TCE and PCE concentrations in Runs 7 and 8 shows that both TCE and PCE concentrations in Reactor 1 effluent were higher in Run 7 than in Run 8. Effluent TCA concentrations were about the same in both runs (3.9 and 4.0 µg/L in Runs 7 and 8, respectively). The higher Reactor 1 effluent TCE concentration in Run 7 may be attributed to higher influent TCE concentrations in that run. Reactor 1 effluent TCE concentrations correspond to 99.5 and greater than 99.9 percent TCE removal in Runs 7 and 8, respectively. Similarly, the Reactor 1 effluent PCE concentrations correspond to 92.9 and greater than 99.2 percent PCE removal in Runs 7 and 8, respectively. These data indicate that higher doses of hydrogen peroxide may have scavenged hydroxyl radicals or excess hydrogen peroxide reduced UV transmittance through water, resulting in lower removal efficiencies for Run 7 than those for Run 8.

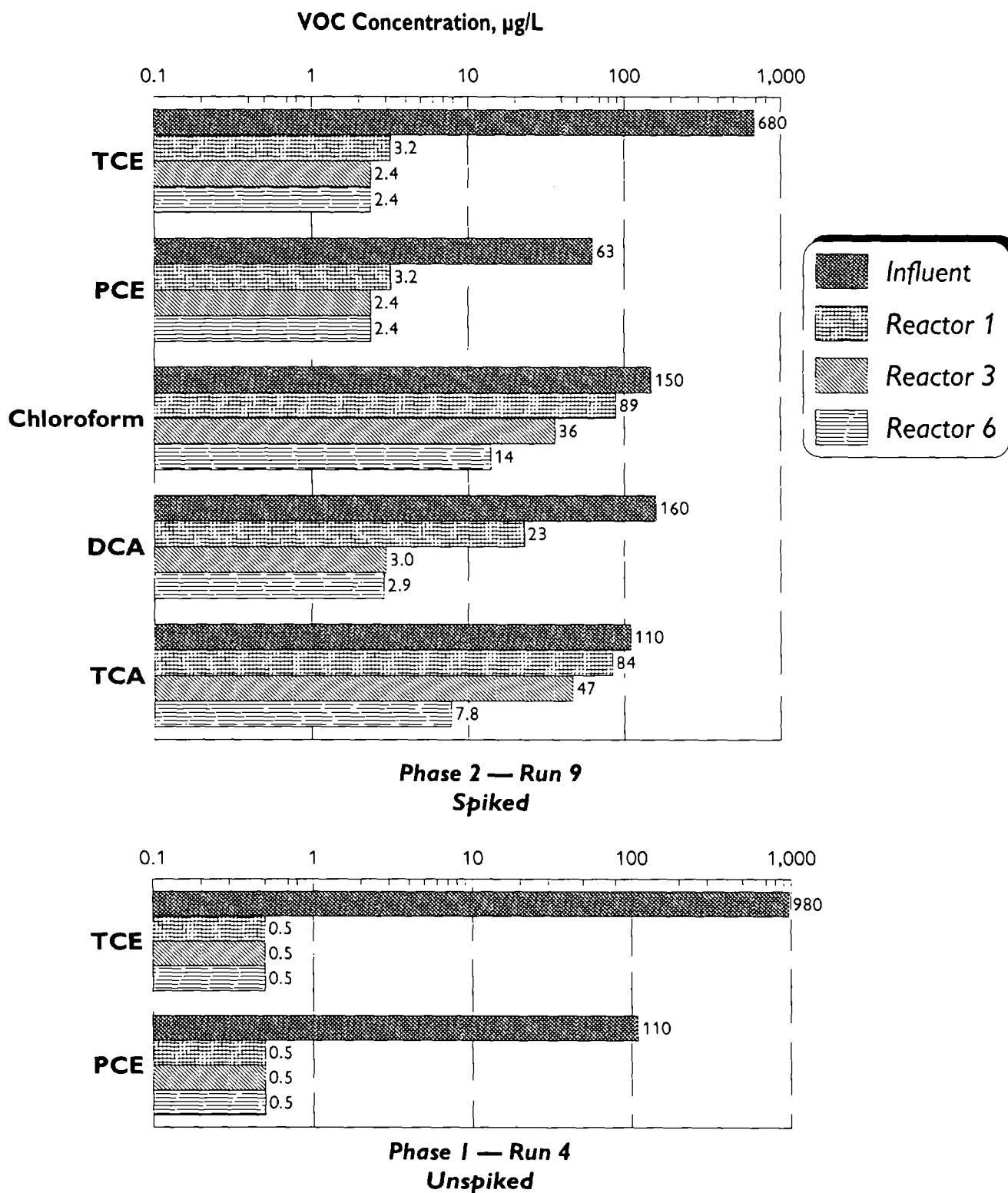
Based on quick turnaround analyses performed during Runs 1 through 6, PSI selected Run 3 operating conditions as preferred for spiked groundwater. As a result, Runs 10 through 14 were performed using Run 3 operating conditions.

## Phase 2 Results

Phase 2 (Runs 9 through 12) results for VOC removal in the perox-pure™ system are presented in Figures 7 through 9. Figure 7 presents a comparison of the system's performance in treating spiked groundwater (Run 9) and unspiked groundwater (Run 4). Figure 7 shows that TCE and PCE concentrations in treated groundwater were higher in Run 9 (spiked groundwater) than in Run 4 (unspiked groundwater). These data suggest that spiking compounds (chloroform, DCA, and TCA) affected the perox-pure™ system's performance in removing TCE and PCE, perhaps because of the additional oxidant demand. However, treated groundwater TCE and PCE concentrations plotted in Figure 7 are estimated concentrations. Because the detection limit for TCE and PCE in Run 9 was 5 µg/L and in Run 4 was 1 µg/L, and because TCE and PCE were present at nondetectable levels in treated groundwater in both runs, the estimated concentrations in Run 9 are higher than in Run 4. Therefore, the data are inconclusive with regard to the effect of spiking compounds on the removal of TCE and PCE.

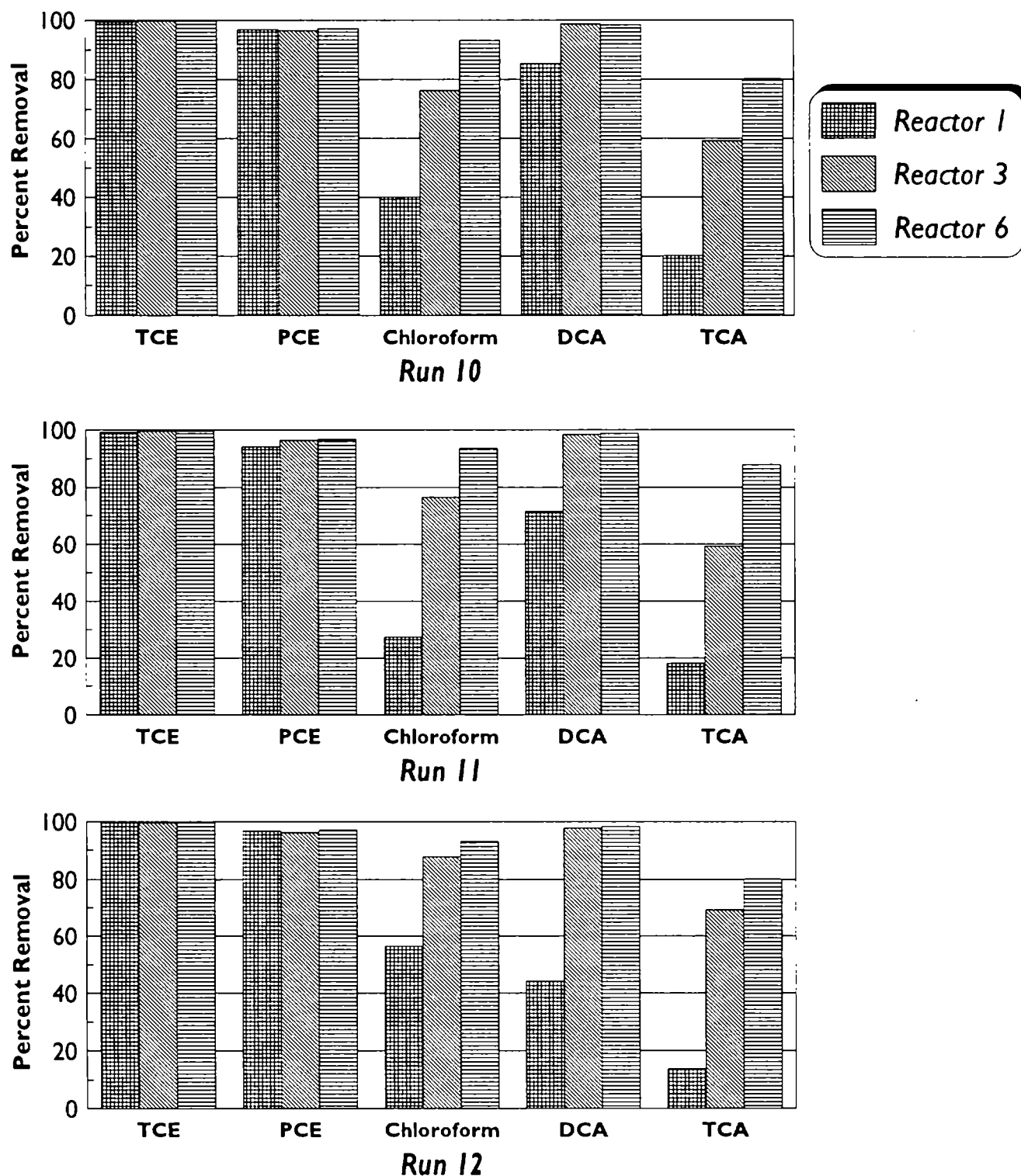
During the reproducibility runs (Runs 10, 11, and 12), the effluent TCE, PCE, and DCA levels were generally below detection limit (5 µg/L) and effluent chloroform and TCA levels ranged from 15 to 30 µg/L. VOC removal efficiencies in reproducibility runs are plotted in Figure 8. Figure 8 shows that for TCE and PCE, which are relatively easily oxidized, most of the removal occurred in Reactor 1, leaving only trace quantities of TCE and PCE to be removed in the rest of the perox-pure™ system. However, for chloroform, DCA, and TCA, which are more difficult to oxidize, considerable removal occurred beyond Reactor 1. During the three reproducibility runs, average removal efficiencies for TCE, PCE, chloroform, DCA, and TCA after Reactor 1 were 99.5, 95.9, 41.3, 67.0, and 17.4 percent, respectively. Effluent samples showed overall removal efficiencies for TCE, PCE, chloroform, DCA, and TCA were 99.7, 97.1, 93.1, 98.3, and 81.8 percent, respectively. The overall removal efficiencies of the perox-pure™ system were reproducible for all VOCs. However, for certain compounds, the removal efficiencies after Reactor 1 were quite variable (for example, chloroform removal efficiencies ranged from 27.4 to 56.3 percent). This variability may be associated with sampling and analytical precision.

Figure 9 compares the 95 percent UCL of effluent VOC concentrations with target levels in reproducibility runs. For this project, the target level for a given VOC was set at the most stringent limit in cases where the VOC has multiple regulatory limits. For all VOCs but

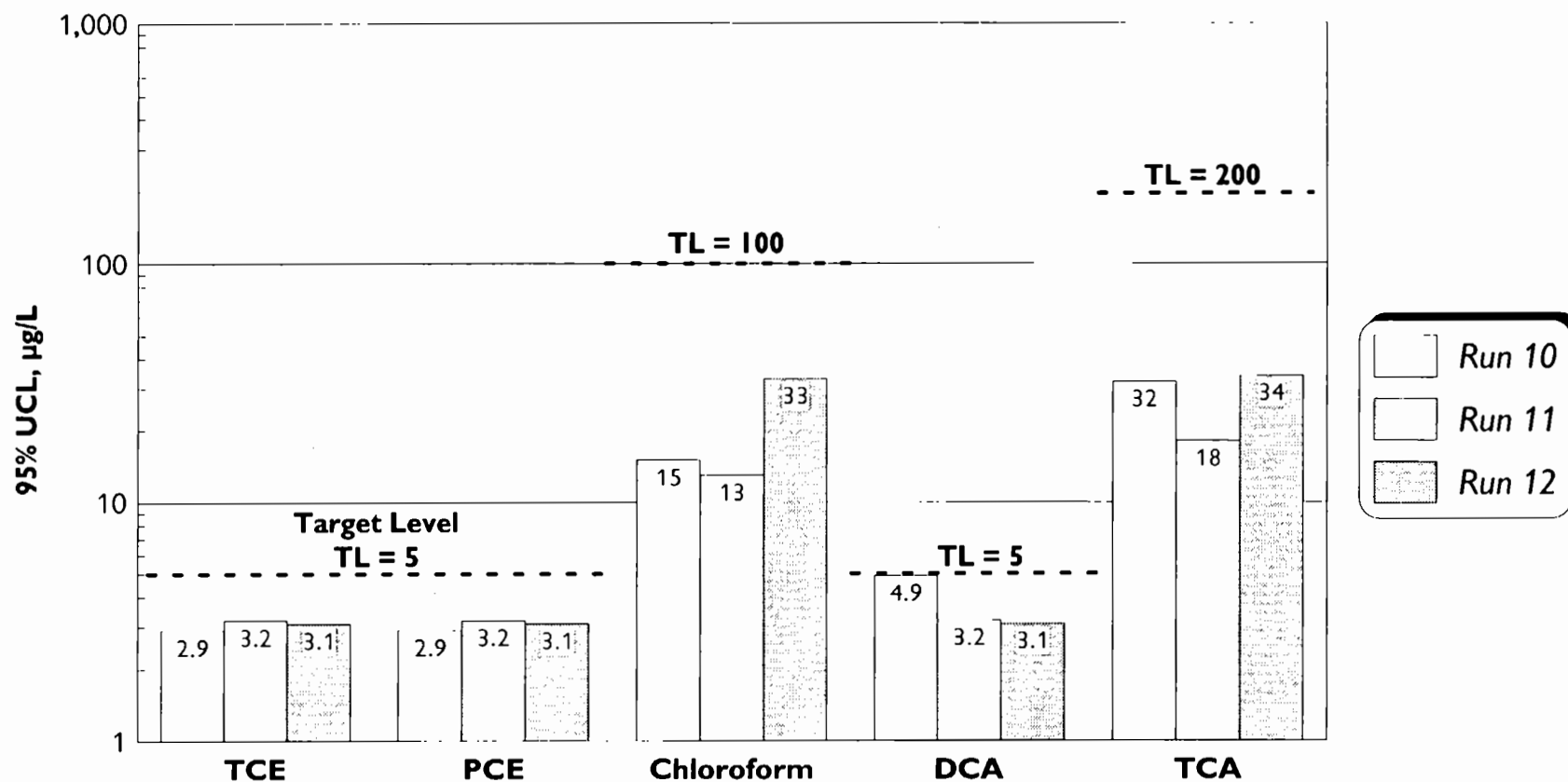


**Figure 7. Comparison of VOC Concentrations in Spiked and Unspiked Groundwater**  
 (Influent pH = 5.0; Hydrogen Peroxide Level at Reactor 1 = 70 mg/L; Hydrogen Peroxide Level at Reactors 2 through 6 = 50 mg/L; Flow Rate = 10 gpm)





**Figure 8. VOC Removal Efficiencies in Reproducibility Runs**  
 (Influent pH = 5.0; Hydrogen Peroxide Level at Reactor 1 = 40 mg/L; Hydrogen Peroxide Level at Reactors 2 through 6 = 25 mg/L; Flow Rate = 10 gpm)



**Figure 9. Comparison of 95 Percent UCLs for Effluent VOC Concentrations with Target Levels in Reproducibility Runs** (Influent pH = 5.0; Hydrogen Peroxide Level at Reactor 1 = 40 mg/L; Hydrogen Peroxide Level at Reactors 2 through 6 = 25 mg/L; Flow Rate = 10 gpm)

chloroform, the most stringent limit is the California drinking water action level. For chloroform, the most stringent limit is the MCL specified in the Safe Drinking Water Act (SDWA). Figure 9 shows that the perox-pure™ system effluent met the target levels at the 95 percent confidence level in all three reproducibility runs, indicating that the system performance was reproducible.

### Phase 3 Results

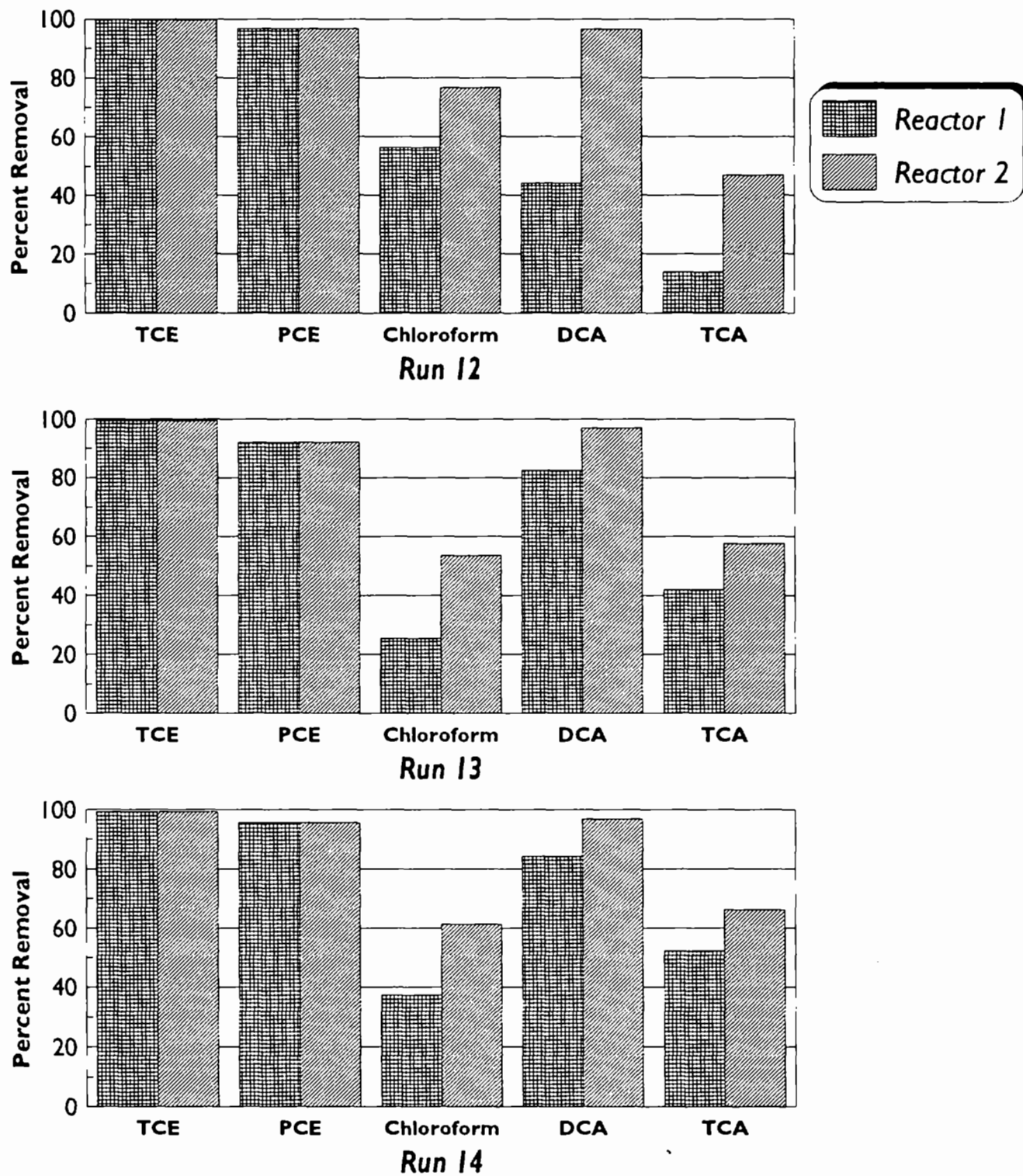
Figure 10 presents VOC concentrations in Runs 12, 13, and 14, conducted to evaluate quartz tube cleaning. In Run 12, quartz tubes from the previous demonstration runs were used. In Run 13, scaled quartz tubes were used. These tubes had been exposed to an environment that encouraged scaling and had not been maintained with cleaners or wipers. In Run 14, quartz tubes that had been maintained by cleaners or wipers were used.

A comparison of removal efficiencies for TCE in Reactors 1 and 2 shows that TCE removal efficiencies were about the same in all runs. PCE removal efficiencies were about 3 percent less in Run 13 than that in Runs 12 or 14. Removal efficiencies for chloroform, DCA, and TCA were uniformly lower in Run 13 than in Run 14, indicating that periodic cleaning of quartz tubes by wipers is required to maintain the perox-pure™ system's performance. Without such cleaning, removal efficiencies in the system will likely decrease in an aqueous environment that would cause scaling of quartz tubes. For example, after Reactor 2, chloroform removal efficiency in Run 13 was 53.4 percent, compared to 61.3 percent in Run 14. Because the quartz tubes used in Run 12 had little coating, removal efficiencies in Run 12 were expected to be higher than those in Run 13. However, the demonstration did not confirm this for all VOCs. For example, Run 12 TCA removal efficiencies were less than Run 13 TCA removal efficiencies; reasons for this inconsistency cannot be identified from the data.

### **Summary of Results for Noncritical Parameters**

The technology demonstration also evaluated analytical results of several noncritical parameters. These results are summarized below.

GC/MS analysis of influent and effluent samples for VOCs indicated that new target compounds or tentatively identified compounds (TIC) were not formed during the treatment.



**Figure 10. VOC Removal Efficiencies in Quartz Tube Cleaner Runs**  
(Influent pH = 5.0; Hydrogen Peroxide Level at Reactor 1 = 40 mg/L; Hydrogen Peroxide Level at Reactors 2 through 6 = 25 mg/L; Flow Rate = 10 gpm)

GC/MS analysis of influent and effluent samples for SVOCs showed that target SVOCs were not present at detectable levels. However, several unknown TICs were present in both the influent and effluent samples.

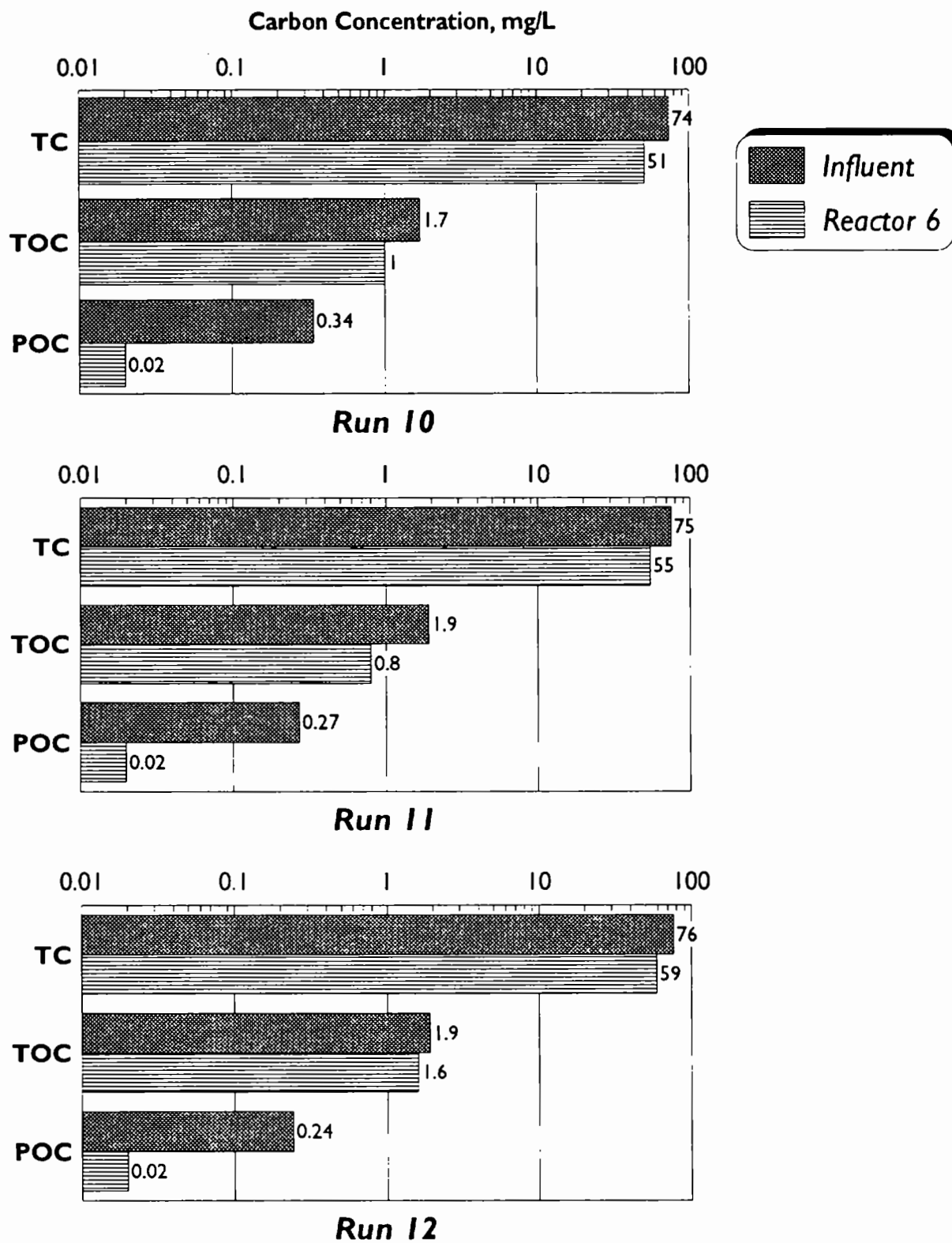
Average influent TOX and AOX concentrations were 800 µg/L and 730 µg/L, respectively. The perox-pure™ system achieved TOX removal efficiencies that ranged from 93 to 99 percent and AOX removal efficiencies that ranged from 95 to 99 percent.

The TC, TOC, and POC concentrations in influent and effluent samples in Runs 10, 11, and 12 are presented in Figure 11. Average TC concentrations in the influent and effluent were 75 mg/L and 55 mg/L, respectively. The decrease in TC concentration in the perox-pure™ system may be attributable to the loss of dissolved carbon dioxide as a result of the turbulent movement of contaminated groundwater in the perox-pure™ system.

Figure 11 shows an average decrease in TOC concentrations of about 40 percent during treatment. The decrease corresponds to the amount of organic carbon that was converted to inorganic carbon during treatment, suggesting that about 40 percent of the organic carbon was completely oxidized to carbon dioxide. However, the TOC data does not indicate whether the organic carbon that was completely oxidized originated from the VOCs or from some other compounds present in groundwater.

Effluent POC concentration was about 0.02 mg/L which is below the reporting limit of 0.035 mg/L. POC concentration data show that the average POC removal efficiency was about 93 percent. Assuming that the majority of organic carbon associated with VOCs could be measured as POC, this indicates that about 93 percent of volatile organic carbon was converted to either carbon dioxide or nonpurgeable organic carbon.

During Runs 10, 11, and 12, bioassay tests were performed to evaluate the acute toxicity of influent to and effluent from the perox-pure™ systems. Two freshwater test organisms, a water flea (*ceriodaphnia dubia*) and a fathead minnow (*pimephales promelas*), were used in the bioassay tests. Toxicity was measured as the lethal concentration at which 50 percent of the organisms died (LC<sub>50</sub>), and expressed as the percent of effluent (or influent) in the test water. One influent and one effluent sample were tested in each run. One control sample was also tested to evaluate the toxicity associated with hydrogen peroxide residual present in the effluent. The control sample



**Figure 11. Carbon Concentrations in Reproducibility Runs**  
 (Influent pH = 5.0; Hydrogen Peroxide Level at Reactor 1 = 40 mg/L; Hydrogen Peroxide Level at Reactors 2 through 6 = 25 mg/L; Flow Rate = 10 gpm)

had about 10.5 mg/L of hydrogen peroxide (average effluent residual in Runs 10, 11, and 12), and had characteristics (alkalinity, hardness, and pH) similar to that of effluent in Runs 10, 11, and 12.

In general, the influent was not found to be acutely toxic to either test organism. The effluent was found to be acutely toxic to both test organisms. The influent  $LC_{50}$  values for both organisms indicated that in the undiluted influent sample more than 50 percent of the organisms survived. However,  $LC_{50}$  values for the water flea were estimated to be 35, 13, and 26 percent effluent in Runs 10, 11, and 12, respectively; and  $LC_{50}$  values for the fathead minnow were estimated to be 65 and 71 percent effluent in Runs 10 and 11, respectively. In Run 12, more than 50 percent of the fathead minnows survived in the undiluted effluent. The  $LC_{50}$  value for the water flea was estimated to be 17.7 percent in the control sample, indicating that the sample contained hydrogen peroxide at a concentration that was acutely toxic to water fleas. However, more than 50 percent of the fathead minnows survived in the undiluted control sample indicating hydrogen peroxide was not acutely toxic to fathead minnows at a concentration of 10.5 mg/L. This observation, however, is not entirely consistent with observations made by the Connecticut Department of Environmental Protection (CDEP). The CDEP Water Toxics Section of Water Management Division reports  $LC_{50}$  value of 18.2 mg/L of hydrogen peroxide with 95 percent confidence limits of 10 mg/L and 25 mg/L (CDEP, 1993).

Comparison of the  $LC_{50}$  value of the control sample with  $LC_{50}$  values of effluent samples for water fleas indicates the toxicity associated with the effluent samples is probably due to hydrogen peroxide residual in the effluent. However, no conclusion can be drawn on the effluent toxicity to fathead minnows because the control sample toxicity results from the SITE demonstration data are not entirely consistent with the data collected by CDEP.

Iron and manganese were present at trace levels in the influent. In general, iron was present at levels less than 45  $\mu\text{g/L}$ , and manganese was present at an average level of 15  $\mu\text{g/L}$ . Significant removal of iron or manganese did not occur in the perox-pure™ system, because these metals were present only at trace levels in the influent.

No changes in pH, alkalinity, hardness, or specific conductance were observed during treatment.

Average influent temperature was about 72 °F. Average effluent temperatures were about 90 °F and 76 °F, at influent flow rates of 10 gpm and 40 gpm, respectively. Because 10 gpm corresponds to a hydraulic retention time of 1.5 minutes and 40 gpm corresponds to a retention time of 0.4 minutes for the perox-pure™ system evaluated, the average temperature increase due to 1 minute of UV radiation exposure in the perox-pure™ system is about 12 °F.

## CONCLUSIONS

For the spiked groundwater, PSI determined the following preferred operating conditions: (1) influent hydrogen peroxide concentration of 40 mg/L, (2) hydrogen peroxide concentration of 25 mg/L at the influent to Reactors 2 through 6, (3) influent pH of 5.0, and (4) flow rate of 10 gpm. At these conditions, the effluent TCE, PCE, and DCA levels were generally below detection limit (5 µg/L) and effluent chloroform and TCA levels ranged from 15 to 30 µg/L. The average removal efficiencies for TCE, PCE, chloroform, DCA, and TCA were about 99.7, 97.1, 93.1, 98.3, and 81.8 percent, respectively.

For the unspiked groundwater, the effluent TCE and PCE levels were generally below detection limit (1 µg/L) with corresponding removal efficiencies of about 99.9 and 99.7 percent. The effluent TCA levels ranged from 1.4 to 6.7 µg/L with corresponding removal efficiencies ranging from 35 to 84 percent.

The perox-pure™ system effluent met California drinking water action levels and federal drinking water MCLs for TCE, PCE, chloroform, DCA, and TCA at the 95 percent confidence level.

The quartz tube wipers were effective in keeping the tubes clean, and they appear to reduce the adverse effect scaling has on contaminant removal efficiencies.

TOX removal efficiencies ranged from 93 to 99 percent. AOX removal efficiencies ranged from 95 to 99 percent.

For spiked groundwater, during reproducibility runs, the perox-pure™ system achieved average removal efficiencies of 38 percent and about 93 percent for TOC and POC, respectively.



The temperature of groundwater increased at a rate of 12 °F per minute of UV exposure in the perox-pure™ system. Since the oxidation unit is exposed to the surrounding environment, the temperature increase may vary depending upon the ambient temperature or other atmospheric conditions.

## **FIELD OPERATIONAL AND EQUIPMENT PROBLEMS**

The PRC SITE team experienced a few operational and equipment problems during the demonstration. Some of these problems resulted in changes in the demonstration schedule, while the others required making decisions in the field to solve the problems. These problems and solutions include the following:

- Based on the 8-hour drawdown test performed in May 1992, LLNL estimated that during the demonstration, contaminated groundwater could be extracted from Wells W-7-O and W-875-08 at approximately 9 gpm and 3 gpm, respectively. The demonstration tests were designed assuming that the combined stream would be the influent to the perox-pure™ system. However, based on the observations made in early September 1992, LLNL informed the SITE team that the wells may not provide the estimated yield throughout the demonstration. The SITE team resolved this issue by reducing the extraction rates from both wells in the same proportion, so that the influent characteristics would be approximately the same as those estimated before the demonstration. The SITE team extracted groundwater from Wells W-7-O and W-875-08 at 6 gpm and 2 gpm, respectively. This approach did not affect the demonstration schedule or the technology evaluation.
- Flow rates through the perox-pure™ system for Runs 7 and 8 were planned to be 50 gpm. In order to maintain the preferred influent pH conditions of approximately five, the system flow rate was reduced to 40 gpm. PSI's acid feed pumps were not capable of providing enough acid to the process flow to increase the system flow rate. This deviation did not alter the selection of preferred conditions from Phase 1 of the technology evaluation despite the increased hydraulic retention time (inversely proportional to flow rate) resulting from the change in flow rate.
- PSI requested that one of its operating facilities ship three scaled (coated) and three clean (uncoated) quartz tubes to perform Phase 3 test runs. However, of the six quartz tubes, one tube was broken in transit. PSI did not have enough time to replace the broken tube. Therefore, Phase 3 tests (Runs 13 and 14) were performed with only two UV lamps on, instead of three. As a result, perox-pure™ system performance with coated tubes and uncoated tubes was compared based on the removals achieved in two reactors, instead of those achieved in three reactors.

- Late arrival of the perox-pure™ system (particularly the hydrogen peroxide feed tank) and other auxiliary equipment (such as the bladder tank, pumps, and other miscellaneous items) delayed the technology demonstration by 3 days. However, the PRC SITE team completed the demonstration on schedule by working late evenings and weekends.
- At the beginning of the demonstration, while setting the operating parameters, water inside the oxidation unit overheated and burned the gaskets that maintain a water-tight seal in two of the reactors. As a result, water leaked out of the treatment unit. PSI collected this water in a 55-gallon drum. PSI explained that because of its oversight, a few pneumatically operated valves did not have an air supply, resulting in a stagnant volume of water that overheated. PSI also stated that the temperature sensor inside the unit, which is located in the top reactor, did not detect the high water temperature because the unit was only partially filled. Later, PSI connected an air compressor to the unit to avoid reoccurrence of this situation. Replacement gaskets arrived the following day, causing the demonstration to be postponed 1 day.
- During the initial stage of the demonstration due to improper operation of valves downstream of the perox-pure™ system, the pressure inside the perox-pure™ unit exceeded the design limit and the pressure relief gasket gave way. PSI immediately collected the leaking water in a drum and shut off the influent. Because PSI had a replacement gasket on site, this operational problem did not cause a significant delay.
- Halfway through the demonstration, while one test run was in progress, the sulfuric acid level in the acid feed tank decreased significantly. As a result, the influent pH could not be lowered to the desired level, and the PRC SITE team discontinued the run. The run was repeated after PSI filled the acid feed tank with sulfuric acid.
- The PRC SITE team initially encountered problems measuring the effluent pH at the sampling location downstream of sodium hydroxide addition point. Because no static mixer was used, the sodium hydroxide added to raise the effluent pH did not adequately mix with the effluent. Lack of proper mixing caused problems in measuring the true effluent pH after sodium hydroxide addition. The PRC SITE team resolved this issue by installing another sampling port about 100 feet downstream, just before the treated water entered the storage tanks. This modification significantly reduced fluctuations in pH and provided a good measure of effluent pH.

## SECTION 7

### COST OF DEMONSTRATION

The cost (rounded to the nearest \$1,000) of conducting the EPA SITE demonstration of the perox-pure™ chemical oxidation technology on the contaminated ground water at the LLNL site was approximately \$760,000. This cost includes site characterization and preparation, demonstration planning and field work, chemical analyses, and report preparation. The PSI portion of this cost was \$11,000 and the balance of \$749,000 was allocated to the SITE program.

#### EPA SITE CONTRACTOR COSTS

Each SITE project is divided into two phases: planning (Phase I) and demonstration (Phase II). Costs (rounded to the nearest \$1,000) for each phase are presented below along with a list of the activities performed during each phase. Phase I costs are actual costs previously incurred; Phase II costs include actual costs plus estimates for labor to complete the Technology Evaluation Report (TER), Applications Analysis Report (AAR), and technology demonstration videotape.

#### Phase I: Planning

Phase I activities included the following:

- Chemical oxidation technology literature review
- Ground water sampling and testing
- Sampling and analysis plan development
- Demonstration plan development

Costs for Phase I are summarized below by cost category:

Labor	\$80,000
Equipment and supplies	5,000
Travel	4,000
Chemical analyses	5,000
TOTAL	<u>\$94,000</u>

## **Phase II: Demonstration**

Phase II activities included the following:

- Site preparation, mobilization, and demobilization
- Sample collection and field oversight
- Chemical analyses (field and off-site)
- Support for the U.S.-German bilateral program
- TER, AAR, and videotape preparation

Costs for Phase II are summarized below by cost category:

Labor	\$300,000
Sampling equipment and supplies	30,000
Travel/transportation	25,000
Chemical analyses	200,000
Subcontractors (including rental of tanks, pumps, trailer, and enclosure and waste disposal)	<u>100,000</u>
TOTAL	\$655,000

## **DEVELOPER COSTS**

Developer costs are the actual costs incurred by PSI in preparing for and conducting the SITE demonstration.

PSI's costs (rounded to the nearest \$1,000) are presented below:

Labor	\$ 3,000
Laboratory	1,000
Travel	2,000
Equipment (using retail rate)	<u>5,000</u>
TOTAL	\$ 11,000

## SECTION 8

### CONCLUSIONS AND RECOMMENDATIONS

#### CONCLUSIONS

For the spiked groundwater, PSI determined the following preferred operating conditions: (1) influent hydrogen peroxide concentration of 40 mg/L, (2) hydrogen peroxide concentration of 25 mg/L at the influent to Reactors 2 through 6, (3) influent pH of 5.0, and (4) flow rate of 10 gpm. At these conditions, the effluent TCE, PCE, and DCA levels were generally below detection limit (5 µg/L) and effluent chloroform and TCA levels ranged from 15 to 30 µg/L. The average removal efficiencies for TCE, PCE, chloroform, DCA, and TCA were about 99.7, 97.1, 93.1, 98.3, and 81.8 percent, respectively.

For the unspiked groundwater, the effluent TCE and PCE levels were generally below detection limit (1 µg/L) with corresponding removal efficiencies of about 99.9 and 99.7 percent. The effluent TCA levels ranged from 1.4 to 6.7 µg/L with corresponding removal efficiencies ranging from 35 to 84 percent.

The perox-pure™ system effluent met California drinking water action levels and federal drinking water MCLs for TCE, PCE, chloroform, DCA, and TCA at the 95 percent confidence level.

The quartz tube wipers were effective in keeping the tubes clean, and they appear to reduce the adverse effect scaling has on contaminant removal efficiencies.

TOX removal efficiencies ranged from 93 to 99 percent. AOX removal efficiencies ranged from 95 to 99 percent.

For spiked groundwater, during reproducibility runs, the perox-pure™ system achieved average removal efficiencies of 38 percent and about 93 percent for TOC and POC, respectively.

The temperature of groundwater increased at a rate of 12 °F per minute of UV exposure in the perox-pure™ system. Since the oxidation unit is exposed to the surrounding environment, the temperature increase may vary depending upon the ambient temperature or other atmospheric conditions.

## RECOMMENDATIONS

The following recommendations are made based on the SITE demonstration results. These recommendations should be taken into account when the perox-pure™ chemical oxidation system is considered for treating contaminated liquid wastes.

During the SITE demonstration, although the effluent VOC levels were well below the target levels (federal drinking water MCLs and California drinking water action levels), bioassay test indicated that the effluent was toxic while the influent was not toxic to freshwater test organisms (*Ceriodaphnia dubia* and *Pimephales promelas*). However, these bioassay tests were inconclusive regarding whether the toxicity was because of hydrogen peroxide residual or the perox-pure™ treatment. Because hydrogen peroxide appears to be toxic to certain aquatic organisms at levels greater than 10 mg/L, it is recommended that the effluent hydrogen peroxide residual be kept well below 10 mg/L. After this, in addition to performing physicochemical analyses, the bioassay tests should be performed on the effluent to determine if the effluent can be discharged to aquatic bodies.

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**APPENDIX A**  
**ANALYTICAL DATA FOR REPRODUCIBILITY RUNS**



**TABLE A-1**  
**ANALYTICAL DATA FOR VOCs BY GC ANALYSIS IN RUN 10**

VOC**	Unit	Influent		Reactor 1 - Effluent		Reactor 2 - Effluent		Reactor 3 - Effluent		Reactor 6 - Effluent	
		Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation
Chloroform	µg/L	140	8.16	84.0*	9.5*	NA	NA	43.0	7.07	10.4	3.7
1,1-Dichloroethane	µg/L	163	20.6	26.3*	5.5*	NA	NA	2.9	0.85	2.9	0.85
Tetrachloroethene	µg/L	92	7.93	3.0	1.41	NA	NA	2.4	0.48	2.4	0.48
1,1,1-Trichloroethane	µg/L	114	21.4	90.7*	4.9*	NA	NA	59.5	10.2	25.8	4.7
Trichloroethene	µg/L	1020*	76.4*	6.1	7.26	NA	NA	2.4	0.48	2.4	0.48

Notes: \* Mean and standard deviation were calculated using data for three of four replicates.  
 \*\* VOCs present above detection limit.

**TABLE A-2**  
**ANALYTICAL AND MEASUREMENT DATA FOR MISCELLANEOUS PARAMETERS IN RUN 10**

Parameter	Unit	Sampling/Measurement Locations					
		Chemical Feed Tank	Influent - Before H <sub>2</sub> SO <sub>4</sub>	Influent - After H <sub>2</sub> SO <sub>4</sub>	Reactor 2 Effluent	Reactor 6 Effluent	Effluent - After NaOH
Alkalinity	mg/L as CaCO <sub>3</sub>	NA	280	88	NA	112	NA
Bioassay, LC <sub>50</sub>	NA	NA	NA	NA	NA	NA	NA
<i>Ceriodaphnia dubia</i>	% Sample	NA	NA	> 100	NA	17	NA
<i>Pimephales promelas</i>	% Sample	NA	NA	> 100	NA	65	NA
Electricity Consumption*	kW	NA	NA	NA	NA	NA	NA

TABLE A-2

## ANALYTICAL AND MEASUREMENT DATA FOR MISCELLANEOUS PARAMETERS IN RUN 10 (Continued)

Parameter	Unit	Sampling/Measurement Locations					
		Chemical Feed Tank	Influent - Before H <sub>2</sub> SO <sub>4</sub>	Influent - After H <sub>2</sub> SO <sub>4</sub>	Reactor 2 Effluent	Reactor 6 Effluent	Effluent - After NaOH
Flow Rate	NA	NA	NA	NA	NA	NA	NA
Ground Water Flow Rate	gpm	NA	NA	10	NA	NA	NA
H <sub>2</sub> O <sub>2</sub> Flow Rate	mL/min	9.1	NA	NA	NA	NA	NA
Acid Flow Rate	mL/min	3.2	NA	NA	NA	NA	NA
Base Flow Rate	mL/min	10.3	NA	NA	NA	NA	NA
Hardness	mg/L as CaCO <sub>3</sub>	NA	310	315	NA	310	NA
Hydrogen Peroxide	mg/L	598,000	NA	NA	NA	13.1	NA
Iron	μg/L	NA	<46.0	NA	NA	<46.0	NA
Manganese	μg/L	NA	15.7	NA	NA	16.5	NA
pH <sup>b</sup> , Mean	pH Units	NA	7.47	5.58	NA	5.76	7.65
pH <sup>b</sup> , Range	pH Units	NA	7.47-7.47	5.39-5.76	NA	5.62-5.90	6.37-8.93
Purgeable Organic Carbon	mg/L	NA	0.34	NA	NA	0.04	NA
Semivolatile Organic Compounds <sup>c</sup>	NA	NA	NA	NA	NA	NA	NA
Hexathiepane (14.80-14.82)	μg/L	NA	8.8	NA	NA	ND	NA
Pentanoic acid (4.73)	μg/L	NA	ND	NA	NA	ND	NA
Unknown (3.64-7.68)	μg/L	NA	18	NA	NA	ND	NA
Unknown (5.01)	μg/L	NA	ND	NA	NA	ND	NA
Unknown (16.90-16.91)	μg/L	NA	66	NA	NA	ND	NA
Unknown (17.59-17.62)	μg/L	NA	ND	NA	NA	ND	NA

TABLE A-2

## ANALYTICAL AND MEASUREMENT DATA FOR MISCELLANEOUS PARAMETERS IN RUN 10 (Continued)

Parameter	Unit	Sampling/Measurement Locations					
		Chemical Feed Tank	Influent - Before H <sub>2</sub> SO <sub>4</sub>	Influent - After H <sub>2</sub> SO <sub>4</sub>	Reactor 2 Effluent	Reactor 6 Effluent	Effluent - After NaOH
Unknown (19.98-19.99)	µg/L	NA	66	NA	NA	ND	NA
Unknown (21.00-21.04)	µg/L	NA	ND	NA	NA	ND	NA
Unknown (21.93-21.94)	µg/L	NA	ND	NA	NA	ND	NA
Sodium Hydroxide Concentration	N	18.4	NA	NA	NA	NA	NA
Specific Conductance	µmho/cm	NA	NA	1740	NA	1770	NA
Sulfuric Acid Concentration	N	33.4	NA	NA	NA	NA	NA
Total Carbon	mg/L	NA	74	NA	NA	51	NA
Total Organic Carbon	mg/L	NA	1.7	NA	NA	1.0	NA
Temperature	°C	NA	21.8	NA	NA	31.5	NA
Total Organic Halides	µg/L	NA	1200	NA	NA	8.9	NA
Turbidity	NTU	NA	NA	0.35	NA	.20	NA
Volatile Organic Compounds (GC/MS)	NA	NA	NA	NA	NA	NA	NA
Target Analytes	NA	NA	NA	NA	NA	NA	NA
Acetone	µg/L	NA	3	NA	NA	9	NA
2-Butanone	µg/L	NA	ND	NA	NA	ND	NA
Chloroform	µg/L	NA	180	NA	NA	10	NA
1,1-Dichloroethane	µg/L	NA	190	NA	NA	ND	NA
1,1-Dichloroethene	µg/L	NA	15	NA	NA	ND	NA
1,2-Dichloroethene (total)	µg/L	NA	13	NA	NA	ND	NA

TABLE A-2

## ANALYTICAL AND MEASUREMENT DATA FOR MISCELLANEOUS PARAMETERS IN RUN 10 (Continued)

Parameter	Unit	Sampling/Measurement Locations					
		Chemical Feed Tank	Influent - Before H <sub>2</sub> SO <sub>4</sub>	Influent - After H <sub>2</sub> SO <sub>4</sub>	Reactor 2 Effluent	Reactor 6 Effluent	Effluent - After NaOH
Tetrachloroethene	μg/L	NA	120	NA	NA	ND	NA
Toluene	μg/L	NA	6	NA	NA	ND	NA
1,1,1-Trichloroethane	μg/L	NA	170	NA	NA	21	NA
Trichloroethene	μg/L	NA	810	NA	NA	ND	NA
Tentatively Identified Compound (retention time, minutes)	NA	NA	NA	NA	NA	NA	NA
Tetrahydrofuran (14.36-14.46)	μg/L	NA	7	NA	NA	ND	NA

## Notes:

- a The mean electricity consumption was 32.19 kW.
- b Readings were taken 2 or 3 times for pH measurement. Range of readings is also listed.
- c None of the semivolatile organic target analytes were detected. Only tentatively identified compounds (TIC) are given in this table. Retention time in minutes for each TIC is given in parentheses.
- d The flow rate was monitored throughout the run, and the volume remained constant.
- NA Not applicable
- ND Not detected
- °C Degree Celsius
- gpm Gallons per minute
- GC/MS Gas chromatography and mass spectrometry
- kW Kilowatts
- μg/L Micrograms per liter
- μmho/cm Micromhos per centimeter
- mg/L Milligrams per liter
- mL/min Milliliters per minute
- NTU Nephelometric Turbidity Unit
- N Normal (equivalents per liter) solution

**TABLE A-3**  
**ANALYTICAL DATA FOR VOCs BY GC ANALYSIS IN RUN 11**

VOC**	Unit	Influent		Reactor 1 - Effluent		Reactor 2 - Effluent		Reactor 3 - Effluent		Reactor 6 - Effluent	
		Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation
Chloroform	µg/L	147*	5.8*	107*	8.5*	NA	NA	34.8	5.97	9.4*	2.9*
1,1-Dichloroethane	µg/L	167*	5.8*	47.5*	7.6*	NA	NA	2.4	0.48	2.1	0.94
Tetrachloroethene	µg/L	66	3.86	3.8	1.56	NA	NA	2.4	0.48	2.1	0.94
1,1,1-Trichloroethane	µg/L	130	24.5	107	19.0	NA	NA	53.0	8.12	16.0*	1.7*
Trichloroethene	µg/L	730	11.6	3.8	1.56	NA	NA	2.4	0.48	2.1	0.94

Notes: \* Mean and standard deviation were calculated using data for three of four replicates.  
 \*\* VOCs present above detection limit.

**TABLE A-4**  
**ANALYTICAL AND MEASUREMENT DATA FOR MISCELLANEOUS PARAMETERS IN RUN 11**

Parameter	Unit	Sampling/Measurement Locations					
		Chemical Feed Tank	Influent - Before H <sub>2</sub> SO <sub>4</sub>	Influent - After H <sub>2</sub> SO <sub>4</sub>	Reactor 2 Effluent	Reactor 6 Effluent	Effluent - After NaOH
Alkalinity	mg/L as CaCO <sub>3</sub>	NA	270	17	NA	18	NA
Bioassay, LC <sub>50</sub>	NA	NA	NA	NA	NA	NA	NA
<i>Ceriodaphnia dubia</i>	% Sample	NA	NA	> 100	NA	13	NA
<i>Pimephales promelas</i>	% Sample	NA	NA	> 100	NA	71	NA
Electricity Consumption*	kW	NA	NA	NA	NA	NA	NA

TABLE A-4

## ANALYTICAL AND MEASUREMENT DATA FOR MISCELLANEOUS PARAMETERS IN RUN 11 (Continued)

Parameter	Unit	Sampling/Measurement Locations					
		Chemical Feed Tank	Influent - Before H <sub>2</sub> SO <sub>4</sub>	Influent - After H <sub>2</sub> SO <sub>4</sub>	Reactor 2 Effluent	Reactor 6 Effluent	Effluent - After NaOH
Flow Rate	NA	NA	NA	NA	NA	NA	NA
Ground Water Flow Rate	gpm	NA	NA	10	NA	NA	NA
H <sub>2</sub> O <sub>2</sub> Flow Rate	mL/min	9.7	NA	NA	NA	NA	NA
Acid Flow Rate	mL/min	3.2	NA	NA	NA	NA	NA
Base Flow Rate	mL/min	10.3	NA	NA	NA	NA	NA
Hardness	mg/L as CaCO <sub>3</sub>	NA	320	315	NA	315	NA
Hydrogen Peroxide	mg/L	644,000	NA	NA	NA	12.0	NA
Iron	μg/L	NA	<46.0	NA	NA	51.7	NA
Manganese	μg/L	NA	15.8	NA	NA	16.4	NA
pH <sup>b</sup> , Mean	pH Units	NA	7.46	5.05	NA	5.33	7.16
pH <sup>b</sup> , Range	pH Units	NA	7.45-7.47	4.75-5.34	NA	5.07-5.51	6.86-7.45
Purgeable Organic Carbon	mg/L	NA	0.27	NA	NA	0.04	NA
Semivolatile Organic Compounds <sup>c</sup>	NA	NA	NA	NA	NA	NA	NA
Hexathiepane (14.80-14.82)	μg/L	NA	4.0	NA	NA	ND	NA
Pentanoic acid (4.73)	μg/L	NA	30	NA	NA	ND	NA
Unknown (3.64-7.68)	μg/L	NA	ND	NA	NA	ND	NA
Unknown (5.01)	μg/L	NA	ND	NA	NA	ND	NA
Unknown (16.90-16.91)	μg/L	NA	ND	NA	NA	ND	NA
Unknown (17.59-17.62)	μg/L	NA	28	NA	NA	ND	NA

TABLE A-4

## ANALYTICAL AND MEASUREMENT DATA FOR MISCELLANEOUS PARAMETERS IN RUN 11 (Continued)

Parameter	Unit	Sampling/Measurement Locations					
		Chemical Feed Tank	Influent - Before H <sub>2</sub> SO <sub>4</sub>	Influent - After H <sub>2</sub> SO <sub>4</sub>	Reactor 2 Effluent	Reactor 6 Effluent	Effluent - After NaOH
Unknown (19.98-19.99)	μg/L	NA	ND	NA	NA	ND	NA
Unknown (21.00-21.04)	μg/L	NA	30	NA	NA	ND	NA
Unknown (21.93-21.94)	μg/L	NA	ND	NA	NA	ND	NA
Sodium Hydroxide Concentration	N	18.6	NA	NA	NA	NA	NA
Specific Conductance	μmho/cm	NA	NA	1750	NA	1760	NA
Sulfuric Acid Concentration	N	35.2	NA	NA	NA	NA	NA
Total Carbon	mg/L	NA	75	NA	NA	55	NA
Total Organic Carbon	mg/L	NA	1.9	NA	NA	0.8	NA
Temperature	°C	NA	22.6	NA	NA	NA	NA
Total Organic Halides	μg/L	NA	800	NA	NA	29	NA
Turbidity	NTU	NA	NA	0.20	NA	.15	NA
Volatile Organic Compounds (GC/MS)	NA	NA	NA	NA	NA	NA	NA
Target Analytes	NA	NA	NA	NA	NA	NA	NA
Acetone	μg/L	NA	4	NA	NA	19	NA
2-Butanone	μg/L	NA	ND	NA	NA	ND	NA
Chloroform	μg/L	NA	160	NA	NA	10	NA
1,1-Dichloroethane	μg/L	NA	180	NA	NA	ND	NA
1,1-Dichloroethene	μg/L	NA	11	NA	NA	ND	NA
1,2-Dichloroethene (total)	μg/L	NA	10	NA	NA	ND	NA

TABLE A-4

## ANALYTICAL AND MEASUREMENT DATA FOR MISCELLANEOUS PARAMETERS IN RUN 11 (Continued)

Parameter	Unit	Sampling/Measurement Locations					
		Chemical Feed Tank	Influent - Before H <sub>2</sub> SO <sub>4</sub>	Influent - After H <sub>2</sub> SO <sub>4</sub>	Reactor 2 Effluent	Reactor 6 Effluent	Effluent - After NaOH
Tetrachloroethene	µg/L	NA	79	NA	NA	ND	NA
Toluene	µg/L	NA	4	NA	NA	ND	NA
1,1,1-Trichloroethane	µg/L	NA	140	NA	NA	16	NA
Trichloroethene	µg/L	NA	670	NA	NA	ND	NA
Tentatively Identified Compound (retention time, minutes)	NA	NA	NA	NA	NA	NA	NA
Tetrahydrofuran (14.36-14.46)	µg/L	NA	5	NA	NA	ND	NA

## NOTES:

- <sup>a</sup> The mean electricity consumption was 32.19 kW.
- <sup>b</sup> Readings were taken 2 or 3 times for pH measurement. Range of readings is also listed.
- <sup>c</sup> None of the semivolatile organic target analytes were detected. Only tentatively identified compounds (TIC) are given in this table. Retention time in minutes for each TIC is given in parentheses.
- <sup>d</sup> The flow rate was monitored throughout the run, and the volume remained constant.

NA Not applicable  
 ND Not detected  
 °C Degree Celsius  
 gpm Gallons per minute  
 GC/MS Gas chromatography and mass spectrometry  
 kW Kilowatts  
 µg/L Micrograms per liter  
 µmho/cm Micromhos per centimeter  
 mg/L Milligrams per liter  
 mL/min Milliliters per minute  
 NTU Nephelometric Turbidity Unit  
 N Normal (equivalents per liter) solution



**TABLE A-5**  
**ANALYTICAL DATA FOR VOCs BY GC ANALYSIS IN RUN 12**

VOC**	Unit	Influent		Reactor 1 - Effluent		Reactor 2 - Effluent		Reactor 3 - Effluent		Reactor 6 - Effluent	
		Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation
Chloroform	µg/L	243	9.57	106	15.2	56.5	5.92	29.5	7.94	17.0	13.4
1,1-Dichloroethane	µg/L	119	72.2	66.5	22.4	4.1	3.28	2.8	1.71	2.1	0.85
Tetrachloroethene	µg/L	72	11.6	2.4	0.48	2.4	0.48	2.8	1.71	2.1	0.85
1,1,1-Trichloroethane	µg/L	130	8.16	112	23.7	69.0	4.90	40.0*	5.0*	25.8	6.65
Trichloroethene	µg/L	680	49.7	2.4	0.48	2.4	0.48	2.8	1.71	2.1	0.85

Notes: \* Mean and standard deviation were calculated using data for three of four replicates.  
 \*\* VOCs present above detection limit.

**TABLE A-6**  
**ANALYTICAL AND MEASUREMENT DATA FOR MISCELLANEOUS PARAMETERS IN RUN 12**

Parameter	Unit	Sampling/Measurement Locations					
		Chemical Feed Tank	Influent - Before H <sub>2</sub> SO <sub>4</sub>	Influent - After H <sub>2</sub> SO <sub>4</sub>	Reactor 2 Effluent	Reactor 6 Effluent	Effluent - After NaOH
Alkalinity	mg/L as CaCO <sub>3</sub>	NA	270	25	51	26	NA
Bioassay, LC <sub>50</sub>	NA	NA	NA	NA	NA	NA	NA
<i>Ceriodaphnia dubia</i>	% Sample	NA	NA	> 100	NA	26	NA
<i>Pimephales promelas</i>	% Sample	NA	NA	> 100	NA	> 100	NA
Electricity Consumption*	kW	NA	NA	NA	NA	NA	NA

TABLE A-6

## ANALYTICAL AND MEASUREMENT DATA FOR MISCELLANEOUS PARAMETERS IN RUN 12 (Continued)

Parameter	Unit	Sampling/Measurement Locations					
		Chemical Feed Tank	Influent - Before H <sub>2</sub> SO <sub>4</sub>	Influent - After H <sub>2</sub> SO <sub>4</sub>	Reactor 2 Effluent	Reactor 6 Effluent	Effluent - After NaOH
Flow Rate	NA	NA	NA	NA	NA	NA	NA
Ground Water Flow Rate	gpm	NA	NA	10	NA	NA	NA
H <sub>2</sub> O <sub>2</sub> Flow Rate	mL/min	9.5	NA	NA	NA	NA	NA
Acid Flow Rate	mL/min	3.2	NA	NA	NA	NA	NA
Base Flow Rate	mL/min	10.3	NA	NA	NA	NA	NA
Hardness	mg/L as CaCO <sub>3</sub>	NA	320	320	320	320	NA
Hydrogen Peroxide	mg/L	615,000	NA	NA	22.0	7.4	NA
Iron	μg/L	NA	<46.0	NA	NA	<46.0	NA
Manganese	μg/L	NA	15.1	NA	NA	15.4	NA
pH <sup>b</sup> , Mean	pH Units	NA	7.48	5.12	5.36	5.34	7.22
pH <sup>b</sup> , Range	pH Units	NA	7.46-7.49	5.11-5.13	5.35-5.36	5.34-5.34	7.19-7.25
Purgeable Organic Carbon	mg/L	NA	0.24	NA	NA	0.04	NA
Semivolatile Organic Compounds <sup>c</sup>	NA	NA	NA	NA	NA	NA	NA
Hexathiepane (14.80-14.82)	μg/L	NA	ND	NA	NA	ND	NA
Pentanoic acid (4.73)	μg/L	NA	ND	NA	NA	ND	NA
Unknown (3.64-7.68)	μg/L	NA	ND	NA	NA	ND	NA
Unknown (5.01)	μg/L	NA	ND	NA	NA	12	NA
Unknown (16.90-16.91)	μg/L	NA	20	NA	NA	ND	NA
Unknown (17.59-17.62)	μg/L	NA	ND	NA	NA	ND	NA

TABLE A-6

## ANALYTICAL AND MEASUREMENT DATA FOR MISCELLANEOUS PARAMETERS IN RUN 12 (Continued)

Parameter	Unit	Sampling/Measurement Locations					
		Chemical Feed Tank	Influent - Before H <sub>2</sub> SO <sub>4</sub>	Influent - After H <sub>2</sub> SO <sub>4</sub>	Reactor 2 Effluent	Reactor 6 Effluent	Effluent - After NaOH
Unknown (19.98-19.99)	µg/L	NA	ND	NA	NA	ND	NA
Unknown (21.00-21.04)	µg/L	NA	ND	NA	NA	ND	NA
Unknown (21.93-21.94)	µg/L	NA	23	NA	NA	ND	NA
Sodium Hydroxide Concentration	N	18.5	NA	NA	NA	NA	NA
Specific Conductance	µmho/cm	NA	NA	1700	NA	1640	NA
Sulfuric Acid Concentration	N	34.2	NA	NA	NA	NA	NA
Total Carbon	mg/L	NA	76	NA	NA	59	NA
Total Organic Carbon	mg/L	NA	1.9	NA	NA	1.6	NA
Temperature	°C	NA	23.8	NA	28.4	33.8	NA
Total Organic Halides	µg/L	NA	740	NA	160	24	NA
Turbidity	NTU	NA	NA	<0.1	NA	<0.1	NA
Volatile Organic Compounds (GC/MS)	NA	NA	NA	NA	NA	NA	NA
Target Analytes	NA	NA	NA	NA	NA	NA	NA
Acetone	µg/L	NA	49	NA	NA	7	NA
2-Butanone	µg/L	NA	ND	NA	NA	ND	NA
Chloroform	µg/L	NA	180	NA	NA	13	NA
1,1-Dichloroethane	µg/L	NA	190	NA	NA	ND	NA
1,1-Dichloroethene	µg/L	NA	9	NA	NA	ND	NA
1,2-Dichloroethene (total)	µg/L	NA	8	NA	NA	ND	NA

TABLE A-6

## ANALYTICAL AND MEASUREMENT DATA FOR MISCELLANEOUS PARAMETERS IN RUN 12 (Continued)

Parameter	Unit	Sampling/Measurement Locations					
		Chemical Feed Tank	Influent - Before H <sub>2</sub> SO <sub>4</sub>	Influent - After H <sub>2</sub> SO <sub>4</sub>	Reactor 2 Effluent	Reactor 6 Effluent	Effluent - After NaOH
Tetrachloroethene	µg/L	NA	71	NA	NA	ND	NA
Toluene	µg/L	NA	2	NA	NA	ND	NA
1,1,1-Trichloroethane	µg/L	NA	150	NA	NA	19	NA
Trichloroethene	µg/L	NA	430	NA	NA	ND	NA
Tentatively Identified Compound (retention time, minutes)	NA	NA	NA	NA	NA	NA	NA
Tetrahydrofuran (14.36-14.46)	µg/L	NA	2	NA	NA	ND	NA

Notes:

<sup>a</sup> The mean electricity consumption was 32.19 kW.<sup>b</sup> Readings were taken 2 or 3 times for pH measurement. Range of readings is also listed.<sup>c</sup> None of the semivolatile organic target analytes were detected. Only tentatively identified compounds (TIC) are given in this table. Retention time in minutes for each TIC is given in parentheses.<sup>d</sup> The flow rate was monitored throughout the run, and the volume remained constant.

NA Not applicable

ND Not detected

°C Degree Celsius

gpm Gallons per minute

GC/MS Gas chromatography and mass spectrometry

kW Kilowatts

µg/L Micrograms per liter

µmho/cm Micromhos per centimeter

mg/L Milligrams per liter

mL/min Milliliters per minute

NTU Nephelometric Turbidity Unit

N Normal (equivalents per liter) solution

**TABLE A-5**  
**ANALYTICAL DATA FOR VOCs BY GC ANALYSIS IN RUN 12**

VOC**	Unit	Influent		Reactor 1 - Effluent		Reactor 2 - Effluent		Reactor 3 - Effluent		Reactor 6 - Effluent	
		Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation
Chloroform	µg/L	243	9.57	106	15.2	56.5	5.92	29.5	7.94	17.0	13.4
1,1-Dichloroethane	µg/L	119	72.2	66.5	22.4	4.1	3.28	2.8	1.71	2.1	0.85
Tetrachloroethene	µg/L	72	11.6	2.4	0.48	2.4	0.48	2.8	1.71	2.1	0.85
1,1,1-Trichloroethane	µg/L	130	8.16	112	23.7	69.0	4.90	40.0*	5.0*	25.8	6.65
Trichloroethene	µg/L	680	49.7	2.4	0.48	2.4	0.48	2.8	1.71	2.1	0.85

Notes: \* Mean and standard deviation were calculated using data for three of four replicates.  
 \*\* VOCs present above detection limit.

**TABLE A-6**  
**ANALYTICAL AND MEASUREMENT DATA FOR MISCELLANEOUS PARAMETERS IN RUN 12**

Parameter	Unit	Sampling/Measurement Locations					
		Chemical Feed Tank	Influent - Before H <sub>2</sub> SO <sub>4</sub>	Influent - After H <sub>2</sub> SO <sub>4</sub>	Reactor 2 Effluent	Reactor 6 Effluent	Effluent - After NaOH
Alkalinity	mg/L as CaCO <sub>3</sub>	NA	270	25	51	26	NA
Bioassay, LC <sub>50</sub>	NA	NA	NA	NA	NA	NA	NA
<i>Ceriodaphnia dubia</i>	% Sample	NA	NA	> 100	NA	26	NA
<i>Pimephales promelas</i>	% Sample	NA	NA	> 100	NA	> 100	NA
Electricity Consumption*	kW	NA	NA	NA	NA	NA	NA

TABLE A-6

## ANALYTICAL AND MEASUREMENT DATA FOR MISCELLANEOUS PARAMETERS IN RUN 12 (Continued)

Parameter	Unit	Sampling/Measurement Locations					
		Chemical Feed Tank	Influent - Before H <sub>2</sub> SO <sub>4</sub>	Influent - After H <sub>2</sub> SO <sub>4</sub>	Reactor 2 Effluent	Reactor 6 Effluent	Effluent - After NaOH
Flow Rate	NA	NA	NA	NA	NA	NA	NA
Ground Water Flow Rate	gpm	NA	NA	10	NA	NA	NA
H <sub>2</sub> O <sub>2</sub> Flow Rate	mL/min	9.5	NA	NA	NA	NA	NA
Acid Flow Rate	mL/min	3.2	NA	NA	NA	NA	NA
Base Flow Rate	mL/min	10.3	NA	NA	NA	NA	NA
Hardness	mg/L as CaCO <sub>3</sub>	NA	320	320	320	320	NA
Hydrogen Peroxide	mg/L	615,000	NA	NA	22.0	7.4	NA
Iron	μg/L	NA	<46.0	NA	NA	<46.0	NA
Manganese	μg/L	NA	15.1	NA	NA	15.4	NA
pH <sup>b</sup> , Mean	pH Units	NA	7.48	5.12	5.36	5.34	7.22
pH <sup>b</sup> , Range	pH Units	NA	7.46-7.49	5.11-5.13	5.35-5.36	5.34-5.34	7.19-7.25
Purgeable Organic Carbon	mg/L	NA	0.24	NA	NA	0.04	NA
Semivolatile Organic Compounds <sup>c</sup>	NA	NA	NA	NA	NA	NA	NA
Hexathiepane (14.80-14.82)	μg/L	NA	ND	NA	NA	ND	NA
Pentanoic acid (4.73)	μg/L	NA	ND	NA	NA	ND	NA
Unknown (3.64-7.68)	μg/L	NA	ND	NA	NA	ND	NA
Unknown (5.01)	μg/L	NA	ND	NA	NA	12	NA
Unknown (16.90-16.91)	μg/L	NA	20	NA	NA	ND	NA
Unknown (17.59-17.62)	μg/L	NA	ND	NA	NA	ND	NA

TABLE A-6

## ANALYTICAL AND MEASUREMENT DATA FOR MISCELLANEOUS PARAMETERS IN RUN 12 (Continued)

Parameter	Unit	Sampling/Measurement Locations					
		Chemical Feed Tank	Influent - Before H <sub>2</sub> SO <sub>4</sub>	Influent - After H <sub>2</sub> SO <sub>4</sub>	Reactor 2 Effluent	Reactor 6 Effluent	Effluent - After NaOH
Unknown (19.98-19.99)	µg/L	NA	ND	NA	NA	ND	NA
Unknown (21.00-21.04)	µg/L	NA	ND	NA	NA	ND	NA
Unknown (21.93-21.94)	µg/L	NA	23	NA	NA	ND	NA
Sodium Hydroxide Concentration	N	18.5	NA	NA	NA	NA	NA
Specific Conductance	µmho/cm	NA	NA	1700	NA	1640	NA
Sulfuric Acid Concentration	N	34.2	NA	NA	NA	NA	NA
Total Carbon	mg/L	NA	76	NA	NA	59	NA
Total Organic Carbon	mg/L	NA	1.9	NA	NA	1.6	NA
Temperature	°C	NA	23.8	NA	28.4	33.8	NA
Total Organic Halides	µg/L	NA	740	NA	160	24	NA
Turbidity	NTU	NA	NA	<0.1	NA	<0.1	NA
Volatile Organic Compounds (GC/MS)	NA	NA	NA	NA	NA	NA	NA
Target Analytes	NA	NA	NA	NA	NA	NA	NA
Acetone	µg/L	NA	49	NA	NA	7	NA
2-Butanone	µg/L	NA	ND	NA	NA	ND	NA
Chloroform	µg/L	NA	180	NA	NA	13	NA
1,1-Dichloroethane	µg/L	NA	190	NA	NA	ND	NA
1,1-Dichloroethene	µg/L	NA	9	NA	NA	ND	NA
1,2-Dichloroethene (total)	µg/L	NA	8	NA	NA	ND	NA

TABLE A-6

## ANALYTICAL AND MEASUREMENT DATA FOR MISCELLANEOUS PARAMETERS IN RUN 12 (Continued)

Parameter	Unit	Sampling/Measurement Locations					
		Chemical Feed Tank	Influent - Before H <sub>2</sub> SO <sub>4</sub>	Influent - After H <sub>2</sub> SO <sub>4</sub>	Reactor 2 Effluent	Reactor 6 Effluent	Effluent - After NaOH
Tetrachloroethene	µg/L	NA	71	NA	NA	ND	NA
Toluene	µg/L	NA	2	NA	NA	ND	NA
1,1,1-Trichloroethane	µg/L	NA	150	NA	NA	19	NA
Trichloroethene	µg/L	NA	430	NA	NA	ND	NA
Tentatively Identified Compound (retention time, minutes)	NA	NA	NA	NA	NA	NA	NA
Tetrahydrofuran (14.36-14.46)	µg/L	NA	2	NA	NA	ND	NA

## Notes:

<sup>a</sup> The mean electricity consumption was 32.19 kW.

<sup>b</sup> Readings were taken 2 or 3 times for pH measurement. Range of readings is also listed.

<sup>c</sup> None of the semivolatile organic target analytes were detected. Only tentatively identified compounds (TIC) are given in this table. Retention time in minutes for each TIC is given in parentheses.

<sup>d</sup> The flow rate was monitored throughout the run, and the volume remained constant.

NA Not applicable

ND Not detected

°C Degree Celsius

gpm Gallons per minute

GC/MS Gas chromatography and mass spectrometry

kW Kilowatts

µg/L Micrograms per liter

µmho/cm Micromhos per centimeter

mg/L Milligrams per liter

mL/min Milliliters per minute

NTU Nephelometric Turbidity Unit

N Normal (equivalents per liter) solution