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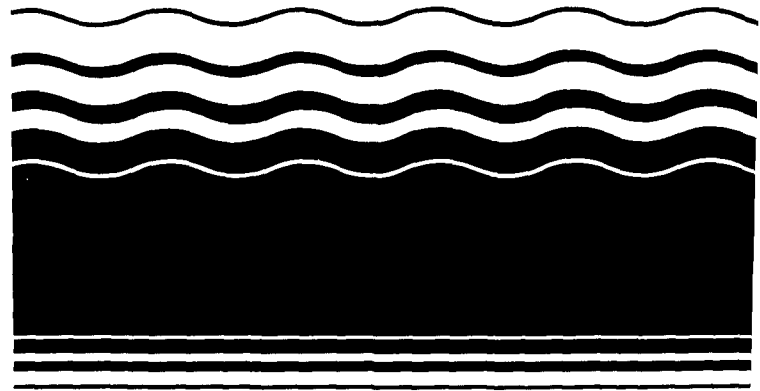
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# Technology Evaluation Report:

## SITE Program Demonstration of the Ultrax International Ultraviolet Radiation/Oxidation Technology

**SITE**  
*SUPERFUND INNOVATIVE  
TECHNOLOGY EVALUATION*



EPA/540/5-89/012  
January 1990

# **Technology Evaluation Report:**

## **SITE Program Demonstration of the Ultrox International Ultraviolet Radiation/Oxidation Technology**

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## **NOTICE**

The information in this document has been funded by the U.S. Environmental Protection Agency under Contract No. 68-03-3484 and the Superfund Innovative Technology Evaluation (SITE) Program. This document has been subjected to the Agency's peer review and administrative review, and has been approved for publication as a U.S. EPA document. Mention of trade names or commercial products does not constitute an endorsement or recommendation for use.

## **FOREWORD**

The Superfund Innovative Technology Evaluation (SITE) Program was authorized in the 1986 Superfund amendments. 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 hazardous waste treatment technologies necessary to implement new cleanup standards which require greater reliance on permanent remedies. This is accomplished through technology demonstrations which are designed to provide engineering and cost data on selected technologies.

This project is a field demonstration under the SITE Program and designed to analyze the Ultrox International's ultraviolet radiation/oxidation technology. The technology demonstration took place at a former drum recycling facility in San Jose, California. The demonstration effort was directed at obtaining information on the performance and cost of the technology for assessing its use at this as well as other uncontrolled hazardous waste sites. Documentation will consist of two reports: (1) a Technology Evaluation Report that describes the field activities and laboratory results; and (2) an Applications Analysis Report that provides an interpretation of the data and discusses the potential applicability of the technology.

A limited number of copies of this report will be available at no charge from EPA's Center for Environmental Research Information, 26 West Martin Luther King Drive, Cincinnati, Ohio, 45268. Requests should include the EPA document number found on the report's front cover. When the limited supply is exhausted, additional copies 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 their Hazardous Waste Collection. You can also call the SITE Clearinghouse hotline at 1-800-424-9346 or 202-382-3000 in Washington, D.C., to inquire about the availability of other reports.

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E. Timothy Oppelt, Director  
Risk Reduction Engineering Laboratory

## ABSTRACT

In support of EPA's Superfund Innovative Technology Evaluation (SITE) Program, this report presents the results of the Ultrox International technology demonstration. The Ultrox® technology (a registered trademark of Ultrox International) simultaneously uses ultraviolet (UV) radiation, ozone, and hydrogen peroxide to oxidize dissolved organic contaminants, including chlorinated hydrocarbons and aromatic compounds, found in groundwater or wastewater. Experiments were conducted in which hydraulic retention time, ozone dose, hydrogen peroxide dose, UV radiation intensity, and influent pH level were varied over a wide range to evaluate the ability of the technology to treat contaminated groundwater at a Superfund site at different operating conditions.

Under the SITE program, the Ultrox technology demonstration was conducted at the Lorentz Barrel and Drum (LB&D) site, San Jose, California, in February and March of 1989. The objectives of the demonstration were to: (1) evaluate the Ultrox technology's ability to treat organic contaminants found in the groundwater at the site; (2) evaluate the effects of major process parameters on the technology's performance; (3) evaluate the efficiency of the ozone decomposer (Decompozon) unit in treating the off-gas from the Ultrox reactor; and (4) develop information useful for evaluating whether this technology is suitable for other hazardous waste sites with similar conditions.

Liquid samples were collected from various locations of the Ultrox system to assess its ability to remove groundwater contaminants. Air samples were taken to measure the effectiveness of the Decompozon unit in reducing ozone levels in the reactor off-gas prior to venting it to the atmosphere. Liquid samples were analyzed for volatile organic compounds (VOC), semivolatile organics, pesticides, metals, and other constituents in the groundwater. Air samples were analyzed for VOCs and ozone.

The Ultrox system achieved VOC removals greater than 90 percent. The majority of VOCs were removed through chemical oxidation. However, stripping also contributed toward removal of a few VOCs, such as 1,1,1-trichloroethane (1,1,1-TCA) and 1,1-dichloroethane (1,1-DCA). The treated groundwater met the applicable National Pollutant Discharge Elimination System (NPDES) standards for discharge into a local waterway at the 95 percent confidence level. There were no harmful air emissions to the atmosphere from the Ultrox system, which is equipped with an off-gas treatment unit.

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## **ACKNOWLEDGEMENT**

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This report was prepared for EPA's SITE Program by Dr. Gary Welshans and Dr. Kirankumar Topudurti of PRC Environmental Management, Inc., under Contract No. 68-03-3484.

PRC utilized the services of its SITE team subcontractor, Engineering-Science, to collect water and air samples, perform all analytical tests in the field and in the laboratory, and prepare sections of the Demonstration Plan and this Technology Evaluation Report.

## SECTION 1 EXECUTIVE SUMMARY

### DEMONSTRATION OVERVIEW

The Ultrox International ultraviolet (UV) radiation/oxidation technology (Ultrox<sup>®</sup>, a registered trademark of Ultrox International) was evaluated under the U.S. Environmental Protection Agency's (EPA) Superfund Innovative Technology Evaluation (SITE) Program during February and March of 1989. The Ultrox treatment process uses a combination of UV radiation, ozone, and hydrogen peroxide to oxidize organic compounds in water. The developer claims that the final products of the reaction are salts, water, carbon dioxide, and possibly some organic products.

The Ultrox technology demonstration was conducted at the Lorentz Barrel and Drum (LB&D) site in San Jose, California. The objectives of the demonstration were to: (1) evaluate the technology's ability to treat organic contaminants in the groundwater at the site; (2) evaluate the effects of major process parameters on the technology's performance; (3) evaluate the efficiency of the ozone decomposer (Decompozon) unit in treating ozone in the off-gas from the Ultrox reactor; and (4) develop information useful for evaluating whether this technology is suitable for other hazardous waste sites with similar conditions.

The shallow groundwater at the LB&D site was selected as the waste stream for evaluating the Ultrox treatment process. This groundwater was primarily contaminated with volatile organic compounds (VOC) such as trichloroethylene (TCE) and vinyl chloride, at levels of 100 and 40  $\mu\text{g/L}$ , respectively. Other VOCs present at relatively low concentrations (in the range of 5 to 15  $\mu\text{g/L}$ ) included 1,1-dichloroethane (1,1-DCA), 1,1,1-trichloroethane (1,1,1-TCA), 1,2-dichloroethane (1,2-DCA), benzene, chloroform, and tetrachloroethylene. Semivolatiles and polychlorinated biphenyls (PCB)/pesticides were not detected.

The total organic carbon (TOC) concentration of the groundwater was about 25 mg/L. However, the concentration of priority pollutants (VOCs and semivolatiles) was only about 2 percent of the TOC concentration.

The pH and alkalinity of the groundwater were about 7.2 and 600 mg/L as  $\text{CaCO}_3$ , respectively. These measurements indicated that the bicarbonate ion ( $\text{HCO}_3^-$ ), which acts as an oxidant scavenger, was present at high levels. Other oxidant scavengers such as bromide, cyanide, and sulfide were not detected.

The experimental demonstration program evaluated the performance of the Ultrox technology in removing VOCs from the groundwater under various operating conditions. During the demonstration program, hydraulic retention times, oxidant doses and ratios, UV radiation intensities, and influent pH levels were adjusted to evaluate the system under various operating conditions. This technology evaluation report contains a comprehensive description of the Ultrox technology demonstration and its results. A thorough discussion of the technology, characteristics of the site and waste stream used for the demonstration, the sampling and analytical procedures, the data generated, and the associated costs to conduct the demonstration are provided in this report.

## **SUMMARY AND CONCLUSIONS**

The groundwater treated by the Ultrox system met the applicable National Pollutant Discharge Elimination System (NPDES) standards for discharge into a local waterway, at the 95 percent confidence level under certain operating conditions. Success was obtained by using a hydraulic retention time of 40 minutes; ozone dose of 110 mg/L; hydrogen peroxide dose of 13 mg/L; all 24 UV lamps operating; and influent pH of 7.2 (unadjusted).

There were no volatile organics detected in the exhaust from the Decompozon unit.

The Decompozon unit destroyed ozone in the Ultrox reactor off-gas to levels less than 0.1 ppm (OSHA Standards). The ozone destruction efficiencies were observed to be greater than 99.99 percent.

The Ultrox system achieved removal efficiencies as high as 90 percent for the total VOCs present in the groundwater. The removal efficiencies for TCE were greater than 99 percent. However, the maximum removal efficiencies for 1,1-DCA and 1,1,1-TCA under optimal operating conditions were about 65 and 85 percent, respectively.

Within the treatment system, the removals of 1,1-DCA and 1,1,1-TCA appear to be due to both chemical oxidation and stripping. Specifically, stripping accounted for 12 to 75 percent of the total removals for 1,1,1-TCA, and for 5 to 44 percent of the total removals for 1,1-DCA. However, stripping accounted for less than 10 percent of the total removals for TCE and vinyl chloride. For other VOCs such as 1,1-dichloroethene, benzene, acetone, and 1,1,2,2-tetrachloroethane, stripping was negligible. Volatile organics present in the gas phase within the reactor at levels of approximately 0.1 to 0.5 ppm were removed to below detection levels in the Decompozon unit.

The Ultrox system's average electrical energy consumption was about 11 kilowatt-hours/hour of operation.

## **ORGANIZATION OF THE REPORT**

Two major reports are produced for each SITE demonstration: a Technology Evaluation Report and an Applications Analysis Report. This Technology Evaluation Report, which documents the performance data from the demonstration, is divided into several sections: Section 2 (Introduction), Section 3 (Description of Technology), Section 4 (Demonstration Procedures), Section 5 (Performance Data and Evaluation), Section 6 (Costs of Demonstration), and Section 7 (Conclusions and Recommendations). References are provided at the end of this report.

[An Applications Analysis Report is prepared to provide additional information for the general use of the demonstrated technology for other sites. The report includes all available information on the specific technology and the applicability of the technology to sites with other characteristics, waste types, and waste matrices. In addition, the report provides cost information and identifies cost-controlling factors when appropriate.]

## **SECTION 2 INTRODUCTION**

### **BACKGROUND**

The Superfund Amendments and Reauthorization Act of 1986 (SARA) (Section 209(b)) amends Title III of the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) 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."

### **SITE Program**

In response to SARA, EPA has established a formal program to accelerate the development, demonstration, and use of new or innovative treatment technologies. This program is called the Superfund Innovative Technology Evaluation (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 have been fully proven and are available for commercial or private use.
- Innovative alternative technologies have been fully developed but lack complete cost or performance information.
- Emerging alternative technologies are in an early stage of development involving laboratory or pilot testing.

One of the most important aspects of the SITE Program is the Demonstration Program which 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 technologies evaluated are close to being available for remediation of Superfund sites. The main objective of the Demonstration Program is to develop extensive performance engineering and cost information

for new 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 applicability of the technology for 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.

### **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.

Ultrox International submitted a proposal to EPA to demonstrate their technology and equipment under the SITE-003 Program in March 1988.



## **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 is initiated. 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 sites for target demonstrations 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 and water sources, and sewers)
- Support of community, state and local governments, and potentially responsible parties

The process typically begins with OSWER contacting the regions and providing information to them on the potential technologies. Next, the process for selecting sites for demonstration of the technologies continues with the EPA regional offices submitting information on the type of waste(s) and additional applicable site characteristics. This information is screened and potential sites are given to the developers for comments.

The advantages and disadvantages of each site are compiled based on considerations and preferences provided by the developer and four principal program goals. These goals are:

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

The applicability of the Ultrox technology for remediating the contamination at the Lorentz Barrel and Drum (LB&D) site was evaluated by EPA Region IX as a part of the engineering evaluation/cost analysis of remedial alternatives and through a treatability study.

The primary purpose of the treatability study was to demonstrate whether the technology could treat the contaminated groundwater at the LB&D site. The treatability study was carried out by Ultrox according to the specifications developed by Region IX (Ebasco Services, 1988). Based on the promising results of the treatability study and the desire by the Region to gain additional data to complete its decision-making for the Phase I remediation of groundwater at the site, the Ultrox technology demonstration was put on an accelerated schedule.

### **Project Organization**

The staff of ORD and OSWER evaluates the technology proposals and, with the assistance of EPA regional offices, matches the technologies to appropriate sites. OSWER and ORD establish the criteria for the waste site selection for each demonstration. Sites are selected cooperatively by OSWER, ORD, EPA regional offices, and the states. The final site is selected in close cooperation with the technology developer.

To demonstrate the ultraviolet (UV) radiation/oxidation treatment of contaminated groundwater at the LB&D site, a Cooperative Agreement was signed between EPA and Ultrox International. Ultrox was responsible for equipment delivery, set up, operation, and demobilization. EPA was responsible for preparing the Demonstration Plan, coordinating the site activities necessary to conduct the technology demonstration, collecting field samples, arranging for laboratory analyses, evaluating the data, preparing the Technology Evaluation Report, participating in community relations efforts, and performing other related tasks.

Region IX assisted the SITE Program by installing groundwater collection wells, collecting groundwater samples, preparing specifications for the treatability study, and performing other support activities.

### **DEMONSTRATION OBJECTIVES**

In addition to meeting the general objectives of the SITE Program during Ultrox technology demonstration, the following specific goals were identified to serve the needs of both the SITE Program and Region IX:

- Demonstrate the ability of the Ultrox system to treat volatile organic compounds (VOC) present in the groundwater at the LB&D site
- Evaluate the efficiency of the ozone decomposer unit in treating ozone in the reactor off-gas

- Develop capital and operating costs for the Ultrox system that can be used in Superfund decision-making processes at other sites
- Develop information useful to Region IX for site remediation

## **EVALUATION CRITERIA AND REGULATORY CONSIDERATIONS**

EPA used the following technical criteria to evaluate the effectiveness of the Ultrox process to treat organic contaminants at the LB&D site:

- Compliance of the treated groundwater with regulatory requirements (see Section 5)
- Efficiency of the off-gas treatment unit in removing ozone and VOCs

For purposes of conducting SITE demonstrations, EPA follows procedures regarding on- and off-site remedial actions taken under CERCLA. A 1985 memorandum from J. Winston Porter, Assistant Administrator for OSWER, states that application for and receipt of permits is not required for on-site response actions performed under the authorities of CERCLA. Although the normal permitting processes are not required for the demonstrations, the memorandum requires that CERCLA removal and remedial activities must be in compliance with all applicable or relevant and appropriate requirements (ARAR) of federal and state environmental and public health laws.

To ensure compliance, several regulatory agencies were contacted to inform them of the planned demonstration, discuss relevant issues related to the expected field tests, and determine the requirements, procedures, and applications needed to receive regulatory permits. The following state and local agencies were contacted:

- San Francisco Bay Regional Water Quality Control Board
- Santa Clara County Health Department
- Bay Area Air Quality Management District
- Department of Consumer Affairs, San Jose
- Department of Public Works, San Jose

## **DESCRIPTION OF OPERATIONS**

This subsection describes the technical operations performed during the field demonstration. The operations are described in detail in subsequent sections.

Initially, background information on the technology was obtained from the developer, Ultrox International, and from literature. Subsequently, the technology Demonstration Plan, which describes the Ultrox process and details the demonstration procedures, was prepared. The demonstration procedures included preparing a schedule for the project; obtaining information on the site description and contamination, and on the treatability study from Region IX; characterizing the groundwater at the site; mobilizing equipment and materials to the site; collecting and storing groundwater for the 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, 1989).

This report summarizes the procedures followed and notes deviations from the Demonstration Plan. In addition, health and safety considerations identified during the demonstration are described in this report. During the demonstration, a Visitors Day was organized so that the community, government officials and the media could witness the demonstration activities and learn first-hand about the technology. In addition, during the demonstration EPA conducted quality assurance/quality control audits of the field operations and also of the analytical laboratory.

Analytical data was obtained for all samples collected during the demonstration. A performance evaluation summary of the technology was then prepared. The cost of the demonstration and the conclusions and recommendations based on the technology demonstration were prepared and are also presented in this report.

### **SECTION 3**

#### **DESCRIPTION OF TECHNOLOGY**

This section provides an overview of the Ultrox technology and a description of the treatment system equipment, support equipment, and utility requirements. Detailed descriptions of the Ultrox treatment technology are presented in the Demonstration Plan (PRC, 1989).

#### **PROCESS DESCRIPTION**

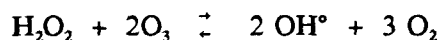
The use of oxidants such as ozone, hydrogen peroxide, and ultraviolet (UV) radiation to destroy organic contaminants present in groundwater is gaining considerable attention, mainly because the oxidants destroy the contaminants instead of transferring them to another phase. Alternative treatments, such as air stripping, granular activated carbon (GAC) adsorption, and reverse osmosis, require additional treatment.

Ultrox International developed a technology that uses three oxidants: ozone, hydrogen peroxide, and UV radiation. The Ultrox technology is best suited for destroying dissolved organic contaminants, including chlorinated hydrocarbons and aromatic compounds, in water with low suspended solids levels. This technology is currently treating contaminated groundwater at facilities located in Kansas City, Missouri; Nashua, New Hampshire; and Muskegon, Michigan. Groundwater at these sites is contaminated with trichloroethylene, tetrachloroethylene, vinyl chloride, pentachlorophenol, phenol, and various other organics. The design flow rates of these facilities are in the range of 20 to 210 gpm.

#### **Process Chemistry**

Processes in which ozone is used in combination with hydrogen peroxide or UV radiation may be categorized as catalytic ozonation processes. These processes accelerate ozone decomposition, thereby increasing the hydroxyl radical ( $\text{OH}^\bullet$ ) concentration and promoting the oxidation rate of the compounds of interest. Specifically, hydrogen peroxide, hydroxide ion, UV radiation, and some transition metal ions such as ferrous iron ( $\text{Fe}^{+2}$ ) have been found to initiate ozone decomposition and accelerate the oxidation of refractory organics via the free radical reaction pathway (Glaze, 1987). Natural water components such as carbonate ions, bicarbonate ions, cyanide ions, nitrite ions, and several other species that consume oxidants act as free radical scavengers and effectively consume hydroxyl radicals.

The ozone-hydrogen peroxide process is affected by the molar ratio of the oxidants used. For example, the expected stoichiometry for hydroxyl radical formation from ozone and hydrogen peroxide is two, as shown in the following equation:



In the treatment of water containing trichloroethylene and tetrachloroethylene, Aieta and others (1988), observed maximum removals at a molar ratio of 2 or a 2.86 weight ratio of ozone to hydrogen peroxide, which agrees with the expected stoichiometry. The removals were significantly less when the molar ratio was not 2. Although in this case the expected stoichiometry for pure water agreed with the molar ratio at which optimum removal was observed, several factors may influence the molar ratio (Aieta and others, 1988). These factors are summarized below:

- Hydrogen peroxide can act as a free radical scavenger itself, thereby decreasing the hydroxyl radical concentration if it is present in excess.
- Ozone can directly react with hydroxyl radicals, consuming both ozone and hydroxyl radicals.
- Ozone and hydroxyl radicals may be consumed by other constituents, known as scavengers, of the water to be treated.

In the ozone-UV process, the UV photolysis of ozone in water yields hydrogen peroxide rather than two hydroxyl radicals. Thus, the ozone-UV process resembles the ozone-hydrogen peroxide process, but offers the additional advantage that direct photolysis and photosynthesized processes also decompose organic substrates.

The Ultrox process, therefore, can be viewed as a catalytic ozonation process and the oxidation of contaminants is likely to occur either by direct reaction of the oxidants added or by reaction of the hydroxyl radicals with the contaminants. The optimum proportion of the oxidants for maximum removals cannot be predetermined; rather, the proportion must be experimentally determined for each waste stream. The following section identifies specific factors that influence the effectiveness of the Ultrox technology in treating the groundwater at the LB&D site.

#### **Factors Affecting the Ultrox Technology**

The factors that affect the Ultrox technology can be grouped into three categories: (1) performance evaluation parameters, (2) operating parameters, and (3) miscellaneous parameters. The performance evaluation parameters of the Ultrox technology at the LB&D site under

specified conditions were specific chemical constituents. These constituents are volatile organic compounds (VOC), semivolatile organics, polychlorinated biphenyls (PCB), and pesticides. The influent concentrations of these constituents can significantly influence the treatment efficiency of the technology.

Operating parameters are those parameters that were manually varied during the treatment process to achieve a desired degree of treatment efficiency. Such parameters included hydraulic retention time, ozone dose, hydrogen peroxide dose, UV radiation intensity, and influent pH level.

Since the Ultrox technology is an oxidation process and is intended for the destruction of organic contaminants, any other species present in the contaminated water which consume oxidants were viewed as an additional load for the system. These species, called scavengers, include anions such as carbonates, bicarbonates, sulfides, nitrites, bromides, and cyanides. Also, metals present in reduced states such as trivalent chromium ( $\text{Cr}^{+3}$ ), ferrous iron ( $\text{Fe}^{+2}$ ), and several others, are likely to be oxidized. In addition, physical characteristics of the influent, such as temperature and pH, also influence the Ultrox process.

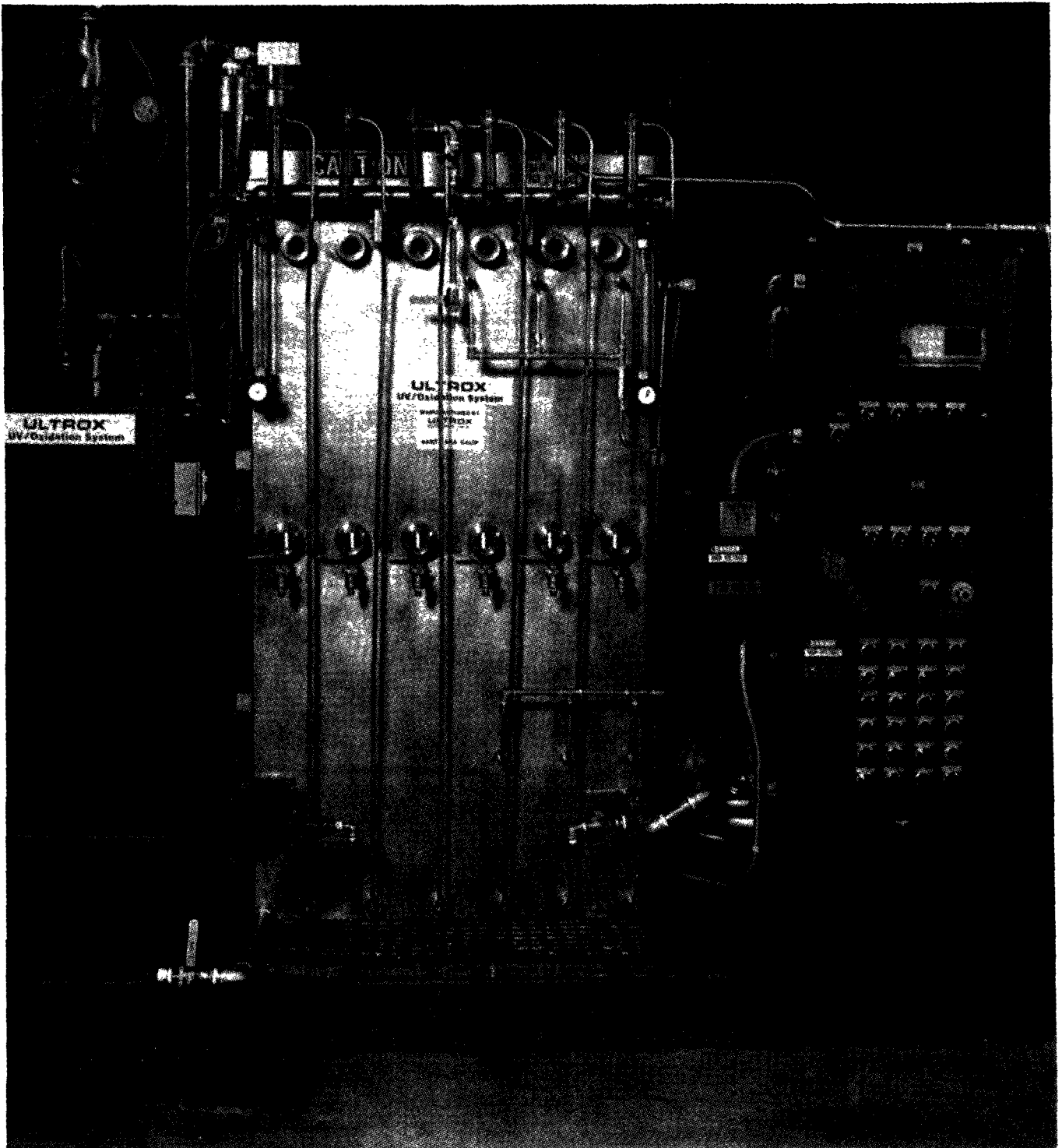
## **TREATMENT SYSTEM EQUIPMENT**

The treatment system used to demonstrate the Ultrox process is shown in Figure 3-1. This system (Model PM-150) uses UV radiation, ozone, and hydrogen peroxide to oxidize the organic chemicals in the collected groundwater. The treatment system has four skid-mounted modules designed for transport with either a flatbed truck or in an enclosed trailer. The major components of the system include the following:

- UV radiation/oxidation reactor module
- Ozone generator module
- Hydrogen peroxide feed system
- Catalytic ozone decomposer unit

An isometric view of the Ultrox system is given in Figure 3-2. The UV radiation/oxidation reactor used for this demonstration has a wet volume of 150 gallons and is 3 feet long by 1.5 feet wide by 5.5 feet high. The reactor is divided by five vertical baffles into six chambers and contains 24 UV lamps (65 watts each) in quartz sheaths. These lamps are installed vertically and are evenly distributed throughout the reactor (four lamps per chamber). Each chamber also has one sparger that covers the width of the reactor. These spargers provide a supply of uniformly diffused ozone gas from the base of the reactor into the treated groundwater.

FIGURE 3-1  
ULTROX SYSTEM DEMONSTRATION UNIT





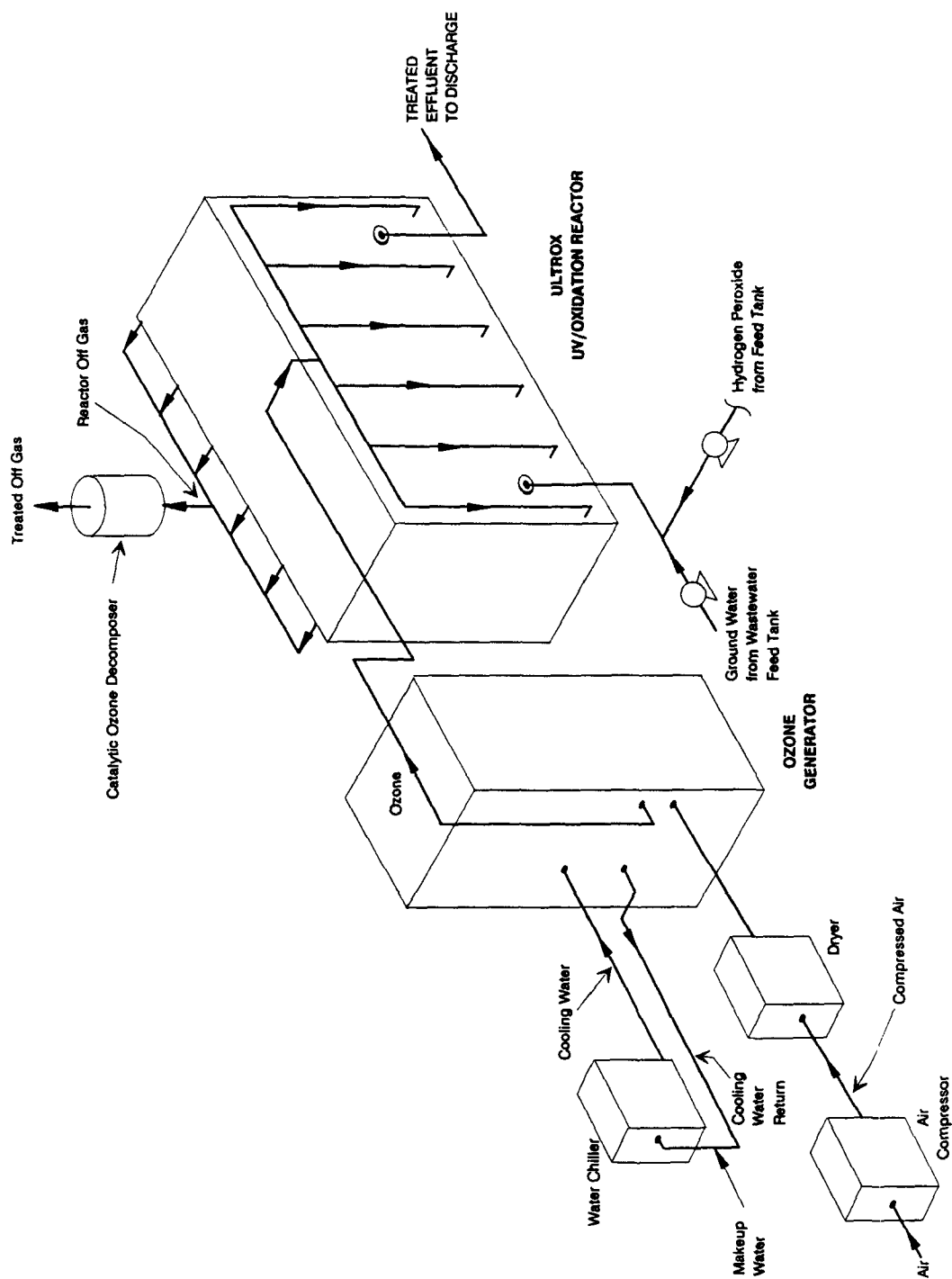


FIGURE 3-2  
ISOMETRIC VIEW OF ULTROX SYSTEM

The ozone generator requires compressed air as a source of oxygen for on-site generation of ozone. The air compressor operates in association with an air dryer which removes moisture. In addition, a water cooler recirculates cooling water supplied to the ozone generator.

The hydrogen peroxide feed system introduces a predetermined concentration of hydrogen peroxide to the reactor via an influent feed line. Commercial-grade hydrogen peroxide of known concentration (about 35 percent) was purchased from a chemical supplier and diluted with distilled water to the appropriate concentration. An in-line static mixer disperses the hydrogen peroxide from the feed tank into the groundwater as groundwater is pumped through the influent feed line.

The catalytic ozone decomposer unit (Ultrox Model 3014 FF ozone decomposer) catalytically decomposes ozone to oxygen using a nickel catalyst. The ozone decomposer (Decompozon) unit can accommodate flows of up to 10 standard cubic feet per minute. The unit is rated to decompose ozone concentrations ranging from 1 to 20,000 ppm (by weight) to less than 0.1 ppm.

A flow schematic diagram of the Ultrox system is given in Figure 3-3. During the demonstration operation, contaminated groundwater came in contact first with hydrogen peroxide as it flowed through the influent line to the reactor. It then came in contact with UV radiation and ozone while it flowed through the reactor at a specified rate to achieve the desired hydraulic retention time. The hydrogen peroxide dose was controlled by varying the ratio of the hydrogen peroxide feed flow rate to the influent contaminated water flow rate. Similarly, the ozone dose was controlled by varying the ratio of the ozone gas flow rate to the contaminated water flow rate and, also, the ozone feed gas concentration. The treatment system was designed so that ozone present in the off-gas from the reactor could be destroyed using a catalyst by the Decompozon unit. Treated groundwater effluent was pumped from the reactor to a storage tank.

## **TREATMENT SYSTEM SUPPORT EQUIPMENT**

Typically, support equipment is needed depending on the site logistics, required operating procedures, and equipment limitations. Submersible discharge pumps may be needed to bring groundwater from the source to the Ultrox system. In addition, a submersible pump is commonly needed to pump the effluent from a small capacity container to a storage tank. As discussed previously, an air compressor is frequently used to generate ozone from air. However, in some applications an alternative air source is used, such as compressed air or oxygen cylinders.

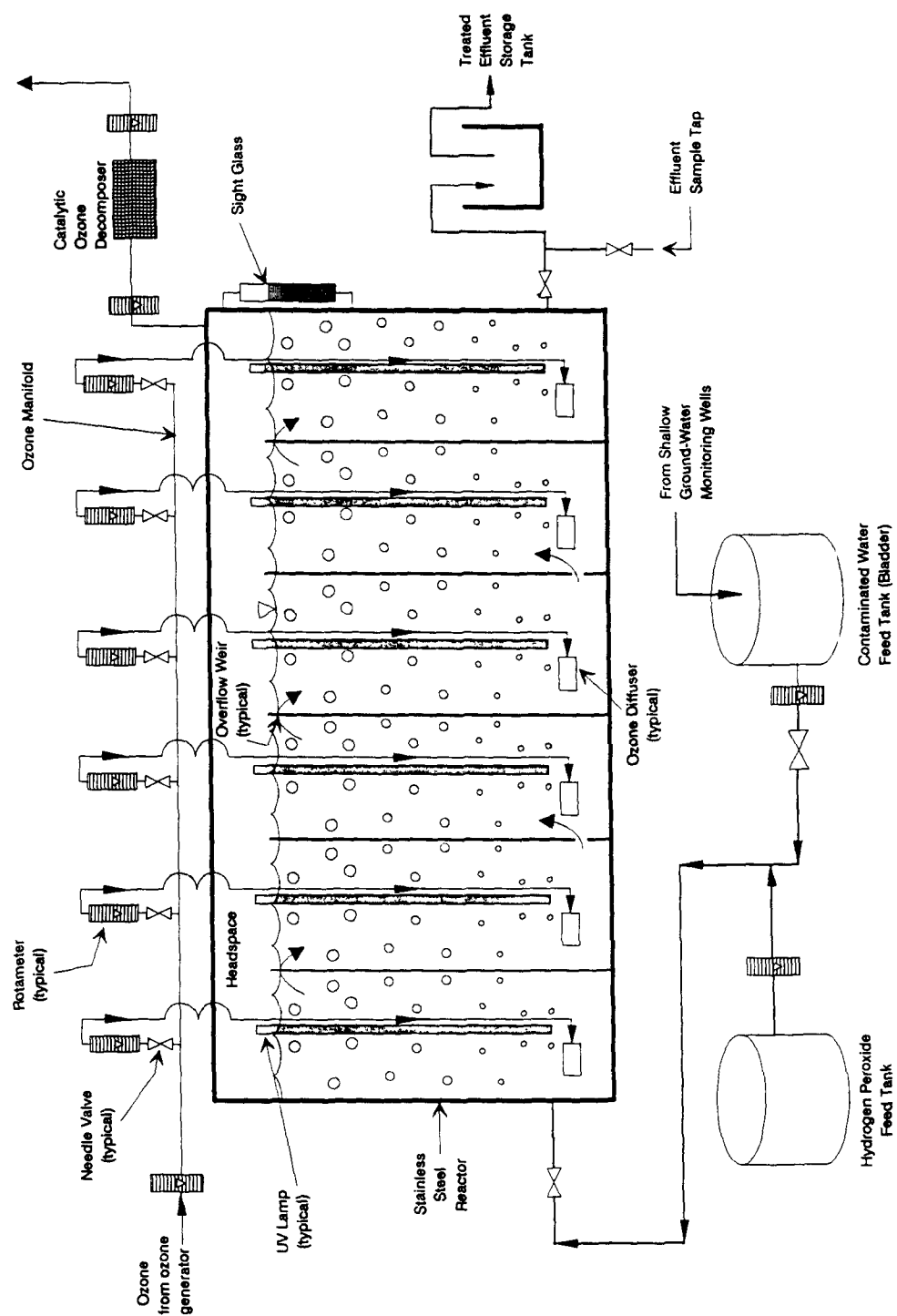


FIGURE 3-3

ULTROX SYSTEM FLOW DIAGRAM

For the demonstration, two collapsible bladder tanks were used to store site groundwater in order to reduce VOC losses. The treated water was pumped from an effluent collection tank to an effluent storage tank in all test runs. The combined effluent from all the runs was stored in the storage tank until the effluent was analyzed and found to be acceptable for discharge into Coyote Creek, a nearby watercourse.

## **UTILITY REQUIREMENTS**

Utilities required for the Ultrox system demonstration included water, electricity, and telephone service.

- **Water --** Tap water was required for the Ultrox process and for equipment and personnel decontamination. During operation, the Ultrox system required less than 3.5 gallons per minute (gpm) of cooling water. A recirculating chiller enabled reuse of cooling water. Water used for equipment and personnel decontamination was provided using existing site pipelines.
- **Electricity --** Electricity was required to operate the Ultrox system, the office trailer, and the laboratory equipment. The Ultrox system required 480-volt, 3-phase, electrical service. Also 110-volt, single-phase power was needed for lighting the field trailer and operating the on-site laboratory equipment.
- **Telephone Service --** Telephone service was required to order supplies, coordinate site activities, and provide communication.

Additional equipment, facilities, and services used during the demonstration are discussed in the following section.

## **SECTION 4**

### **DEMONSTRATION PROCEDURES**

The procedures followed during the Ultrox demonstration were developed to allow the Ultrox technology to be tested on wastes at the LB&D site. Based on the LB&D site characteristics, waste stream characteristics, and results of treatability studies, a Demonstration Plan detailing the sampling and analysis procedures, quality assurance plans, and health and safety procedures was prepared. This section summarizes the LB&D site characteristics and site preparation activities, and discusses the test runs, demonstration procedures (i.e., sampling and analysis procedures), and deviations from Demonstration Plan (PRC, 1989). This section also discusses technical systems reviews and health and safety procedures followed during the demonstration, as well as the community relations efforts.

#### **SITE DESCRIPTION AND CHARACTERISTICS**

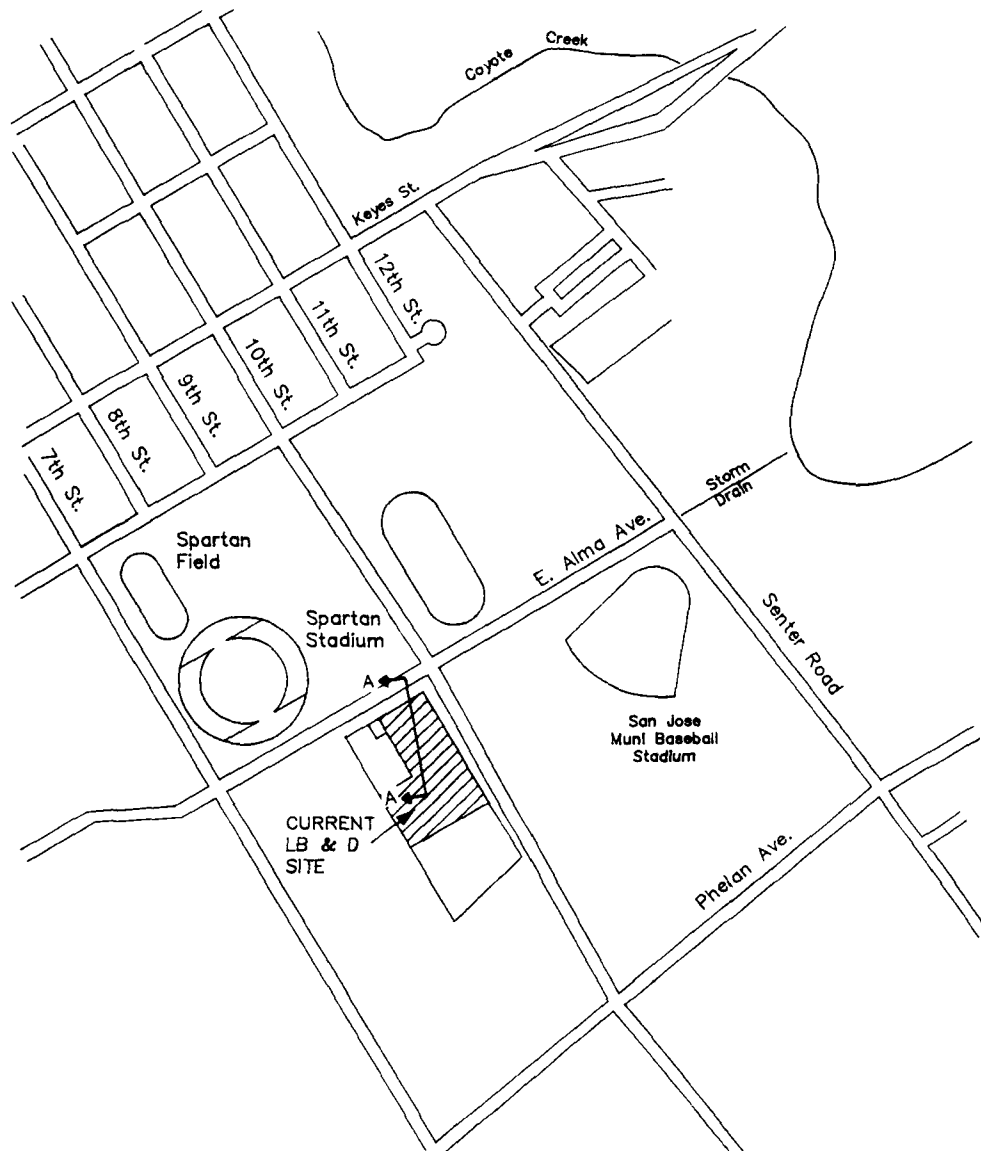
The LB&D site is located at the southwest corner of East Alma Avenue and South Tenth Street in the southern portion of San Jose, Santa Clara County, California. LB&D began a drum recycling operation in 1947. At that time, the LB&D site consisted of 10.5 acres. Since that time, some of the property has been sold, resulting in the current L-shaped site which covers 5.25 acres. This area is suspected to contain the highest levels of contamination. A site location map is presented in Figure 4-1.

The site is zoned for manufacturing and is located just south of land zoned as residential. This residential zone includes San Jose State University's (SJSU) football stadium (Spartan Field and Spartan Stadium) and recreation fields, as well as the San Jose Muni Baseball Stadium. SJSU University student housing (the closest residential area) is about a quarter mile north of the site.

The LB&D site is nearly level. The slope at the site is from the southwest corner to the northeast corner. The highest elevation at the southwest corner is 106 feet, and the lowest point at the northeast corner is 102 feet above mean sea level.

The climate is characterized by warm, dry summers and cool, wet winters. Normal January and July daily average temperatures are 49.5°F and 68.8°F, respectively. Annual minimum temperatures are generally a few degrees below freezing, while maximum temperatures in excess of 100°F are common. Normally, average annual rainfall in the area is 13.9 inches, most of which occurs from November through April.

**FIGURE 4-1**  
**LORENTZ BARREL & DRUM SITE LOCATION**



Surface water runoff from the site enters a 60-inch diameter storm drain at the corner of East Alma Avenue and South Tenth Street and flows to Coyote Creek under Alma Avenue. A secondary 18-inch storm drain runs northwest under South Tenth Street and connects with the 60-inch diameter storm drain.

Coyote Creek is less than 1/2 mile east of the site. Coyote Creek flow rates are regulated by the Coyote and Anderson reservoirs. An average flow rate of 45 cubic feet per second (cfs) has been recorded between 1970 and 1983. A maximum flow rate of 5000 cfs was recorded in March 1983. Zero flow rate has been recorded for short durations in the fall.

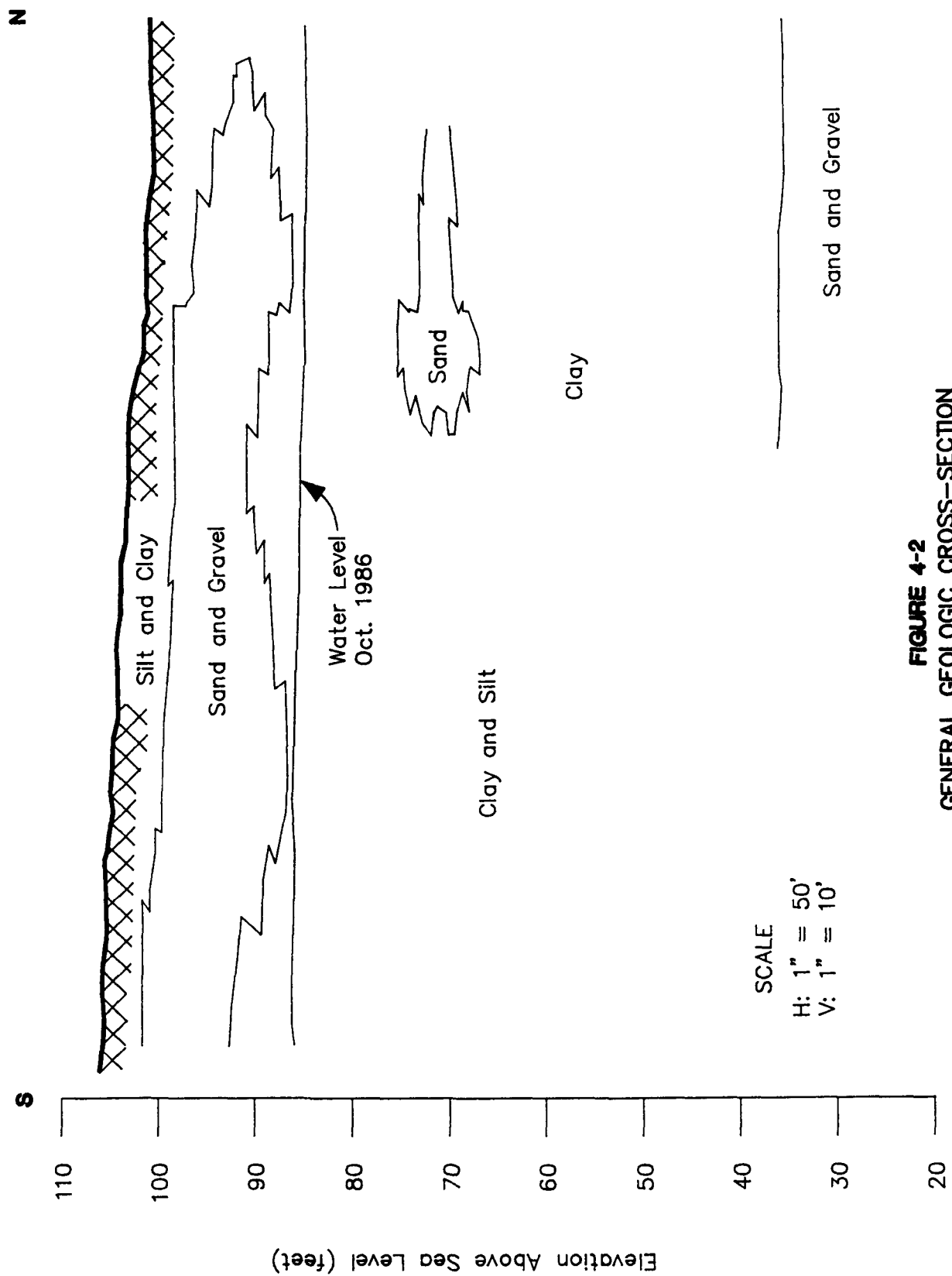
A generalized cross-section of the site-specific hydrogeology is shown in Figure 4-2. The water table at the site is approximately 20 feet below ground surface. Seasonal variations of the water table, the actual aquifer thickness, and the hydraulic characteristics of the clay aquitard are unknown. As is typical with water table aquifers, the shallow groundwater flow appears to follow the ground surface topography, flowing north toward Coyote Creek.

#### **SITE CONTAMINATION AND TREATABILITY STUDY**

Contaminated groundwater characteristics and treatability study results were used to design the demonstration plan for the Ultrox UV radiation/oxidation technology. Contaminated groundwater characterization data were used to select analytical parameters while treatability study results were used to prepare the test run matrix.

The preliminary site assessment report for the LB&D site (CH2M Hill, 1986) shows that groundwater and soil are contaminated with organics and metals. A limited sampling program conducted at the LB&D site verified contamination of soil and groundwater; however, indication that the contaminants had originated from the LB&D site was not conclusive (Ebasco, 1988).

Based on the results of a treatability study on LB&D's groundwater, the site was selected for demonstrating the Ultrox technology. The maximum contaminant levels detected in the groundwater at the LB&D site are summarized in Table 4-1. This table shows that the groundwater at the site is contaminated with VOCs, pesticides, PCBs, and metals, while groundwater downgradient of the site is contaminated with VOCs. The organic contaminants measured in the on-site groundwater range in concentration from 0.2 parts per billion (ppb) for chlordane (a pesticide) to 2,108 ppb for trichloroethylene (TCE, a VOC). Organic contaminants measured in the off-site groundwater range from 0.5 ppb for chloroform to 311 ppb for TCE.



**FIGURE 4-2**  
GENERAL GEOLOGIC CROSS-SECTION



**TABLE 4-1**  
**GROUNDWATER ANALYTICAL DATA SUMMARY**  
(November 1983 to July 1988)

Analyte	Highest Level Detected On-Site (ppb <sup>a</sup> )	Highest Level Detected Off-Site (ppb <sup>b</sup> )
Arsenic	4.0	ND
Barium	160.0	141.0
Chromium	10.0	2.4
Cobalt	60.0	15.0
Molybdenum	20.0	NA
Nickel	130.0	72.0
Vanadium	30.0	32.0
Zinc	20.0	NA
<u>Volatile Organics</u>		
Benzene	26.0 <sup>c</sup>	8.0
Chloroethane	24.0	ND
Chloroform	29.0	0.5
1,1-Dichloroethane	85.0	16.0
1,2-Dichloroethane	270.0	20.0
1,1-Dichloroethene	160.0	86.0
Trans-1,2-Dichloroethene	750.0	56.0
1,2-Dichloropropane	170.0	19.0
Tetrachloroethene	140.0	19.0
Methylene Chloride	26.0	ND
1,1,2,2-Tetrachloroethane	140.0	ND
1,1,1-Trichloroethane	220.0	34.0
Trichloroethylene	2108.0	311.0
Vinyl Chloride	1100.0	72.0
Freon 113	41.0	NA
<u>Pesticides</u>		
Chlordane	0.2	ND
Toxaphene	2.0	ND
Polychlorinated Biphenyls	4.2	ND

Source: Ebasco, 1988.

Notes: Phthalates were omitted from this table due to the unreliability of supporting data.  
(They appear to be laboratory or field contaminants.)

ND = Not detected; detection limits were not given in the source.

NA = Not analyzed.

<sup>a</sup> Chemical data from monitoring well sampling on-site and nearby off-site.

<sup>b</sup> Chemical data from off-site Tracer Research mobile laboratory study.

<sup>c</sup> Estimated trace value.

In December 1988, additional groundwater samples were collected from wells at and near the LB&D site. Samples were collected from three off-site wells (MW16B, MW18A, and MW19) and two on-site wells (MW4 and MW5) near the planned location of the technology demonstration. The analytical results are summarized in Table 4-2. The data indicates that 14 VOCs were detected at least once in the well samples. However, neither semivolatiles nor PCBs were detected. VOCs detected at relatively high levels include acetone (160 ppb at MW16B); 1,1-dichloroethene (180 ppb at MW19); 1,2-trans-dichloroethene (200 ppb at MW19); TCE (920 ppb at MW4); and vinyl chloride (240 ppb at MW19). VOCs detected in all five wells include 1,1-dichloroethene; 1,2-trans-dichloroethene; 1,1,1-trichloroethane; and TCE.

In addition to the pre-demonstration sampling results, the analytical results of influent samples collected during the test runs were also used to characterize groundwater contamination at the LB&D site. Laboratory analytical parameters measured during the test runs included the following: VOCs, total organic carbon, metals, semivolatile organics, PCBs, and pesticides. Field parameters included pH, conductivity, temperature, alkalinity, and turbidity.

The applicability of the Ultrox technology for remediating the contamination at the LB&D site was evaluated by EPA Region IX through a treatability study. The study was conducted as part of the engineering evaluation/cost analysis. The treatability study was carried out by Ultrox in July 1988 according to specifications developed by Region IX (Ebasco, 1988). Groundwater used for the treatability study was collected and composited from two off-site wells.

The treatability study used a 2-liter reactor that was operated in a batch mode. The treatability study indicated that the Ultrox process could remove the toxic organics in the contaminated groundwater to allowable levels for discharge into Coyote Creek, a nearby watercourse. However, the concentration of nickel in the treated groundwater exceeded the California Regional Water Quality Control Board recommended level for discharge to surface water.

The treatability study also identified the initial values for operating parameters used in the demonstration testing. Based on the results, Ultrox recommended a hydraulic retention time of 40 minutes; an ozone dose of 75 mg/L; a hydrogen peroxide dose of 25 mg/L; and a lamp density of three UV lamps (65 watts each) per square foot of reactor plan area for the demonstration (PRC, 1989).

**TABLE 4-2**  
**1988 GROUNDWATER ANALYTICAL DATA SUMMARY**

	Concentrations				
	On-Site		Off-Site		
<u>Volatile Organic Compounds</u>	<u>MW4</u>	<u>MW5</u>	<u>MW16B</u>	<u>MW18A</u>	<u>MW19</u>
Acetone	ND (100)	ND (100)	160	ND (100)	ND (100)
Benzene	ND (5)	16	8	ND (5)	20
Chloroform	8	ND (5)	ND (5)	ND (5)	ND (5)
1,1-Dichloroethane	16	41	24	ND (5)	42
1,2-Dichloroethane	ND (5)	ND (5)	ND (5)	ND (5)	17
1,1-Dichloroethene	17	120	40	22	180
1,2-trans-Dichloroethene	68	42	59	19	200
1,2-Dichloropropane	36	18	16	ND (5)	38
Tetrachloroethene	43	ND (5)	27	ND (5)	32
Toluene	ND (5)	7	ND (5)	ND (5)	ND (5)
1,1,1-Trichloroethane	10	20	11	15	54
Trichloroethene	920	280	370	86	730
Vinyl chloride	51	146	120	ND (5)	240
Xylenes, total	ND (5)	10	ND (5)	ND (5)	ND (5)
<u>Metals</u>					
Arsenic	7.9	35.5	ND (5)	ND (5)	ND (5)
Chromium, hexavalent	ND (50)	ND (50)	ND (50)	ND (50)	
Lead	13.3	5.3	5.8	ND (5)	13.7
Mercury	ND (0.2)	ND (0.2)	ND (0.2)	ND (0.2)	
Selenium	ND (2)	ND (2)	ND (2)	ND (2)	
<u>Miscellaneous</u>					
Alkalinity, mg/L as CaCO <sub>3</sub>	515	621	551	451	669
Bromide	ND (2000)	ND (2000)	ND (2000)	ND (2000)	ND (2000)
Cyanide, total	ND (20)	46	ND (20)	ND (20)	ND (20)
Sulfide	ND (1000)	ND (1000)	ND (1000)	ND (1000)	ND (1000)
Total organic halides	NA	NA	540	140	1000
Phenolics	13	150	NA	NA (2)	NA (2)
2,4-Dichlorophenol	ND (0.39)	ND (0.39)	9.33	ND (0.39)	ND (0.39)
2-Nitrophenol	1-68	1-68	8.55	ND (0.045)	ND (0.045)
Beta-BHC	ND (0.006)	ND (0.006)	0.21	ND (0.006)	ND (0.006)
4,4'-DDD	0.034	ND (0.011)	ND (0.011)	ND (0.011)	ND (0.011)
4,4'-DDT	ND (0.012)	0.186	ND (0.012)	ND (0.012)	ND (0.012)
Turbidity, NTU	270	60	95	115	9200
pH, pH units	7.0	7.2	7.0	7.1	7.2

Source: Engineering-Science, Inc., 1989.

Notes: Concentrations are in ppb, unless otherwise stated.

ND =Not detected; detection limits are shown in parentheses.

NA =Not analyzed

## **DEMONSTRATION PROGRAM SCHEDULE**

The schedule and duration for the Ultrox technology demonstration is shown in Table 4-3. Following EPA approval of the final Demonstration Plan, site preparation and equipment mobilization for the Ultrox system demonstration began in early February 1989. The actual demonstration of the commercial-size Ultrox system began in late February 1989.

The test demonstration was divided into three phases: (1) site preparation (about 3 weeks), (2) technology system demonstration (about 2 weeks), and (3) site demobilization (about 3 weeks). Upon EPA approval, Ultrox may conduct follow-up, long-term testing for 4 months during the actual site remediation, scheduled for fall 1989. Except for the follow-up study, all demonstration activities, including the test data analysis and the draft Technology Evaluation Report and Applications Analysis Report submittals, are expected to be completed by early September 1989.

To accommodate the SITE team's demonstration program schedule, Region IX installed four groundwater extraction wells at the LB&D site in January 1989. The wells were necessary to obtain sufficient groundwater for the technology demonstration test runs. Once installed, the four wells were pump-tested to estimate expected groundwater yields. Of the four wells installed, only three were needed to obtain the necessary groundwater, which was stored in two bladder tanks.

## **FIELD ACTIVITIES**

A suitable location was selected at the LB&D site to conduct the field demonstrations. After deciding on the field demonstration location, numerous required support services, facilities, and major pieces of material and equipment were ordered and installed. Specifically, EPA arranged utility connections, ordered and rented specialty equipment, supervised and directed subcontractors, and arranged for security protection. Following the demonstration, the site support equipment and facilities were demobilized.

The following subsections discuss the location selected for the demonstration and the major pieces of support equipment and services used during the effort.

### **Site Location**

The northeast corner of the LB&D site (approximately 100 ft by 200 ft) was selected for the SITE demonstration for the following reasons:

**TABLE 4-3**  
**DEMONSTRATION CHRONOLOGY**

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**Site Preparation**

Prepared layout design for demonstration area	late January, 1989
Met with electric utility company	February 1, 1989
Trailer and chemical toilets were delivered	February 1, 1989
Connected telephone line	February 2, 1989
Sent announcement letters for visitors day	February 6, 1989
Met with electrical subcontractor	February 7, 1989
Steel storage tank was delivered	February 10, 1989
Bladder-type storage tanks delivered	February 14, 1989
Miscellaneous plumbing connections were completed	February 17, 1989
Pumped groundwater and filled bladder tanks	February 20-23, 1989
Ultrox unit was delivered	February 21, 1989
Electrical service was connected	February 23, 1989
Held health and safety orientation meeting	February 23, 1989
Established support, contaminant reduction, and exclusion zones	February 23, 1989

**Technology Demonstration**

Pre-demonstration Run 0	February 24, 1989
Run 1	February 27, 1989
Run 2	February 28, 1989
Run 3	March 1, 1989
Runs 4 and 5	March 2, 1989
Run 6	March 3, 1989
Run 7	March 4, 1989
Runs 8 and 9	March 6, 1989
Electrical power pole damaged and repaired	March 6-7, 1989
Audio-visual camera crew taping	March 6-8, 1989
Run 10	March 7, 1989
Run 11	March 8, 1989
Visitors Day	March 8, 1989
Runs 12 and 13	March 9, 1989
Remaining liquids treated	March 9, 1989

**Site Demobilization**

Ultrox unit decontaminated and disassembled	March 10, 1989
Support equipment removal completed	March 30, 1989

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- Allowed convenient site access through existing driveway and locking gate
- Allowed possible utility service with power and telephone lines across the street
- Provided storm drain access at adjacent street intersection for discharging treated wastewater after laboratory analyses
- Provided ample parking and support for truck deliveries and equipment because of its level asphaltic surface
- Allowed convenient access to nearby groundwater monitoring and extraction wells

### **Major Support Equipment, Facilities, and Services**

Numerous support items were needed for the field demonstration, including equipment to collect and store site groundwater and treated effluent; facilities for field and office personnel; a field laboratory; and utility connections for the Ultrox unit and the office and field laboratory trailer. The major support equipment, facilities, and services are described below.

#### **Bladder Tanks--**

Two, 7,500-gallon bladder-type tanks were purchased to store the contaminated site groundwater pumped from on-site wells. Approximately 13,000 gallons were collected and stored in the flexible tanks, which had been selected specifically to minimize VOC losses during the test period. The tank's membrane material was approved by the U.S. Food and Drug Administration to store potable water.

#### **Submersible Pumps--**

Three dedicated, submersible pumps were used to pump site groundwater into the two bladder tanks. Approximately 13,000 gallons were pumped over a 2½-day period. The maximum pumping rate was approximately 5 gpm per pump; the average, approximately 1 gpm. The bladder tanks and pumps were connected using piping manifolds so that the two tanks could be filled simultaneously.

#### **Metal Storage Tank--**

A 21,000-gallon storage tank was used to store all treated effluent. The tank had been steam cleaned prior to delivery to the LB&D site. In addition to holding the effluent from the test runs, groundwater remaining in the bladder tanks after the final test run was treated and pumped to the storage tank. Similarly, miscellaneous liquid wastes which had been stored in 55-gallon drums during the test period were treated by the Ultrox unit and pumped to the storage tank. These miscellaneous liquids consisted of well development water, excess sample volumes

generated during sampling operations, and spent chemical reagent wastes produced from the on-site laboratory analyses.

#### **Electrical Service--**

Electrical service was connected to the site from a public utility. The Ultrox system required 480-volt, 3-phase electrical service, which was provided through a 100-amp electrical service using a dedicated meter and a transformer. An additional 110-volt, 100-amp service line was connected to another dedicated meter to provide power to the office and laboratory trailer.

#### **Office and Laboratory Trailer--**

A field trailer provided space for laboratory personnel to conduct field analyses. It also served as an office for field personnel, provided shelter and storage for small equipment and supplies, and acted as a base for site security personnel. A single telephone line was installed in the trailer. Two chemical toilets were located near the trailer.

#### **Portable Tent--**

A portable tent was installed to protect personnel, the Ultrox system and sampling equipment, and site visitors from bad weather. The tent, which measured 20 by 30 by 8 feet high, was rented for a 3-day period.

#### **Security Service--**

Although the LB&D site perimeter is enclosed by a fence, a commercial security service was hired to provide additional protection from equipment vandalism during evening hours and over weekends.

### **TEST RUNS**

During the demonstration program, the operating parameters (such as hydraulic retention time, oxidant doses, and influent pH level) were adjusted to evaluate the Ultrox system under various operating conditions. At the end of the demonstration, two additional test runs were performed to determine if the performance levels were reproducible. The test runs performed during the demonstration are summarized in Table 4-4. Runs 1 through 11, given in the table, were designed to evaluate the Ultrox system under varying operating conditions. Runs 12 and 13 were performed to verify the performance of Run 9. All of the runs were performed over a period of two weeks, as listed and described in Table 4-5. The Ultrox system was shut down at the end of each run.

**TABLE 4-4**  
**OPERATING PARAMETERS MATRIX FOR THE ULTROX SYSTEM DEMONSTRATION**

Run No.	Influent pH	Retention Time (Minutes)	Ozone Dose (mg/L)	H <sub>2</sub> O <sub>2</sub> Dose (mg/L)	UV Lamps (24 tubes 65 watts each)
1 <sup>a</sup>	7.2	40	75	25	All ON
2	6.2	40	75	25	All ON
3	5.2	40	75	25	All ON
4	Preferred <sup>b</sup>	60	75	25	All ON
5	Preferred	20	75	25	All ON
6	Preferred	Preferred	110	25	All ON
7	Preferred	Preferred	38	25	All ON
8	Preferred	Preferred	Preferred	38	All ON
9	Preferred	Preferred	Preferred	13	All ON
10	Preferred	Preferred	Preferred	Preferred	Only ON in the first three chambers
11	Preferred	Preferred	Preferred	Preferred	Only ON in the last three chambers
12 <sup>c</sup>	Preferred	Preferred	Preferred	Preferred	Preferred
13 <sup>c</sup>	Preferred	Preferred	Preferred	Preferred	Preferred

**Notes:**

- <sup>a</sup> The operating conditions used in Run 1 were determined by Ultrox International to be the optimum conditions for treating groundwater in the treatability study at the LB&D site.
- <sup>b</sup> "Preferred" operating conditions are those for which (1) the concentrations of effluent indicator VOCs are below their respective NPDES limits and (2) the relative operating costs are the lowest.
- <sup>c</sup> Verification runs performed to check the reproducibility of the data collected at the "preferred" operating conditions (Run 9). See Section 5 for the demonstration program results.



**TABLE 4-5**  
**SUMMARY OF THE EXPERIMENTAL PROGRAM SCHEDULE**

Week	Day	<u>Number of the Run Performed</u>		Parameter Varied
		AM	PM	
1	1	1		None
	2	2		Influent pH level
	3	3		Influent pH level
	4	4	5	Hydraulic retention time
	5		6	Ozone dose
	6	7		Ozone dose
2	7	8	9	Hydrogen peroxide dose
	8		10	UV radiation intensity
	9	11		UV radiation intensity
	10	12	13	None (reproducibility runs)

To meet the demonstration program objectives, the data were obtained in accordance with specific testing approaches. Samples were collected at the sampling locations described under Sampling Procedures. The testing approaches for the operating parameters study and the verification runs are described as follows.

### **Operating Parameters Study**

The demonstration was designed to evaluate the Ultrox system by controlling five operating parameters: hydraulic retention time, ozone dose, hydrogen peroxide dose, UV radiation intensity, and influent pH level. The experimental program began under the operating conditions established by Ultrox. These initial operating conditions were expected to approximate the optimum conditions, based on the results of groundwater treatability study conducted by Ultrox for the LB&D site. The operating parameters study consisted of the first eleven test runs.

The performance of each test run was determined based on the effluent concentrations of selected indicator VOCs. Specifically, two of the six replicate samples collected at each of three liquid sampling locations (influent, midpoint, and effluent of the reactor) were analyzed overnight by gas chromatography for three indicator VOCs. The three indicator VOCs selected for this purpose were trichloroethylene (TCE, a major volatile contaminant at the site), 1,1-dichloroethane (1,1-DCA), and 1,1,1-trichloroethane (1,1,1-TCA). The latter two VOCs were selected because Ultrox's experience indicated that they are relatively difficult to oxidize. The indicator VOCs were limited to three primarily because of analytical time constraints.

In the first three test runs of the demonstration program, the influent pH level was varied by adding sulfuric acid. The system's performance was evaluated for each of these runs to determine the "preferred" influent pH (see Table 4-4 footnotes). Once the "preferred" influent pH was determined, the influent pH remained at that level for the remaining runs. In a similar manner, other parameters were varied one at a time, as shown in Table 4-4, to determine the "preferred" values for those parameters. The criteria were the same as those used in determining the "preferred" value for influent pH. After the "preferred" values were determined for all five operating parameters, two verification runs were performed to check the results at the "preferred" operating conditions.

### **Verification Runs**

Two identical runs (12 and 13) were performed to verify the reproducibility of the Ultrox system's performance levels. By duplicating the "preferred" operating conditions developed

during the operating parameters study, the two verification runs served to ensure that the results could be based on repeated observations, with comparable findings.

## **SAMPLING PROCEDURES**

This section of the report describes the standard procedures used to collect samples for on- and off-site analyses. Strategies for collecting samples to fulfill the sampling objectives are discussed first, followed by more detailed discussions of sampling procedures, process control measurements, and quality assurance procedures.

### **Sampling Strategies**

To meet the objectives of the Ultrox demonstration, five types of sampling and monitoring were performed: (1) water samples for off-site analysis; (2) air samples for off-site analysis; (3) water samples for on-site analysis; (4) ozone monitoring in air; and (5) process control measurements associated with the Ultrox treatment system. The remainder of this section summarizes these sampling and monitoring procedures and identifies deviations from the procedures described in the Demonstration Plan (PRC, 1989). Tables 4-6 to 4-8 summarize the sampling locations, types, blanks, and the number of samples for all analytical parameters.

#### **Water Samples for Off-Site Analysis--**

##### **Sampling Locations**

All water samples analyzed off-site were collected directly into sampling bottles from the four sampling ports of the Ultrox treatment system via attached faucets (Figures 4-3 and 4-4). Influent samples were collected from the influent sampling port, which was located between the bladder storage tanks and the hydrogen peroxide addition point. The influent samples were collected to determine the waste characteristics before the addition of acid or hydrogen peroxide.

Another port was used to collect samples after acid or hydrogen peroxide was added. Midpoint samples were collected from the sampling port approximately at the midpoint of the reactor. These samples were collected to determine the analytical characteristics of the waste during the treatment process in the reactor.

To determine the analytical characteristics of the treated waste as well as the overall treatment efficiencies for specific constituents, effluent samples were collected from the effluent sampling port at the reactor outlet.

**TABLE 4-6**  
**LOCATIONS, PARAMETERS, AND NUMBERS**  
**OF SAMPLES FOR TREATMENT EVALUATION**

Parameters	Matrix <sup>b</sup>	Analysis <sup>c</sup>	Number of Samples per Location			No. of Equipment Blanks	No. of Trip Blanks	TOTAL <sup>d</sup>
			Influent <sup>d</sup>	Midpoint <sup>d</sup>	Effluent <sup>d</sup>			
Alkalinity	L	F	17	0	14	0	0	81
Conductivity	L	F	30	0	29	0	0	59
Chromium (Cr <sup>+6</sup> )	L	Lab.	0	0	2(1,1)	0	0	2(1,1)
Hydrogen Peroxide	L	F	0	0	14	0	0	14
Metals	L	Lab.	13(6,6)	0	13(7,7)	4	0	30(13,13)
Minerals/ Ions	L	Lab.	0	0	2(1,1)	0	0	2(1,1)
Ozone	L	F	0	0	16	0	0	16
PCBs <sup>a</sup> / Pesticides	L	Lab.	12(1,1)	12	12(1,1)	4	0	40(2,2)
pH	L	F	33	0	29	0	0	62
Semi-Volatiles	L	Lab.	12(1,1)	12	12	4	0	40(1,1)
TOC	L	Lab.	13(1,1)	0	13	0	0	26(1,1)
Turbidity	L	F	15	0	15	0	0	30
VOC (GC)	L	Lab.	78(5,5)	78(4,4)	78(4,4)	4	14	252(13,13)
VOC (GC/MS)	L	Lab.	4(1,1)	4	4	0	0	12(1,1)
<b>TOTAL</b>			<b>227(15,15)</b>	<b>106(4,4)</b>	<b>253(14,14)</b>	<b>16</b>	<b>14</b>	<b><u>616 (33,33)</u></b>

**Notes:**

The total number of samples is for the entire demonstration (13 runs). The total number of samples is used to determine completeness.

- a. PCB = polychlorinated biphenyls
- b. L = Liquid
- c. F = Field Method
- Lab. = Laboratory Method
- d. ( ) = Number of Matrix Spike and Matrix Spike Duplicate Samples

**TABLE 4-7**  
**LOCATIONS, PARAMETERS, AND NUMBERS OF**  
**SAMPLES/MEASUREMENTS FOR PROCESS CONTROL**

Parameters	Matrix <sup>a</sup>	Analysis <sup>b</sup>	<u>Water Chiller</u>		<u>Chemical Feeder</u>			Electric Meter	TOTAL
			Reactor Influent	Inlet	H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> SO <sub>4</sub>	O <sub>3</sub>		
Electricity Consumption	NA	F	0	0	0	0	0	13	13
Flow Rate	L/A	F	15(L)	0	13(L)	2(L)	24(A)	0	54
H <sub>2</sub> O <sub>2</sub> Feed Conc.	L	F	0	0	15	0	0	0	15
Normality (H <sub>2</sub> SO <sub>4</sub> )	L	F	0	0	0	3	0	0	3
Ozone	A	F	0	0	0	0	25	0	25
Temperature	L	F	32	12	0	0	0	0	44
<b>TOTAL</b>			<b>47</b>	<b>12</b>	<b>28</b>	<b>5</b>	<b>49</b>	<b>13</b>	<b><u>154</u></b>

**Notes:**

The total number of samples is for the entire demonstration (13 runs). The total number of samples is used to determine completeness.

a.     NA = Not Applicable  
       L = Liquid  
       A = Air

b.     F = Field Method

**TABLE 4-8**  
**LOCATIONS, PARAMETERS, AND NUMBERS**  
**OF SAMPLES FOR EMISSION CONTROL**

Parameters	Matrix <sup>a</sup>	Analysis <sup>b</sup>	<u>Sampling Locations</u>		No. of Trip Blanks	No. of Field Blanks	TOTAL
			Reactor Off-Gas	Decomposon Exhaust			
Ozone	A	F	25	25	0	0	50
Temperature	A	F	25	25	0	0	50
VOC	A	Lab.	78	78	12	12	180
<b>TOTAL</b>			<b>128</b>	<b>128</b>	<b>12</b>	<b>12</b>	<b><u>280</u></b>

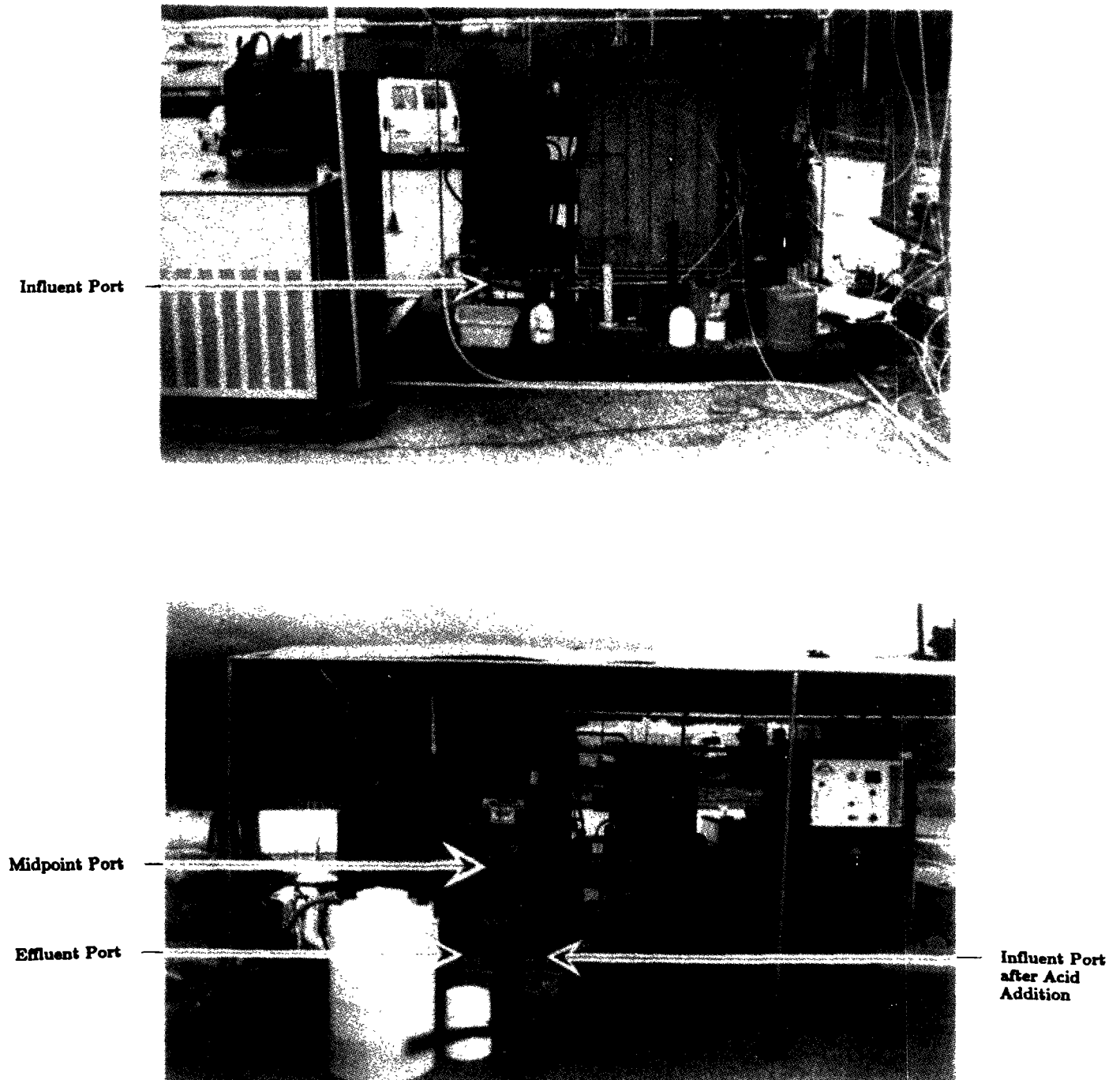
**Notes:**

The total number of samples is for the entire demonstration (13 runs). The total number of samples is used to determine completeness.

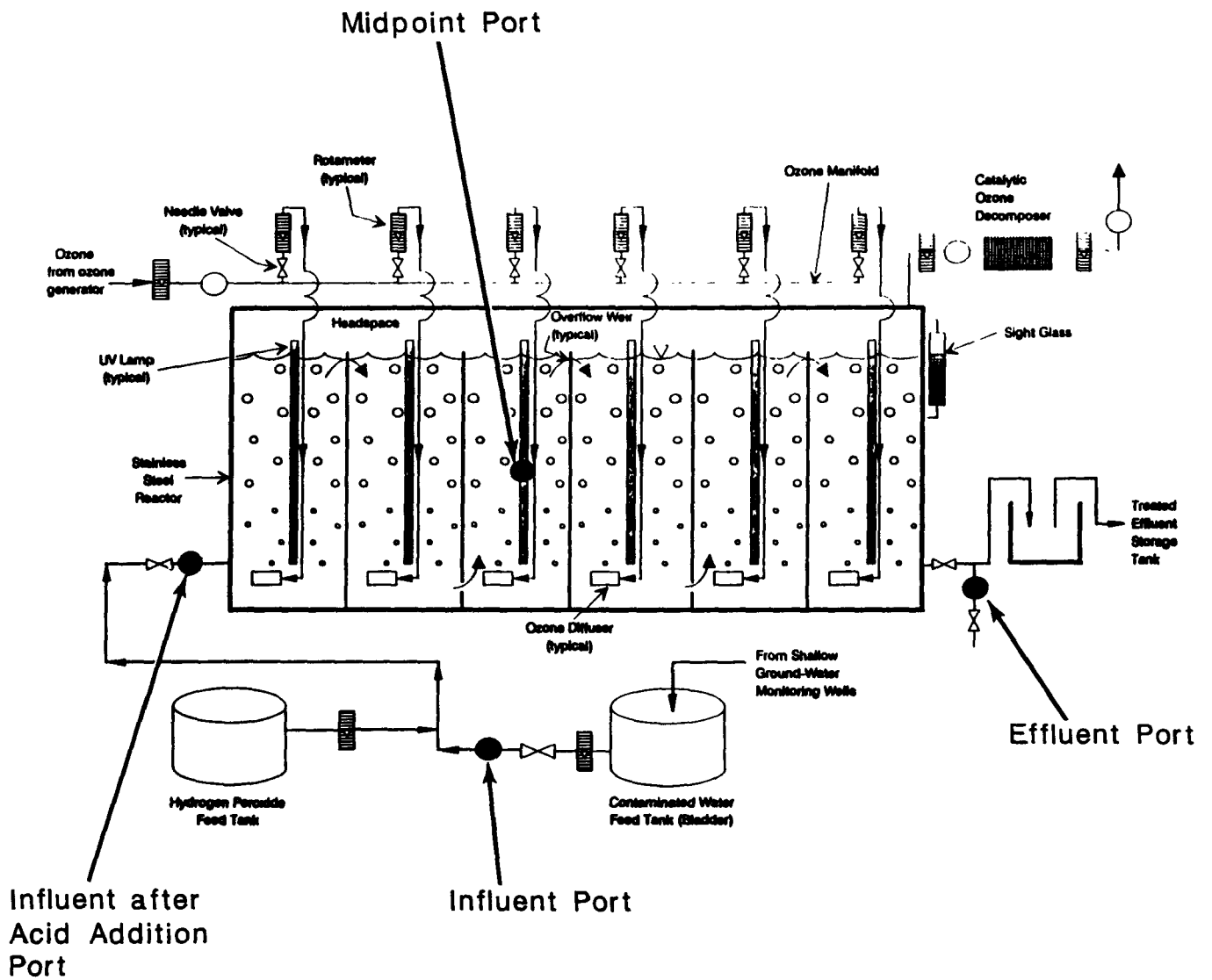
a.           L = Liquid  
               A = Air

b.           F = Field Method  
               Lab. = Laboratory Method

**FIGURE 4-3**  
**WATER SAMPLING LOCATIONS**



**FIGURE 4-4**  
**SCHEMATIC OF WATER SAMPLING PORTS**





### Sample Size and Sampling Frequency

Volatile organic compounds (VOC) were selected as the critical parameters for evaluating the effectiveness of the Ultrox technology, for the following reasons:

- The Ultrox technology was developed primarily to treat organics (such as VOCs, semivolatiles, and PCBs/pesticides).
- Of the organic species mentioned above, only VOCs were found in the groundwater samples collected in December 1988.

VOC samples were collected for both gas chromatography (GC) and GC/mass spectrometry (MS) analysis. The majority of these samples were collected for GC analysis, which allowed quantification of the compounds at lower detection limits. Additional samples were analyzed using the GC/MS method to provide additional compound identification information. Six replicate samples were collected for VOC analysis by GC at each of the three sampling locations per test run. Each sample consisted of three 40-mL vials with Teflon-lined septums.

For each test run a matrix spike (MS) sample and a matrix spike duplicate (MSD) sample were also collected. Sampling locations for the MS/MSD samples were rotated among the three sampling locations. All replicate samples were collected at 15-minute time intervals after the treatment system had reached steady-state (after 3 hydraulic retention times) for each test run. Of the six replicates from each location, two were analyzed within 24 hours. Information provided by this expedited analysis was used to determine operating conditions for subsequent runs.

Additionally, during the last two test runs (12 and 13), a total of 12 replicate samples (three at each location) were collected for GC/MS analysis for VOCs. Also collected for GC/MS analysis was a pair of MS/MSD samples from the influent sampling port.

Liquid samples for metals analyses were collected, one each from the influent and effluent sampling ports after the treatment system had reached steady-state, for all test runs. Amber glass, 1-liter bottles were used for the sample collection. A pair of MS/MSD samples was also collected for each run from the effluent sampling port during Runs 1 through 7 and from the influent sampling port during Runs 8 through 13. All MS/MSD sample pairs collected from the same sampling port were later composited into a pair of MS/MSD samples in the laboratory.

Liquid samples for total organic carbon (TOC) analyses were collected, one each from the influent and effluent sampling ports, for all test runs. Each sample was collected in 40-ml vials (three per sample) with Teflon-lined septums. One pair of MS/MSD samples was also collected from the influent sampling port.

Liquid samples for PCBs/pesticides and semivolatiles analyses were collected only during Runs 12 and 13. Six samples, each of which filled two, amber glass, 1-liter bottles, were collected from the influent, midpoint, and effluent sampling ports. A pair of MS/MSD samples was collected for each of these parameters for the two verification runs.

Liquid samples for hexavalent chromium and minerals/ions analyses were collected, one each, in 500-ml and amber glass, 1-liter bottles, respectively, during the last two verification runs from the effluent sampling port. These samples were collected to confirm that the effluent from the Ultrox demonstration unit meets the specified waste discharge requirements. Also, a pair of MS/MSD samples were collected for each parameter.

### **Blanks**

To evaluate the cleanliness of the Ultrox oxidation reactor prior to the demonstration, approximately 150 gallons of tap water was introduced into and recirculated several times through the reactor. Replicate samples of the tap water were collected as equipment blanks from both the influent and effluent sampling ports. The replicate equipment blanks were analyzed for VOCs, metals, semivolatiles, and PCBs/pesticides.

Trip blanks were also prepared to determine if contamination was introduced through sampling containers or as a result of exposure during shipment to and from the LB&D site. One trip blank for VOCs (consisting of three, 40-ml vials of deionized water) was prepared and shipped with other sampling containers in an ice chest to the demonstration site.

### **Air Samples for Off-Site Analysis--**

#### **Sampling Locations**

Air samplers for collection of VOCs were connected to (1) the reactor off-gas feed line to the Decompozon unit and (2) the off-gas line from the Decompozon unit. The collected samples were drawn through Teflon tubing.

### **Sample Size and Sampling Frequency**

For this study, nine VOCs were identified as potential air contaminants of interest. These nine compounds were divided into the following three sampling groups:

Group I	Vinyl chloride
Group II	1,1-Dichloroethane
	1,1,1-Trichloroethane
Group III	1,1-Dichloroethene
	1,2-Dichloroethene
	1,1,2,2-Tetrachloroethane
	Acetone
	Benzene
	Trichloroethylene

For vinyl chloride sampling, two charcoal tubes were connected in series. The front tube was designated as the sample tube while the back tube was assigned as the breakthrough tube. Single charcoal tubes were used for sampling the second and third groups of the compounds listed above. During each test run, after the treatment system had reached steady-state, two consecutive samples were collected for each of the three groups of compounds at the two sampling locations. Sampling duration for all samples was 33 minutes. Altogether, 12 air samples were collected during each run for VOC analysis.

### **Blanks**

Three equipment blanks were collected during the pre-demonstration run (Run 0), one each for the three analyte groups. Additionally, one trip blank and one field blank were collected each day during the field testing. All samples and blanks collected were delivered during the same day to the laboratory for analysis.

### **Water Samples for On-Site Analysis--**

In accordance with the objectives for the demonstration and the rationale presented in the Demonstration Plan, numerous water samples were analyzed during each test run in the field trailer.

### **Sampling Locations**

Water samples for on-site analyses were collected from three locations: the influent port, the influent port after acid or hydrogen peroxide addition, and the effluent port. These samples were analyzed for the parameters listed below:

<b><u>Sampling Location</u></b>	<b><u>Parameter</u></b>
Influent/effluent	Alkalinity
Influent after acid or hydrogen peroxide addition	Alkalinity
Influent/effluent	Conductivity
Effluent	Hydrogen Peroxide
Effluent	Ozone
Influent/effluent	pH
Influent/effluent	Turbidity
Influent/effluent	Temperature
Influent after acid or hydrogen peroxide addition	Temperature

### **Sampling Frequency**

Alkalinity, turbidity, and ozone measurements were taken for samples collected at their appropriate locations once per run. During Runs 7 and 12, duplicate measurements were taken. The alkalinity measurements were not determined for two locations: influent after acid addition and effluent during Run 1. Hydrogen peroxide measurements were taken once during each run from the effluent location, except for (1) Run 1, where no measurement was taken, and (2) Runs 7 and 12, where duplicate measurements were taken. Analytical duplicate samples were collected for the measurement of conductivity and pH from the influent and effluent locations. Four measurements were missing during Runs 1 and 2.

### **Ozone Monitoring in Air--**

To determine the efficiency of Ultrox's Decompozon unit in destroying ozone, field measurements were made using low and high concentration monitors.

### **Sampling Locations**

Air concentrations of ozone were directly measured using PCI ozone monitors at (1) the intake to the Decompozon unit (off-gas from the reactor) and (2) exhaust from the Decompozon unit (treated off-gas). Samples were drawn through Teflon-lined probes and Teflon tubing to the monitors.

### **Sample Size and Sampling Frequency**

Ozone measurements were coordinated with air sampling for VOCs. Sampling consisted of 30 measurements (approximately one measurement per minute for a 33-minute sampling duration) for each of the two back-to-back sampling periods. Averages of these 30 measurements were reported as air concentration levels of ozone at that location during a given run.

### **Process Control Measurements--**

The following procedures were used during the demonstration to measure operating parameters such as flow rates, electrical energy consumption, hydrogen peroxide and sulfuric acid feed concentrations, and ozone feed gas concentration.

The flow rates of the hydrogen peroxide and the sulfuric acid feeds were determined using flow measuring devices mounted on the Ultrox unit. These devices were graduated plastic cylinders of 250 ml (for acid) and 500 ml (for hydrogen peroxide), with a bypass valve at the bottom of each cylinder. The cylinders were filled with their respective liquids of the same concentrations that were used in a particular run. To measure the hydrogen peroxide feed flow rate, the main valve from the hydrogen peroxide feed tank was turned off and the bypass valve from the cylinder was turned on, simultaneously. By doing so, hydrogen peroxide could be pumped from the graduated cylinder instead of from the feed tank. The time taken to pump a known volume of liquid (about 200 ml) was measured using a stopwatch to calculate the flow rate. The bypass valve was then turned off and the main valve turned on to resume pumping from the feed tank. Similar procedures were followed to measure the acid flow rate.

The flow rate of reactor influent (untreated groundwater, hydrogen peroxide, and sulfuric acid, when used) was measured using a dial-type flow meter provided on the influent line to the Ultrox reactor. The flow meter was graduated and was equipped with a needle that moved at a speed proportional to the flow rate. The time taken for the needle to make one revolution, which corresponded to 10 gallons of influent pumping, was measured to calculate the flow rate. The flow rate was measured three times at the beginning of a run, and the average flow rate was calculated for each run. The flow meter was manually calibrated on-site before the demonstration at three different flow rates, by taking three measurements at each flow rate using a graduated 5-gallon container.

The ozone feed gas flow rate was measured using a rotameter provided on the ozone generator. This rotameter was calibrated on-site using a dry gas meter before and after the demonstration.

The electrical energy consumption was measured using a standard watt meter supplied by the local electric utility company. The meter was dedicated to measuring the electrical energy consumption during the operation of the Ultrox system. The initial reading on the meter at the start of a run and the final reading on the meter at the end of a run were recorded during the demonstration to determine the electrical energy consumption per unit hour of operation. These readings were in kilowatt-hour units.

Samples to measure hydrogen peroxide and sulfuric acid feed concentrations were collected directly from their respective feed tanks. Before the beginning of any run, 200-ml samples were collected in plastic containers. The containers remained closed until they were analyzed on-site. The samples were analyzed using the methods described in Analytical Procedures, usually within 1 hour after collection.

Ozone feed gas sampling was not required, since the concentration was measured directly using an ozone analyzer that was calibrated before the demonstration. At the time of calibration, the ozone gas was bubbled at a rate of 1 liter/minute into 300 ml of 2 percent potassium iodide solution contained in a 500 ml graduated cylinder for 30 to 60 seconds. From this, 50-ml aliquots were withdrawn and titrated with 0.02 M sodium thiosulfate as described in Method 422 of Standard Methods for the Examination of Water and Wastewater (1985).

### **Air Sampling Procedures**

#### **Volatile Organic Compounds--**

Samples of the reactor off-gas and Decompozon unit exhaust gas were taken to determine VOC concentrations. Two samples for each of the three compound groups were collected during each test. The specific compounds selected for sample analysis were chosen based on their presence in previous groundwater samples. The purpose of sampling and analysis of VOC concentrations was to quantify the amount of VOC stripping which occurred in the reactor and the rate of VOC emissions to the atmosphere.

Sampling was performed using modified National Institute of Occupational Safety and Health (NIOSH) methods. The modifications were necessary for two reasons. First, the NIOSH procedures were not developed for point source emissions measurement, so the sampling

apparatus used was not the typical portable personnel sampling pump system. Second, the estimated concentrations of the specific VOCs to be measured were low relative to the concentrations recommended for the NIOSH methods employed; therefore, modifications to the recommended sampling rates, sample volumes, and sorbent masses were made to ensure that method detection limits were met and that sample breakthrough would not occur.

Sample breakthrough is detected through analysis of the back sections of each sorbent tube which is separated from the primary sorbent by a barrier. The tube size designations such as 100/50 and 400/200 indicate the primary sorbent quantities (e.g. 100 and 400 mg) followed by the breakthrough sorbent mass (50 and 200). Two 100/50 tubes were used in series for the vinyl chloride samples with the entire second tube used as the breakthrough section. Ten percent of all breakthrough tubes and tube sections was analyzed. No breakthrough was detected.

Modifications to the methods were necessary to collect two samples per test run within the planned schedule and to achieve the specified analyte mass/absorbent mass ratios, sample volume/absorbent mass ratios, and analyte mass effluent volume ratios necessary to exceed the levels of detection specified by the methods. Changes to the VOC sampling method parameters were made to account for the 33-minute sampling period and to reduce the number of sample tubes and analysis runs.

Separate sampling systems were used for each sampling location. The off-gas was drawn through a Teflon sample line and chilled condensate trap using a diaphragm pump located downstream of all sampling apparatus. A condensate trap was added to each sampling system after moisture was observed in one sample tube during Run 2. Subsequently, neither moisture nor any type of condensation was observed in either the moisture traps or sorbent tubes.

To prevent any ozone present in the gas stream from interfering with VOC adsorption onto the charcoal sample tubes, the sample was also drawn through a bisulfite impregnated filter to reduce the ozone. Since many of the compounds had different sorbent capacities and breakthrough volumes, three different size sorbent tubes containing charcoal sorbent were operated in parallel to ensure that a sufficient quantity of each compound was collected.

Sample flow rate for each tube was controlled using one of three calibrated critical orifices. The downstream side of each orifice was maintained at a vacuum greater than 20" water column (W.C.) to ensure critical flow. The flow rate through each orifice and sorbent tube combination was verified, and the system was also checked for leaks at a vacuum greater than 20" W.C. before and after each sample was collected.

Sample tubes were tagged, opened, installed in the sample train, and recovered by the field team wearing latex gloves. Each tube was immediately capped and packaged in pre-labeled, double polyethylene bags. The samples were then placed in an insulated, iced container.

#### **Field Air Monitoring--**

Treatment process operating parameters were collected twice during each test run. The ozone feed rate was recorded manually before and after each sample run from Ultrox's ozone feed rate rotameter, which was calibrated against a dry gas meter prior to the demonstration.

The gas stream temperature was measured using thermocouples inserted in the off-gas and Decompozon unit exhaust piping. The temperatures were recorded before and after each test run.

The ozone feed concentration was recorded from Ultrox's PCI monitor before and after each sample run. The reactor off-gas and Decompozon unit exhaust ozone concentrations were measured using ozone analyzers and recorded once per minute during each sample run.

#### **Water Sampling Procedures**

##### **Sample Bottle Preparation--**

All water samples analyzed were collected in new sample bottles, as specified in Table 4-9. The specifications for preservatives are also listed in Table 4-9. All required preservatives were added to the sample bottles in the laboratory, prior to shipment to the field. Maximum holding times for the collected samples are provided in the Demonstration Plan. Sample labels were filled in, except for sample collection time and sampler's initial, and pasted on each sample bottle for the field sampling team prior to shipment to the field.

##### **Sample Collection--**

The sampling protocol followed the procedures listed in the Demonstration Plan. In addition, two treated wastewater samples from the steel storage tank were collected prior to testing for regulatory criteria and discharge. One sample was taken at the north end and the other at the south end of the tank. The samples were collected using a bailer-type sampling container with a small orifice for filling. The sampling team lowered the container to the bottom of the tank and raised it to the surface to obtain representative grab samples. All collected samples were stored in ice chests.



**TABLE 4-9**  
**SAMPLE CONTAINERIZATION AND PRESERVATION**  
**OF WATER SAMPLES FOR LABORATORY ANALYSIS**

Parameter	Sample Volume (mL) <sup>a</sup>	Container	Preservative
BNA	1,000	G (TLC/Amber)	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> <sup>c</sup> , Cool, 4° C
Chromium (Cr <sup>+6</sup> )	500	G (Amber)	Cool, 4° C
Metals (except Cr <sup>+6</sup> ) <sup>d</sup>	1,000	G (Amber)	HNO <sub>3</sub> to pH <2
Pesticides/PCBs	2 @ 1,000	G (TLC/Amber)	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> <sup>c</sup> , Cool, 4° C, pH 5-9
Total Organic Carbon (TOC)	3 @ 40	VOA	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> <sup>c</sup> , Cool, 4° C, HCl to pH <2
Volatile Organic Compounds (VOC)	3 @ 40	VOA	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> <sup>c</sup> , Cool, 4° C, HCl to pH <2
Minerals and Ions <sup>b</sup>	1,000	G	Cool, 4° C
Residual Chlorine	1,000	G	Cool, 4° C

**Key:**

BNA	= Base, neutral, and acid extractable semivolatile organics
PCB	= Polychlorinated biphenyls
G	= Glass
G (Amber)	= Amber colored bottle
G (TLC)	= Glass, Teflon-lined cap
VOA	= Volatile organic analysis bottle

**Notes:**

- a Sample volume applies to all samples including replicate samples and various QA/QC samples.
- b Minerals and Ions = chloride, sulfate, and silica.
- c Sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) was added to the samples as a preservative to neutralize the oxidants present in the samples shipped for laboratory analyses so that oxidation of the contaminants would not occur during sample shipment. To a 40-ml VOA sample, 1 ml of 3% sodium thiosulfate was added. To a 1-L bottle, 5 ml of 15% sodium thiosulfate solution was added.
- d Metals = arsenic, barium, calcium, chromium, cobalt, iron, magnesium, manganese, nickel, potassium, sodium, and zinc.

## **Sample Transportation--**

After all samples were collected for each test run, the field team prepared a sample custody form. The ice chests containing samples and the sample custody sheets were transported to the laboratory and transferred to designated laboratory personnel. Sample transportation protocol is described in detail in the sample handling and shipment subsection.

## **Field Measurements**

Field analysis to evaluate the Ultrox treatment system required collecting water samples from the Ultrox unit. Samples were collected only after a steady state condition (three hydraulic retention times) had been reached. Sample collection time was coordinated directly between the field analyst and the field sampler to allow for rapid and efficient analysis of field samples. Water samples were collected in appropriate glass containers, labeled, and delivered to the on-site trailer for field analysis (Table 4-10). Table 4-10 also indicates the type of collection vessel and the critical holding times for water samples collected for each of the field measurement parameters.

## **Sampling Quality Assurance Procedures**

This subsection discusses the quality assurance (QA) procedures implemented to ensure that all sampling activities during the demonstration were carried out as much as possible in accordance with the Demonstration Quality Assurance Project Plan (QAPP). These QA procedures were developed in accordance with HWERL guidance (U.S. EPA, 1987) and SW-846 criteria (U.S. EPA, 1986). They include sample containerization, preservation, handling, and shipment requirements. Each of these QA steps decreases the likelihood of sampling and handling error and increases the certainty that reliable and reproducible quality data will be obtained from each sample.

## **Sample Containerization and Preservation--**

Tables 4-9 and 4-10 present the container and preservation requirements for each parameter which was analyzed. The containers listed are those which are either specified or recommended by each of the analytical methods used. The containers when shipped were grouped by the analytical method to be performed in the field, and each group was accompanied by the appropriately completed labels. All bottles were packed in their original shipping containers for transport to the field.

**TABLE 4-10**  
**SAMPLE CONTAINERIZATION AND HOLDING TIMES**  
**FOR ON-SITE ANALYSES**

Parameters	Collection Vessel	Holding Time
Water Temperature	1 L beaker	immediate analysis
pH	1 L beaker	immediate analysis
Conductivity	1 L bottle	immediate analysis
Turbidity	500 ml beaker	immediate analysis
Ozone*	100 ml glass bottle	immediate analysis
Alkalinity*	250 ml glass bottle	immediate analysis**
Hydrogen Peroxide*	40 ml glass bottle	immediate analysis

**Notes:**

- \* Clean glass collection bottles of different volume were also used depending on availability.
- \*\* Alkalinity samples collected from the influent sampling point were analyzed as soon as practicable.

All samples requiring field analysis were analyzed in an on-site laboratory, immediately after sample collection or as soon as practicable. The parameters which were designated for field analysis required no preservatives. Generally, all effluent measurements or samples were prepared and analyzed immediately after collection. The effluent and midpoint samples had more stringent holding times due to the oxidation rate of the constituents being analyzed. Influent samples were prepared and analyzed prior to the end of the day. They were kept cool and out of direct light until each analysis was complete and confirmed.

Containers for samples which required preservation upon collection were provided to the field team with the appropriate preservatives already included. The QAPP states that the "preservatives will be added to the samples as soon as possible after they are collected." The project team opted to have the bottles arrive on-site with the preservative already included to reduce the field team's responsibilities and to save time during sampling. Even with this step eliminated, the field team was required to collect water samples for VOC analysis every 15 minutes for the duration of the test run. The field team, therefore, was required to collect approximately 18 samples per sample location, every 15 minutes.

All containers were checked by the laboratory scheduling coordinator prior to shipment to the field to ensure that proper preparation, labeling, and packaging had been carried out. During laboratory preparation of samples for analyses, it was determined that some of the samples intended for TOC analysis were not properly acidified or preserved in the field. However, these samples were acidified or preserved in the laboratory prior to analysis. Thus, the quality of the data obtained from the analysis was ensured.

#### **Sample Handling and Shipment--**

Samples were retained at all time in the field sampling team's custody. The field sample custodians were responsible for ensuring that all samples were properly labeled and packed into iced coolers.

During each test run, a standard chain-of-custody form was maintained for each sample as it was collected. Each sample was recorded on the chain-of-custody form as it was packed. The procedures outlined in the QAPP were followed when filling out the chain-of-custody forms. When all line items were completed and all samples were properly packed in the shipping container, the chain-of-custody form was signed, dated (including time), and confirmed to be completed. The completed chain-of-custody form was put in a file folder and carried by the sample custodian with the sample shipment to the laboratory.

When the samples changed hands during transportation and when they were turned over to the laboratory, the field custodian (or designate) signed and dated the form, listed the time, and confirmed completeness of all descriptive information contained on the form. When the sample custodian was unable to transport the samples to the laboratory, each individual who subsequently assumed responsibility for the samples signed the chain-of-custody form and recorded the reason for assuming custody. The field chain-of-custody form terminated when the laboratory received the samples. A copy was returned with the completed analytical data and the field sample custodian (or designate) obtained a copy of the chain-of-custody form for program files.

The Demonstration Plan states that samples intended for laboratory analysis were to be transported by courier to the laboratory at the end of each test run. A courier service, however, was not employed during the demonstration period. The sampling team was responsible for transporting the samples to the laboratory during the entire demonstration. The samples were within the sampling team's custody until they reached the laboratory, where the laboratory assumed custody.

The sample bottles were packed in their original shipping containers. The packaging of inorganic and organic samples together from a single sampling location, however, was not feasible since the sample bottles used were not the same size. To compensate for this, the individual shipping boxes were sectioned off to designate the sample locations. In some cases (primarily Runs 12 and 13), there was not enough space within the shipping boxes for all the samples collected. The extra samples were put in plastic bags and transported to the laboratory in a separate compartment of the shipping cooler. Duplicate samples were also packed in designated (by sampling location) sections within the shipping boxes; they were not put in separate shipping containers.

Custody seals were not applied to the individual sample containers since the samples did not at any time leave the custody of the field sampling team. Custody seals were only applied to the filled, ready-to-transport ice chests and no tracking report was necessary since the chain-of-custody forms were kept for each test run and accompanied the samples to the laboratory. Also, this method of transportation required no DOT markings on the shipping containers.

Separate shipping containers were used when two test runs were conducted on the same day. On those days, samples were shipped immediately after the run was completed. This was especially important since the designated 24-hour sample turnaround was required for both runs, despite the extra work load on the laboratory.

## **ANALYTICAL PROCEDURES**

### **Analytical Methods**

In selecting analytical methods for samples from the Ultrox treatment system, the SITE team considered the specific analytes of interest, the sample matrix, and the minimum detectable concentrations needed for the project. When more than one EPA or other approved method was available and appropriate, the one most consistent with the project objectives was selected.

Table 4-11 summarizes the methods used for analyzing the samples collected during the Ultrox technology demonstration. Most of the parameters were analyzed using EPA-approved methods, Standard Methods for the Examination of Water and Wastewater, or NIOSH Sampling and Analytical Methods. Exceptions included ozone and hydrogen peroxide in the aqueous samples. Also, the NIOSH methods were modified to meet the project needs, as described in previously. Specific non-standard analyses are discussed below.

#### **Ozone--**

Field analysis was necessary for ozone in the effluent due to its reactivity. Ozone in the effluent was analyzed by the Indigo Method (Bader and Hoigne, 1982). In this method, indigo trisulfonate is added to the water sample. Ozone, if present in water, rapidly and stoichiometrically decolorizes the added indigo trisulfonate in acidic solution. The increase in concentration of ozone is linear with the decrease in absorbance.

Ozone concentration was measured using a spectrophotometer. An aliquot of effluent water and distilled water were delivered into two volumetric flasks and a colored reagent was added to each. The spectrophotometer was "zeroed" using a blank which was prepared with distilled water. The sample was then read against this "blank" baseline. A negative absorbance reading indicated that ozone was present in the sample. The absolute value of this negative absorbance reading was then substituted into a formula available in the method to calculate the final concentration in mg/L.

#### **Hydrogen Peroxide--**

Field analysis was necessary for hydrogen peroxide in water due to its highly reactive nature. For the determination of hydrogen peroxide in water, the titanium method was selected (Boltz et al., 1979). The reaction of hydrogen peroxide with titanium (IV) in acid solution produces a yellow peroxytitanic acid. The yellow color of peroxytitanic acid forms immediately

**TABLE 4-11**  
**ANALYTICAL METHODS**  
(Sheet 1 of 3)

Analyte <sup>a</sup>	Matrix <sup>b</sup>	Method Type <sup>c</sup>	Method Reference	Title
Alkalinity	L	F	MCAWW 310.1 <sup>d</sup>	Alkalinity
Arsenic	L	Lab	SW-846 7060 <sup>e</sup>	Arsenic by Furnace Technique
BNA (Semivolatiles)	L	Lab.	SW-846 8270 <sup>e</sup>	GC/MS for Semivolatile Organics
Chromium (Cr <sup>6+</sup> )	L	Lab.	SW-846 7195 <sup>e</sup>	Hexavalent Chromium by AAS
Chloride	L	Lab.	SM 429 <sup>g</sup>	Ion Chromatography
Chromium	L	Lab.	SW-846 7191 <sup>e</sup>	Chromium by Furnace Technique
Conductivity	L	F	Manual <sup>k</sup>	Conductivity
Hydrogen Peroxide	L	F	Boltz et al. (1979) <sup>f</sup>	Titanium Method
Metals (Barium, Cobalt, Iron, Manganese, Nickel, Zinc, Potassium, Calcium, Magnesium, and Sodium)	L	Lab.	SW-846 6010 <sup>e</sup>	Metals by ICP
Ozone	L	F	Bader and Hoigne(1982) <sup>h</sup>	Ozone by Indigo Method
Ozone	A	F	40 CFR Part 50 <sup>i</sup>	Ultraviolet Photometric Procedure
pH	L	F	Manual <sup>k</sup>	pH

**TABLE 4-11**  
**ANALYTICAL METHODS**  
(Sheet 2 of 3)

Analyte <sup>a</sup>	Matrix <sup>b</sup>	Method Type <sup>c</sup>	Method Reference	Title
Pesticides/PCBs	L	Lab.	SW-846 8080 <sup>e</sup>	Organochlorine Pesticides & PCBs
Silica	L	Lab.	SW-846 6010 <sup>e</sup>	Metals by ICP
Sulfate	L	Lab.	SM 429 <sup>s</sup>	Ion Chromatography
Temperature	L	F	Manual <sup>k</sup>	Temperature
Total Organic Carbon	L	Lab.	SM 505A <sup>s</sup>	Carbon Oxidation and IR Detection
Turbidity	L	F	Manual <sup>k</sup>	Turbidity
Volatile Organics	L	Lab.	SW-846 8010 and 8020 <sup>e</sup>	GC for Volatile Organics
Volatile Organics	L	Lab.	SW-846 8240 <sup>e</sup>	GC/MS for Volatile Organics
Volatile Organics:				NIOSH Methods for VOCs in Air
Vinyl Chloride	A	Lab.	NIOSH 1007 <sup>j</sup>	
1,1-Dichloroethene	A	Lab.	NIOSH 1015 <sup>j</sup>	
1,1-Dichloroethane	A	Lab.	NIOSH 1003 <sup>j</sup>	
1,2-Dichloroethene	A	Lab.	NIOSH 1003 <sup>j</sup>	
1,1,1-Trichloroethane	A	Lab.	NIOSH 1003 <sup>j</sup>	
Trichloroethylene	A	Lab.	NIOSH 1022 <sup>j</sup>	
Benzene	A	Lab.	NIOSH 1500 <sup>j</sup>	
1,1,2,2-Tetrachloroethane	A	Lab.	NIOSH 1019 <sup>j</sup>	
Acetone	A	Lab.	NIOSH 1300 <sup>j</sup>	



**TABLE 4-11**  
**ANALYTICAL METHODS**  
(Sheet 3 of 3)

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Notes:

- <sup>a</sup>    BNA    =    Base, neutral, and acid extractable semivolatile organics  
      PCB    =    Polychlorinated biphenyls
  - <sup>b</sup>    L        =    Liquid  
      A        =    Air
  - <sup>c</sup>    F        =    Field Method  
      Lab.    =    Laboratory Method
  - <sup>d</sup>    Methods for the Chemical Analysis of Water and Wastes, EPA-600/4-79-020, revised March 1983, Environmental Monitoring and Support Laboratory, Cincinnati, OH, U.S. EPA, 1983, and subsequent EPA-600/4 Technical Additions thereto.
  - <sup>e</sup>    Test Methods for Evaluating Solid Waste, Volumes 1A-1C: Laboratory Manual, Physical/Chemical Methods; and Volume II: Field Manual, Physical/Chemical Methods, SW-846, Third Edition, Office of Solid Waste, U.S. EPA, Document Control No. 995-001-00000-1, 1986.
  - <sup>f</sup>    Boltz, D.F., and J.A. Howell, Hydrogen Peroxide, Colorimetric Determination of Nonmetals, John Wiley & Sons, 1979, 301-303.
  - <sup>g</sup>    Standard Methods for the Examination of Water and Wastewater, Sixteenth Edition, APHA, AWWA, and WPCF, 1985.
  - <sup>h</sup>    Bader, H., and J. Hoigne, Determination of Ozone in Water by Indigo Method, Ozone Science and Engineering, 4:169, 1982.
  - <sup>i</sup>    The National Primary and Secondary Ambient Air Quality Standards, 40 CFR Part 50, Appendix D -- Measurement of Ozone in the Atmosphere.
  - <sup>j</sup>    NIOSH, Manual of Analytical Methods, Third Edition, U.S. Department of Health and Human Resources, DHHS (NIOSH) Publication No. 84-100, 1984.
  - <sup>k</sup>    Operating instructions provided with the instruments.
-

upon the addition of the titanium in acid solution. Hydrogen peroxide concentration is then determined spectrophotometrically.

A standard curve was prepared daily using a fresh solution of hydrogen peroxide of known concentration to prepare dilutions of three known concentrations. The samples were prepared in the same manner as the standards, noting any dilutions which may have been necessary to allow for reading absorbance within the range available from the standards. Color was developed in the standards and samples using reagents. Standards and samples were then analyzed spectrophotometrically. Each spectrophotometer reading was preceded by "zeroing" the instrument using a blank prepared in the same fashion as the standards without addition of hydrogen peroxide. The amount of hydrogen peroxide in the sample was calculated by reading the concentration from the standard curve which corresponded to the absorbance of the sample as read from the spectrophotometer.

#### **Air Sampling Modifications--**

The NIOSH analytical method was modified by using a capillary column for all analysis in lieu of the packed columns specified in the method. This allowed several compounds to be analyzed from one sample tube. Charcoal tube desorption efficiencies were determined in accordance with the NIOSH methods. Larger charcoal tubes (400/200) than specified in the NIOSH method (100/50) were used for the collection of 1,1-dichloroethane and 1,1,1-trichloroethane to minimize potential breakthrough.

#### **Field Water Sampling Modifications--**

Due to problems encountered in the field when instruments did not function properly or as expected, the following parameters were analyzed by the direct reading instrumentation specified below, using the instructions which came with the instruments rather than the method specified in the Demonstration Plan:

<u>Parameter</u>	<u>Instrument</u>
Conductivity	YSI Conductivity Meter
Turbidity	Hach Turbidity Meter
Water Temperature	Centigrade Mercury Thermometer, graded increments of 1 degree Celsius
Water pH	Orion combination pH/temperature meter

Additional process measurements for the sulfuric acid and hydrogen peroxide feed tank concentrations were also performed during the demonstration. The sulfuric acid feed tank concentration was measured at the beginning of Runs 2 and 3 when acid was added to the influent. The concentration of sulfuric acid in the feed tank was calculated by titrating an aliquot of the acid against a solution of sodium hydroxide of known concentration to a phenolphthalein endpoint. Although this is a standard test method, no method for determining sulfuric acid feed concentration was specified in the QAPP.

The hydrogen peroxide feed tank concentration was measured using a spectrophotometer. A standard curve using three concentrations was prepared daily using a fresh solution of hydrogen peroxide of known concentration. The feed sample was prepared in the same manner as the standards, noting the dilution factor which was necessary to allow for reading of absorbance within the range available from the standards. Color was developed in the standards and samples using reagents.

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

The laboratory data reduction, validation, and reporting procedures used in this technology demonstration are described in Section 3.6 of the Demonstration Plan. Equations presented in the Demonstration Plan for calculating compound or parameter concentrations were followed. However, for metal analytes, a closer control limit of 75 to 125 percent was used instead of the proposed 75 to 150 percent control limit. Data validation and reporting procedures for QA data did not deviate from those proposed in the Demonstration Plan.

#### **Internal Quality Control Checks**

Internal quality control (QC) checks of routine internal procedures were performed to ensure that the data output of a measurement system meets prescribed criteria for data quality. Section 3.7 of the Demonstration Plan details the internal QC check procedures followed for the demonstration. Internal QC control measures included method blanks, duplicate and matrix spike samples, standards, surrogates, and field blanks.

#### **Analytical Quality Assurance**

Analytical quality assurance (QA) is the process of ensuring and confirming the accuracy of the work product. This process includes the establishment of data quality objectives for the project. Development of a sampling plan, selection of analysis methods and associated QC

measurements, and establishment of the criteria to determine the degree of attainment of these objectives are critical elements in the QAPP.

#### **Quality Assurance Objectives--**

The primary analytical QA objective for this demonstration plan was to produce documented data of known quality. To measure the quality of the data obtained, several controls were implemented throughout the analysis process. The QC components employed to determine the fulfillment of this objective were the analytical accuracy, analytical precision, representativeness, and completeness of the results obtained from the analytical methods used in relation to the ultimate use of the analytical data. Detection limit validation and confirmation for the analytical methods and the instrumentation used for this project were also elements of this determination. The fulfillment of this objective was evaluated upon the basis of obtaining analytical results which could be used with confidence in the performance evaluation of the system.

#### **Quality Assurance Procedures--**

Chemical analyses performed in support of this project were conducted in accordance with the QC procedures described in the QAPP section of the Demonstration Plan. These procedures were used to assess the precision, accuracy, completeness, representativeness, and comparability of the analytical data. The results obtained for the analyses of QC samples were reviewed by the laboratory QC coordinator and the Project QA Manager. These QC data were compared to the acceptance limits established for the project to determine the quality of the results.

The precision of analyses of aqueous samples was measured by the analyses of a matrix spike (MS) and a matrix spike duplicate (MSD) for all tests for which this procedure was applicable. Charcoal tubes used for the collection of off-gas from the reactor and the Decompozon unit were not amenable to spike addition. Thus the analyses of duplicate spiked blank tubes from the same source and lot were used to obtain precision data for this test parameter.

The accuracy of the analytical results was evaluated upon the basis of percentage recovery of MS and MSD analyses. Surrogate compounds were used to further assess the accuracy of analyses performed by gas chromatography and gas chromatography/mass spectrometry.

The acceptance criteria for each QC measurement was used to determine the quality of the analysis results obtained for samples analyzed within a sample set. These criteria were based upon EPA-recommended limits for the specific method or laboratory analysis control charts in lieu of published values.

Trip blanks and laboratory prepared blanks were analyzed to provide data regarding potential contamination of samples during collection, transport, storage, and analysis. Spiked blanks (laboratory control samples) were analyzed to determine if the analytical system was operating correctly during the analyses of samples.

The QC data obtained was first evaluated upon the established acceptance criteria for the measurement. If a problem was indicated, corrective actions were taken in accordance with standard procedures for the test. These included checking all calculations and analyses of laboratory control samples, recalibrating equipment, and reanalyzing the sample if sufficient quantities were available.

If the acquisition of analysis results with supporting QC data was not feasible due to sample quantity limitations or other potential problems encountered, the effect of the bias indicated by the QC results upon the analytical results was evaluated with respect to the ultimate use of the data. Data qualifiers were used to flag values for which QC problems were associated. Narrative summaries of these problems, corrective action taken, and potential impact upon the data usability were prepared for each sample set.

The analysis reports were reviewed by the Project QA Manager for completeness, accuracy, and conformance with the project objectives. Problems identified were discussed with the Project Manager and the Laboratory Manager. Corrective action required to provide accurate analysis and QC results was taken to minimize errors in reporting and to provide complete summaries of the results obtained.

#### **Analysis of Quality Assurance Review**

This subsection presents a detailed analysis of the QA data obtained during the field demonstration. QA validation was emphasized for the analyses of water samples for volatile organics, since VOCs were identified as the critical parameter for this project. Data was also collected for other non-critical parameters to provide a comprehensive evaluation of the proposed technology.

## Quality Assurance Review For Critical Parameters--

### Precision

The QAPP specifies that precision is to be evaluated for a set of samples of similar matrix by the analyses and comparison of MS and MSD samples. The relative percentage difference (RPD) of the values obtained for the MS and MSD samples are calculated using the following equation:

$$\% \text{ RPD} = \frac{(\text{MS} - \text{MSD})}{(\text{MS} + \text{MSD})/2} \times 100$$

All values of RPD obtained for the water samples collected and analyzed for volatile halogenated organics and volatile aromatic organics were within the QC acceptance limits.

### Accuracy

The accuracy of the analytical results is evaluated upon the basis of the percent recovery of matrix spike compounds in MS and MSD samples, with a minimum of one sample per 20 samples of similar matrix. The acceptance range for the percent recovery for each matrix spiking compound is presented in the QAPP. The recovery of spiking compounds is an indication of the effect of the sample matrix upon the accuracy of the analysis results. The percent recovery (PR) is calculated by:

$$\text{Percent Recovery, PR} = \frac{(\text{MS or MSD}) - \text{SR}}{\text{SA}} \times 100$$

where:           SR = sample result  
                    SA = spike added

If the results of analyses of the MS or MSD samples are not within the QC acceptance range for PR, a blank spike is analyzed to determine if the problem is matrix-related or if the analytical system is not in control. If the problem is found to be matrix-related, the data is qualified by the use of a flag. If the problem is due to the analytical system, the problem is identified and the affected samples reanalyzed if additional amounts remain.

A surrogate compound is added to each sample to obtain further information about the performance of the analytical system. If the surrogate PR is outside the control limits, the sample is reanalyzed. If the results of the reanalysis do not provide data within the acceptance range, the problem is related to the sample and the result is qualified.

One sample, LBD-1-I-MS (Laboratory Sample No. 89020241) had a PR of 52 percent for trichloroethylene (TCE) in the MS sample which was outside the acceptance range (65 percent to 131 percent). The PR obtained for the MSD sample and the blank spike analyzed with this QC sample provided results within the acceptance limits. The concentration of TCE in the unspiked sample was approximately twice the spiking concentration. Thus, the low spike recovery was considered to be due to the relative concentrations of the compound in the sample and spiked sample. A small absolute error in determining the concentration of the spiked sample could yield a large percent error in the calculation of the PR. The blank spike results showed the system was in control, and further corrective action was not necessary.

The PR for the volatile aromatic compounds surrogate,  $\alpha$ - $\alpha$ - $\alpha$ -trifluorotoluene, in sample LBD-2-M-1 (Laboratory Sample No. 89020269) was slightly higher (155 percent) than the upper limit of the acceptance range (50 percent to 150 percent). Inspection of the chromatogram showed the presence of chromatographic interferences which had a positive bias upon the detector response. The analytical results obtained for this sample were compared to those obtained for samples collected from the same location during the same test run. No significant difference in the concentrations of the volatile aromatics were found. Thus, the problem was determined to be due to an interference in the determination of the surrogate concentration, and no further corrective action was needed.

The results obtained for the PR of matrix spiking compounds and surrogate compounds, with the exception of the instances discussed in the previous paragraphs, were within the QC acceptance limits for determining VOCs in water as presented in the QAPP.

### Holding Times

All analyses for VOCs in water were completed within the holding times specified in the QAPP.

### **Detection Limits**

The detection limit for organic compounds, determined by gas chromatography in accordance with the procedures of a specific method, is the method detection limits (MDL). This is the smallest concentration of analyte that is distinguishable from background by the instrument used for the analysis. The MDL values presented in the QAPP are based upon the values listed in EPA Methods 8010 and 8020. The actual values obtainable are dependent upon the specific instrument used for the analysis and the conditions under which the analysis is performed.

Upon the recommendation of the EPA audit team, an MDL study was performed during the time period in which this project was in progress. The MDL values obtained in this study are reported in the data packages prepared for this project as the laboratory's obtainable detection limits. Some of the values obtained from this study are higher than the values listed in the QAPP. However, the values obtained were less than the practical quantitation limits (PQL). The actual limits of accurate quantitation of target analytes in an environmental sample are dependent upon the sample matrix. The relative analytical error in determining the concentrations of analytes at or near the MDL do not adversely affect the attainment of data quality objectives for this demonstration project.

### **Completeness**

All water samples submitted for volatile organics analyses by EPA Methods 8010 (volatile halogenated organics) and 8020 (volatile aromatic organics) were analyzed within the holding times for the methods.

One matrix spiking compound (TCE) had a PR less than the lower limit of the acceptable range. Review of the data indicated the relative concentration of the spike to the concentration of the analyte in the sample was the most probable cause of the problem. Thus, the integrity of the data was based on both the accurate analysis of the blank spike associated with the sample group and the surrogate recoveries obtained for each sample in the group.

The volatile aromatic hydrocarbon surrogate recovery for one sample was slightly above the upper limit of the acceptable range. Examination of the chromatogram showed the coelutration of interfering substances, which gave a positive bias to the quantitation of the surrogate. All other QC data associated with the sample group was acceptable. Thus, the quantitation of the target analytes in this sample are usable for the intended purpose of the analysis.



All data required for the evaluation of the items identified in the Demonstration Plan as critical parameters were obtained.

#### **Quality Assurance Review For Non-Critical Parameters--**

Non-critical parameters are identified in the Demonstration Plan to provide further information for evaluation of the Ultrox process for destruction of organic compounds. Water samples were collected during the last two test runs for analyses for VOCs by GC and GC/MS, semivolatile organics by GC/MS, and pesticides and aroclors by GC. In addition, analyses were performed to determine the concentrations of selected metals, total organic carbon, and inorganic anions. The QC results obtained for these analyses are summarized below.

##### **Accuracy**

GC/MS (EPA Method 8270) was used to analyze semivolatile organics in samples collected during Run 0, the equipment blank, and the last two test runs. The MS sample was found to contain one of six base/neutral spiking compounds at a concentration less than the acceptable range. The MSD sample had low recoveries for four of these compounds. All acid matrix spiking compounds had recoveries within the acceptance range. A blank spike was analyzed to check for potential interference due to the matrix of the sample.

Four of the six base/neutral matrix-spiked compounds were found to have low recoveries. The most probable cause for this problem is loss of the MS compounds during the concentration of the sample extract. The concentration of the spiking solution was checked to determine if all compounds were present in the appropriate amounts. The results showed the concentration of the four base/neutral compounds in question were low by factors ranging from 70 to 92 percent. The spiking solution was replaced, but insufficient sample was available for reanalysis. Correction of the PR calculation for the low concentration improves the PR values, although the potential for loss during concentration is still the major factor for the low recoveries.

The PR of the surrogate spiking compounds was reviewed to obtain further information regarding potential loss during concentration. Only the sample used for the MS/MSD analyses had surrogates outside the acceptable range. The surrogates for all other samples in the group had recoveries within acceptable ranges.

The acid surrogates for sample O-I (R)-A (Laboratory Sample No. 89020209) were all reported as zero. The MS and MSD samples prepared from these surrogates had acceptable recoveries for both the acid surrogates and the acid matrix spiking compounds. The most

probable cause for loss of the acid surrogates in the sample is error in pH adjustment prior to extraction of the acid phase of the sample.

The analyses of the equipment blank samples showed the presence of only phthalate compounds. These are common contaminants often found in blanks. Thus, for semivolatile organic compounds, the results of the equipment blank samples do not adversely affect the use of the sample results obtained during the test runs.

Samples collected during the last two test runs were analyzed for semivolatile organics by GC/MS Method 8270. The MSD samples collected during Run 12 had a slightly higher recovery for nitrotoluene (101 percent vs. an upper limit of 96 percent). This would indicate a potential for positive bias in the analyses, but compounds of similar characteristics were not found in the samples. Thus, the results of the test are unaffected.

All surrogate recoveries were within the acceptable range with one exception. This sample was reextracted and reanalyzed. The surrogate recoveries for the reanalyses were acceptable and the results of the reanalyses were reported.

The matrix spiking compounds in the pesticide analyses, Method 8080, were found to be lower than the acceptance range for the MS of sample LBD-13-E-5 (Laboratory Sample No. 89030734). The spiking compounds in the MSD of this sample, blank spike, and the MS/MSD for sample LBD-14-I-4 were all in the acceptable range but near the high end. The overall tendency indicated is a positive bias in the analyses for pesticides. Pesticides, however, were not found in the samples. The low recoveries in the one MS sample appear to be an abnormality which was not repeated in any of the other analyses for these compounds.

The equipment blank samples analyzed for pesticides had MS/MSD recoveries which were within the acceptable range of high (positive bias) with the exception of the MS concentration of endrin. The concentration of this compound was acceptable in the MSD and blank spike, indicating an irregularity in the analysis for this compound in the MS. Pesticides were not found in the equipment blank samples.

The PRs for MS/MSD and surrogate spiking compounds used for other analyses performed for water samples were found to be acceptable.

The potential for stripping volatile organics from the water was investigated. Air emissions from the system were collected in charcoal tubes and monitored. GC analyses by NIOSH-approved methods were used to determine the quantity of target analytes collected during

the test run. Results for these analyses were reported in absolute mass of analyte detected ( $\mu\text{g}$ ) vs. concentration of the extract from the tube to facilitate the calculation of concentration of the compounds present in the volume of air passing through the charcoal tube ( $\mu\text{g}/\text{L}$  of air).

The accuracy of analyses for volatile organics adsorbed on the charcoal traps was evaluated by the analyses of MS and MSD blank tubes from the same lot used for the collection of the samples. The PRs were evaluated upon the basis of analysis control charts. The PR for all MS and MSD analyses were found to be within the control limits of  $\pm$  thrice the standard deviation from the mean. This method of evaluation was used in lieu of published acceptance criteria for the NIOSH methods used for these analyses.

In addition, there were PRs out of the control limits for some inorganic analyses. Interferences exist in the use of Method 7195 for the quantification of hexavalent chromium and in the silicon analyses (Method 6010).

Laboratory Sample Nos. 89030730 and 89030757 were prepared and analyzed for hexavalent chromium following Method 7195 (SW-846, 1986). The results indicated extreme interference in the sample/preparation matrix. Sample dilution resulted in the increase in the reporting limit (QC samples were not diluted). To further validate the results, the samples were prepared for total chromium analysis by Method 3020 and analyzed by Method 7191 (SW-846, 1986). Values achieved by this method were below the PQL of  $10 \mu\text{g}/\text{L}$  but above the MDL of  $5 \mu\text{g}/\text{L}$  with matrix interferences requiring the method of standard additions.

Silicon analysis results were subject to interferences due to sample matrix and sample preparation. Interferences were randomly encountered and could not be determined accurately.

### **Precision**

The precision of the analyses is evaluated upon the basis of relative percent difference (RPD) of the results obtained for the analyses of the MS and MSD samples. The RPD values which exceeded the control limits are associated with the MS/MSD problems discussed above. Thus, the same corrective actions and conclusions discussed above are applicable to the evaluation of precision of the QC analyses.

The precision of analyses for volatiles adsorbed on the charcoal traps used for the collection of air samples was evaluated by the relative percent difference of the MS and MSD of blank tubes. The maximum allowable RPD for each compound was determined by calculation of the mean and standard deviation of the MS and MSD analyses performed during this project. A

control limit of thrice the standard deviation from the mean was used. All RPD values obtained were within the acceptance limit.

### **Holding Times**

All water samples were analyzed within the holding times specified in the methods, with two exceptions. Samples extracted for semivolatile analyses for Runs 12 and 13 were extracted 12 to 18 hours past the holding time limit. This delay in sample preparation should not have an adverse effect upon the results.

The analyses for total organic carbon in 14 water samples were repeated due to rejection of the QC results for the initial analyses. The reanalyses exceeded the holding time for the samples. Similar results of the reanalyses of these samples and of those samples completed within the specified holding times were obtained. Thus, the problems encountered should not adversely affect the results of the demonstration.

Fifteen air samples collected on charcoal tubes were analyzed for vinyl chloride outside the 7-day holding time specified in the QAPP. NIOSH Method 1007, used for this analysis, contains stability information indicating the compound is stable on a charcoal tube for 10 days at ambient temperature and  $\leq 19$  days when stored at -20 degrees Celsius. NIOSH Method 1015 provides stability information for 1,1-dichloroethene of 7 days at ambient temperature and 21 days at five degrees Celsius. NIOSH Method 1500 indicates the stability of hydrocarbons is 14 days. The charcoal tubes used for collection of samples during this project were stored at 4 degrees Celsius. Based on this information, the data obtained for the analyses of volatile organics by NIOSH methods do not compromise their validity, although they were not entirely obtained within the 7-day holding time specified in the QAPP.

### **Detection Limits**

A discussion of detection limits is found above regarding the critical parameters.

### **Completeness**

A total of 182 charcoal tubes were submitted to the laboratory for VOC analysis. The samples were collected on charcoal tubes (size 100/50 and 400/200) and included designated QC samples. These QC samples were breakthrough tubes and field and trip blanks. The QAPP specifies that one field blank should accompany each test run and one trip blank should accompany every sample shipment.

All samples were analyzed using NIOSH methods for VOCs. The NIOSH methods specify that for all volatile constituents covered by the methods used, except Method 1007-Vinyl Chloride, the front half of all sample tubes must be analyzed. The back half of the tube is analyzed when the results obtained from the analysis of the front half are out of the control limits. For QC purposes, back halves of 10 percent of the tubes are to be analyzed for breakthrough. Therefore, the 50 part of the 100/50 size tubes and the 200 part of the 400/200 size tubes were analyzed for breakthrough.

Method 1007-Vinyl Chloride specifies that a whole 100/50 size tube be analyzed for vinyl chloride and that another 100/50 size tube be analyzed for breakthrough. The field sampling team designated the sample tubes by adding "ST" onto the end of the sample I.D. and the breakthrough tubes were designated by adding "BT" onto the end of the sample I.D.

The QC results indicate that one field blank was analyzed for every run and that one trip blank was analyzed for every sample shipment. Therefore, 14 field blanks and 12 trip blanks were analyzed and the results reported. There were 13 back halves and 11 whole tubes analyzed for breakthrough, corresponding to 11 percent of the total number of samples submitted. Thus, QC requirements were fulfilled.

All of the samples submitted for analysis were analyzed with the exception of Laboratory Sample No. 89030299. The extract from Laboratory Sample No. 89030299 was spilled during preparation. Therefore, analysis was not performed.

Only a few sample results are considered questionable, as follows. All sample contents of Laboratory Sample No. 89030292 were extracted due to the high moisture collected during sampling. Moisture deactivates the carbon and, thus, could be responsible for no results, except for acetone, being obtained. It is likely that acetone was contained in the Ultrox system during sampling and was carried by the water to the charcoal. The sample extract of Laboratory Sample No. 89030290 evaporated before the second column confirmation could be accomplished.

The previous subsection regarding accuracy discusses four samples (Laboratory Sample Nos. 89020209-89020212) analyzed by Method 8270 (GC/MS) which were found to have low recoveries of four base/neutral matrix spiking compounds. The cause of the problem was hypothesized as due to the loss of the MS compounds during the concentration of the sample extract. If this hypothesis is correct, the data associated with these samples is questionable.

The previous subsection also discusses the low recovery of the matrix spiking compounds in the analysis of Laboratory Sample No. 89030734 using Method 8080. The objective of this analysis was to determine whether or not pesticides or PCBs were present in the samples. All results indicated that pesticides or PCBs were absent from the samples. These results meet the data quality objectives of this analysis. Therefore, the conclusion that a positive bias exists in the quantitation of the surrogate, which in turn qualifies the data obtained from the sample analyses, does not compromise the data quality. Furthermore, these results should not adversely affect the overall data quality objectives for the demonstration project.

#### **Overall Completeness of the Analytical Data--**

The QAPP defines completeness as the ratio of the number of activities that are actually finished to the number of activities initiated. For this project, the first activity was acquiring the samples, and the final activity is reporting the analytical data obtained from the laboratory analysis of these samples. The degree of completeness is calculated by the number of samples with acceptable analytical data, divided by the total number of samples collected and analyzed, and multiplied by 100 percent. The objective for the degree of completeness is 95 percent.

The subsection regarding completeness of the critical parameter (volatile organics) analysis addresses the quality of two samples. One sample (Laboratory Sample No. 89020241) was highly concentrated with TCE and the associated spiked sample was low in TCE recovery. Upon review of these results and the results obtained from the associated blank sample, the low recovery of TCE in the spiked sample was attributed to the relative concentrations of the compound in the sample and the spiked sample. The results obtained from the analysis of the blank spike showed the system to be in control, thus eliminating any question of data quality. The other sample (Laboratory Sample No. 89030269), which had a high surrogate recovery, could indicate a potential for a positive bias to the quantitation of the surrogate. Therefore, the quality of the analytical data associated with this sample is in question.

Overall, the degree of completeness for the critical parameter analysis is 99.8 percent.

As noted previously, some non-critical water and air samples were analyzed after the holding times had expired. All 31 samples which missed their holding times, except for the 14 samples analyzed for TOC, have associated data with questionable quality. In the case of the TOC samples, the original analysis of these samples was within the required holding times; however, the reanalysis was not. Since the data obtained from both analysis sets were consistent, it was determined that the holding time issue did not adversely affect the results of the sample

reanalysis. Hence, the data quality objectives of the demonstration should not be adversely affected by these results.

The previous subsection regarding the completeness of the non-critical parameter analyses addresses the quality of eight samples. Laboratory Sample No. 89030292 had qualified data due to the high moisture contained in the sample. However, this should not adversely affect the quality of the data obtained from the sample analysis. Data obtained from the analysis of Laboratory Sample No. 89030734 was determined to not be in question, especially since the sample results indicated that no pesticides or PCBs were contained in the sample. The other six samples, discussed in the completeness of the non-critical parameters subsection, have associated data of questionable quality.

Consequently, the degree of completeness for the non-critical parameter analyses is 90.8 percent. Considering critical and non-critical parameters, the overall degree of completeness for the analytical data package is 95.5 percent.

#### **Quality Assurance Review of the Field Data--**

##### **Water Samples**

In addition to the water measurements required by the QAPP, the field sampling team also collected temperature data at the influent and effluent to the chiller as well as at the chiller motor. The field sampling team also measured the ambient temperature. The water temperature data are only available for Runs 2 through 13, because it was not decided that these measurements should be taken until the second test day. The chiller motor and ambient temperatures are not presented for Run 12 as these data values were not recorded. Since this was not a water measurement required by the QAPP, the absence of this measurement should not adversely affect the data quality objectives of this demonstration project.

For Run 0, only influent flow rate data is available since this run was primarily conducted to rinse the equipment and to provide equipment blank data.

Several data are not presented for Run 1 because of their unavailability to the data reduction/field team or because of the limited time for analysis during the test run. For example, the acid feed rate and influent flow rate for the early runs are not available because they were not recorded. In addition, because of the limited time for analysis during Run 1, the following data are also not available: (1) the conductivity and alkalinity data collected at the influent after acid addition, (2) the alkalinity and hydrogen peroxide data collected at the

effluent, and (3) the influent temperature after acid addition data. The absence of these data should not adversely affect the data quality objectives of the demonstration project.

In the case of the acid feed rate, data only exists for Run 2. Because the results indicated that no significant change had occurred in the volatile organic contents of the effluent water due to the addition of the acid, acid was not added to the influent water after Run 3. The method employed to determine the acid concentration used in the feed stock to acidify the influent water was not specified in the QAPP.

The missing conductivity measurement for the influent is not of critical concern. Runs 0 through 3 had conductivity data of questionable quality due to the use of an instrument with a defective electrode. All other runs used another instrument of better quality.

The turbidity measurements made during Runs 1 through 3 are of questionable quality because an instrument which could not be calibrated properly was used. For all other runs, another turbidity meter of better quality was employed. Thus, the respective data obtained is of good quality. Also, for all turbidity measurements made during the demonstration, the analytical method specified in the QAPP was not employed because it was not feasible for field use. The quality of data obtained from the use of the field method should not adversely affect the data quality objectives of this demonstration project.

Temperature measurements were not made according to the specifications of the QAPP because the specified instrument was not available for field use. Instead, temperature measurements were made using two different methods that yielded comparable results: an Orion pH/temperature meter and a mercury thermometer. The use of these methods should not compromise the quality of the data obtained and should not adversely affect the data quality objectives of this demonstration project.

The pH meter calibration procedures specified in the QAPP were not employed during the demonstration because the method referenced was not applicable to the type of pH meter in use. Instead, calibration of the pH meter was done prior to each run according to the instrument instructions. Data obtained using these procedures are considered to be of good quality and should not adversely affect the data quality objectives of this demonstration project.

Although the QAPP specified that replicate samples be taken for acid concentration, chiller water flow rate, conductivity, turbidity, influent and effluent temperatures, pH, alkalinity, hydrogen peroxide concentration, and ozone concentration, the absence of these



parameters in duplicate should not adversely affect the data quality objectives of this demonstration project. Several of the parameters required duplicates for analysis.

Most of the electric consumption data were collected as specified in the QAPP. However, the measurements during Runs 0 through 2 require adjustments because the readings included electrical usage in the field trailer as well as the Ultrox unit.

The degree of completeness for the field water data is defined as the number of samples with acceptable data divided by the total number of samples collected and analyzed in the field, multiplied by 100 percent. The objective for the degree of completeness was not specified. The only samples obtained and analyzed in the field with questionable data quality were those taken for turbidity and conductivity measurements during Runs 1 through 3 and electricity measurements taken during Runs 0 through 2. Therefore, the degree of completeness for the field water data is 94 percent.

#### **Air Samples**

Ozone concentrations were measured at the feed, reactor off-gas, and Decompozon unit exhaust (treated off-gas) lines (including replicate samples for each location) as specified in the QAPP. VOC sampling equipment, sampling tubes, and field and trip blanks were used and collected as specified in the QAPP. Flow meter and ozone test meter calibrations were carried out according to the QAPP. Test meter leak tests were performed before and after each test run. The effluent gas temperature was also measured according to the QAPP.

During Runs 0 through 9, only one ozone generator/photometer was used to collect measurements as well as provide reference ozone concentrations. This methodology was employed only until another ozone analyzer could be obtained to collect measurements. The measurements obtained during the first ten runs were, therefore, not collected in accordance with 40 CFR 50, Appendix D, as required by the QAPP. This method specifies that a separate ozone generator/photometer be used as a reference for the ozone measurement analyzer. Since the ozone analyzer provided with the treatment system did not demonstrate acceptable linearity, the reference photometer was used until a separate analyzer could be obtained. Subsequent to testing, the generator/photometer was checked against the Virginia State Air Pollution Control Board, NBS traceable calibration standard and was found to be within the specified linearity criterion with no adjustment. Therefore, although the measurements were not collected as specified by the QAPP, post-calibration proved their validity. Hence, data quality is not an issue.

During Runs 10 through 13, the Decompozon unit malfunctioned and exhaust ozone concentrations exceeded the calibrated range of the ozone analyzer (1 ppm). All measurements of the Decompozon unit exhaust ozone concentrations during these runs are of unknown accuracy. The sporadic odor of ozone was evident to personnel working close to the Ultrox system.

During Run 2, one of the rotameters used for VOC sampling broke. From this point until Run 6, only one rotameter was employed to collect all the flow rate data. This did not adversely affect the quality of the data collected during these runs, but it did increase the time needed to complete all the measurements required per test run.

As with the field water data, the objective for the degree of completeness for the field air data was not specified. The only air measurements made with questionable data quality were the Decompozon unit ozone measurements obtained during Runs 10 through 13 and the large charcoal tube (400/200) sample collected for analyses of 1,1-dichloroethane and 1,1,1-trichloroethane during Run 2. Therefore, the degree of completeness for the field air data is 93 percent.

## **DEVIATIONS FROM THE DEMONSTRATION PLAN**

Deviations from the Demonstration Plan occurred during the Ultrox demonstration due to unforeseen site conditions, broken equipment, or necessary procedural changes. This section summarizes deviations in sampling and analysis procedures.

### **Water Sample Related**

This subsection discusses water sample related deviations from the Demonstration Plan. The deviations concern sample collection, laboratory analysis, and field measurements.

#### **Sample Collection--**

All water samples were collected in accordance with the sample collection program as shown in Table 4-6. In addition, the following samples that were not specified in the Demonstration Plan, were collected:

Two 1L samples from the groundwater extraction wells prior to the initiation of the test runs. These samples were analyzed to provide background information regarding the presence of potentially interfering substances for ozone in water analysis.

Additional MS/MSD samples for metal analysis. Instead of collecting two pairs as specified in the Demonstration Plan, 13 pairs of MS/MSD samples were collected and, later, composited into two pairs.

After the Ultrox unit treated all liquid wastes and was decontaminated, two samples were collected from the steel storage tank in which the treated effluent was stored prior to discharge. Analysis of these samples was performed to ensure that the treated effluent met the regulatory requirement established for the discharge of wastewater.

Some of the samples designated for laboratory analysis required preservation. To ensure that preservatives were added, sample containers were provided to the field team with the appropriate preservatives already included. This was a modification from the specifications of the QAPP which stated that samples would be spiked in the field. This modification was made to reduce the field sampling team's responsibilities and to save time. For the same reason, partially completed sample labels were pasted on each sample bottle prior to shipment to the field.

Several deviations from the QAPP's specifications were implemented during the sample packaging and shipping. The packaging of all organic and inorganic samples together from a single sampling location was found to not be feasible since the sample bottles used were not the same size. Duplicate samples were packed in designated sections (by sampling location) within the shipping containers; however, they were not put in separate shipping containers, as specified in the QAPP.

Custody seals were not applied to the individual sample bottles as specified in the QAPP since the samples did not at any time leave the custody of the field sampling team. Custody seals were applied to the filled shipping containers when they were ready for transport to the laboratory. No tracking report was used since the chain-of-custody forms were kept for each test run and accompanied the samples to the laboratory. The chain-of-custody forms were hand-carried by the sampling team to laboratory along with the collected samples.

#### **Laboratory Analysis--**

Water samples collected during Runs 1 through 11 were analyzed for volatile organics by EPA Methods 8010 and 8020. These samples were initially quantitated using an internal standard, one of two options presented in the QAPP. During the on-site audit, the EPA auditor informed the laboratory of changes to the Demonstration Plan requiring the use of external standards for calibration. Consequently, the previous samples were reanalyzed and recalculated using external calibration procedures. All subsequent samples were analyzed in accordance with this quantification method.

Total organic carbon (TOC) method 505B was specified in the Demonstration Plan with the anticipation of the need for a low limit of detection (0.05 mg/L). However, the samples had a significantly higher concentration of TOC. Method 505A, with a detection limit of 2.5 mg/L, was consequently used for the analyses. All samples, except for the Run 6 effluent sample, contained organic carbon at concentrations of at least 7 times this detection limit. The TOC concentration during Run 6 was less than the detection limit. As such, the use of this alternative method did not have an effect on the results of the analyses.

#### **Field Measurements--**

A flow rate measurement was not made for Run 1. All other measurements were made in accordance with the specifications.

The initial conductivity measurements (Runs 0 through 3) were questionable due to calibration problems encountered in the field. These problems did not occur after Run 3 when a replacement conductivity meter (Markson Conductivity Meter Model 15/16) was secured. The replacement meter was calibrated according to the calibration procedures which accompanied the analytical instrument, rather than the method specified in the Analytical Method Reference SW-846 9050. Analytical duplicate measurements were made for the influent and effluent.

The turbidity meter was replaced after Run 3 due to calibration problems encountered in the field. These problems did not occur after Run 3. The replacement turbidity meter (Hach Turbidity Meter Model #16800) was calibrated using three standard turbidity solutions provided with the instrument, rather than the calibration procedures according to the Analytical Method Reference MCAWW 180.1. Single measurements, rather than duplicate measurements as specified in the Demonstration Plan, were made for the influent and effluent.

Water temperature measurements were not made using a reference NBS thermometer as specified in the Analytical Method Reference MCAWW 170.1. Water temperature data was collected using a mercury analog thermometer. Temperature readings obtained using an Orion combination pH/temperature meter, Model SA 250, were compared to the readings from the laboratory mercury thermometer. These comparisons agreed favorably. In addition, single measurements, rather than duplicate readings as specified in the Demonstration Plan, were made.

Water pH was measured using an Orion combination pH/temperature meter, Model SA 250. The Analytical Method Reference MCAWW 150.1 was not followed for pH meter calibration, because the standards specified in the reference method were not applicable to the type of pH meter(s) used in the demonstration. Replicate samples were collected from both the

influent and effluent for all runs except for Run 1, when only a single sample was collected at each location. Samples from the influent line, after acid addition, were collected for only Runs 1 through 3, since acid was not added in subsequent runs.

Most of the electric consumption data were collected as stated in the QAPP. However, the data for Runs 0 through 2 require adjustment, because a single electric meter measured consumption for both the Ultrox unit and the field trailer during these runs. Subsequently, another meter was installed to isolate the electrical consumption by the Ultrox system.

A simplified field method for hydrogen peroxide, adapted from the QAPP reference method, was used. Single samples, rather than replicates as detailed in the QAPP, were analyzed for hydrogen peroxide in water except for Runs 7 and 13, when replicate analysis was performed. Additionally, due to analytical problems, analysis was not completed for the effluent sample during Run 1.

The QAPP specified that replicate samples for alkalinity be analyzed for the following: influent, influent after acid addition, and effluent samples for all runs. For the influent and effluent, replicate samples were analyzed only for Runs 7 and 13. Alkalinity analysis for influent after acid addition was performed only during Runs 2 and 3.

A simplified field method for ozone adapted from the QAPP reference method was used. The Demonstration Plan specified that replicate samples be analyzed for ozone in the effluent for all runs. However, the replicate samples were analyzed only for Runs 7 and 13.

Sulfuric acid concentration was measured using a standard acid/base titration using phenolphthalein as an indicator. This method was not specified in the QAPP. Sulfuric acid feed stock concentrations were measured only for Runs 1 through 3, since acidification of the influent only took place during these runs.

### **Air Sample Related**

This subsection discusses air sample related deviations from the Demonstration Plan. The deviations concern sample collection, laboratory analysis, and field measurements.

#### **Sample Collection--**

During Run 2, the rotameter used for flow rate verification of the Decompozon unit outlet VOC sample system cracked. The subsequent runs through Run 6 were conducted using a

single rotameter which was shared between the two systems for pre- and post-test flow rate measurement. A replacement rotameter was received and calibrated using a spirometer prior to Run 7.

The second set of VOC samples were not collected during Run 2 due to the cracked rotameter. The EPA auditing team stated that the second set of VOC samples should not be collected due to this rotameter problem.

Also during Run 2, moisture was observed in the 400/200 sorbent tube used for collecting several of the VOC compounds. This could not be explained by any Ultrox process upset or malfunction, and was not anticipated based on preliminary relative humidity estimates. Teflon moisture traps were inserted into the sample line near the sample point of each sampling location to prevent possible condensation in the sorbent tubes which could interfere with the adsorption process. No moisture or other condensation was observed during subsequent sampling.

#### **Laboratory Analysis--**

The analytical method was modified by using a capillary column for all analyses in lieu of the packed columns specified in the method. This allowed several compounds to be analyzed from one sample tube. Charcoal tube desorption efficiencies were determined in accordance with NIOSH methods. Larger charcoal tubes (400/200) than those specified in the NIOSH method (100/50) were used to collect 1,1-dichloroethane and 1,1,1,-trichloroethane to minimize potential breakthrough. The larger quantity of charcoal required a larger volume of solvent (5 ml vs. 1 ml) for the extraction of these tubes. The analysis results were reported in units of  $\mu\text{g}/\text{tube}$  rather than  $\mu\text{g}/\text{L}$  as presented in the Demonstration Plan. This procedure was used to facilitate the conversion to  $\mu\text{g}/\text{cubic meter of air}$ . The detection limits specified for this test were achieved by GC with flame ionization detection.

Charcoal tubes from the same lot were used to prepare blank spikes. All blank spikes were prepared by laboratory personnel. The PRs of target compounds from the 100/50 tubes were within the laboratory control limits. Three blank spikes prepared for the 400/200 tubes had PRs greater than the upper control limit and one blank spike had a percent recovery that was less than the lower limit. Because reextraction and analysis of the sample tubes was not possible, the data were qualified by a flag to identify the potential bias of the analysis data.

A sample stability of one week at 25 degrees Celsius is specified for halogenated hydrocarbons in NIOSH Method 1003, 2/14/84. Revision 1 of this method (8/15/87) lists the sample stability as "not determined". The 7-day holding time specified in the Demonstration Plan was based upon the available information. Samples were collected on charcoal tubes and stored at 4 degrees Celsius. Analyses of several samples occurred after the 7-day period but less than 12 days. Storage at the lower temperature will decrease the rate of degradation of the sample constituents. Thus, the analysis values obtained for this secondary parameter are believed to be within the limits of error achievable for measurements of air volumes passing through the tube and will not adversely affect the quality of the data.

#### **Field Measurements--**

Monitoring of the reactor off-gas and Decompozon unit exhaust gas ozone concentration was to be performed using PCI ozone monitors leased for the project. A transfer standard ozone generator/photometer was used to verify the calibration of the PCI monitor used for Decompozon unit off-gas measurement. The instrument demonstrated a bias of approximately 400 percent of the transfer standard generated test atmosphere. The photometer of the transfer standard was then used to monitor the Decompozon unit exhaust gas ozone concentration until a second 4" monitor could be obtained. The first replacement instrument displayed excessive drift and a second replacement was not available until Run 11. The transfer standard calibration was checked after the demonstration against the Virginia Department of Air Pollution Control, NBS traceable standard. The transfer standard met all linearity and accuracy control limits with no adjustment or corrective action.

Process off-gas flow rate was to be measured during testing. Ultrox personnel indicated that a flow measuring device with a flow restriction of 3 to 4" water column (W.C.) would not cause any interference with process operation. When a dry gas meter imposing a pressure drop of only  $\frac{1}{2}$ " W.C., was installed, the resulting back pressure limited the ozone/air feed rate below that necessary for proper process operation.

As an alternative to the flow rate procedure specified in the QAPP, the process ozone/air feed rate rotameter was calibrated against the dry gas meter while the process was not operating and rotameter indication of flow rate was recorded.

Process off-gas humidity was to be measured using EPA Method 4 (40 CFR 60, Appendix A) as a QA check of moisture interference with VOC adsorption. The gas flow rate for six test runs (0, 1, 2, 3, 4, and 7) was below that required for achieving the minimum sample volume required by the method. Humidity sampling was not conducted during these runs. The results

for all runs for which humidity was measured were below the minimum detection level (2 percent) of that method.

## **TECHNICAL SYSTEMS REVIEWS**

During the demonstration, three technical systems reviews (TSR) were conducted to audit sampling and analytical procedures followed during the demonstration. One focused on field-related activities and the other two focused on laboratory-related activities. The field TSR was in addition to a previous Corrective Action Recommendation (CAR).

The primary concerns of the TSRs are project organization and QA management. Each TSR emphasized the responsibilities of each of the key project personnel and the necessity of maintaining clear communications. The TSRs also emphasized that all communications within the project team should be coordinated through their respective project managers, in order to ensure that all documentation would be appropriately distributed within the SITE project team. Corrective action addressing this concern was immediately implemented informally upon its recognition and formally through documentation at a later date.

CAR and TSR for various field activities resulted from the field audit conducted February 27 through March 1. Responses to these reviews were submitted on March 20 and March 27, 1989, respectively. The reviews noted critical concerns regarding the on-site water analyses for turbidity and conductivity. Both concerns addressed the quality of the standard solutions and the calibration of the instruments used. Because both instruments were defective, new instruments and new standard solutions were obtained. Corrective action was implemented on March 2, 1989, to resolve the field concerns. There were no subsequent concerns regarding data quality after these corrective procedures were implemented.

Another critical concern identified by the TSRs addressed the arithmetical error which incorrectly calculated the hydrogen peroxide concentration. The EPA auditors expressed concern whether adequate analytical training of personnel had occurred prior to commencing the field demonstration. In addition, a review of the proposed on-site analysis procedures indicated that the turbidity methods would not be feasible for the field demonstration. Consequently, another procedure was used which was included in the Data Report submitted to PRC on May 10, 1989. The new procedures were appropriate for the demonstration with the field personnel adequately trained. Corrective action for these concerns was implemented on March 3, 1989, with no further concerns regarding data validity.



The field CAR and TSR also addressed three major concerns regarding the air sampling procedures. The first concern was the use of only one ozone generator/photometer for measuring references as well as collected samples. This methodology was implemented because the original analyzer provided with the treatment system did not demonstrate acceptable linearity. The single generator/photometer was intended to be used for both the reference measurements and the sample collection measurements only until another photometer could be obtained. Corrective action was implemented on March 8, 1989, when another photometer was acquired.

The two other major concerns involved the use of ambient air for the zero point calibration of the ozone monitor. The QAPP had specified that zero grade nitrogen and an adequate number of reference standards were to be used for the ozone instrument calibration. A five-point reference calibration for the ozone monitor was instituted, as recommended by the QAPP. Corrective action was taken on February 27, 1989, prior to the first test run.

There were two TSRs performed at the laboratory. The first, a 2-day review, was conducted on March 9 and 10, 1989. A response to this review was submitted to the EPA auditor on April 6, 1989. The second TSR was performed on March 16, 1989, as a follow-up to the earlier review. A response to this review was submitted to the auditor on April 12, 1989. Both TSRs addressed major concerns involving sample log-in, custody, and preservation, as well as the analytical determination of VOCs using EPA Methods 8010 and 8020. Minor concerns included sample refrigeration, QC checks using standard analyses, document control, extractions used in the laboratory, and the NIOSH analytical procedures.

The concerns involving sample log-in and custody addressed the proper storage of volatile and non-volatile samples and the proper log-in documentation required for all samples during intra-laboratory preparation. Corrective action was implemented informally upon identification of the problem and formally on April 4, 1989, with documentation. All sample receipts and sample custody personnel received additional training to ensure proper implementation of the changed procedures. The laboratory's Standard Operating Procedures (SOP) for sample log-in documentation were amended to include notations for temperature upon sample receipt, proper preservation, physical condition of samples, physical condition of custody seals, and pH.

The major concern involving the determination of VOCs by EPA Methods 8010 and 8020 was the use of an external standard calibration. Although the Demonstration Plan did not specify that the external standard calibration was to be used exclusively, the auditor recommended that only this method of calibration be used. The auditor even recommended that for all samples in which internal standard calibration were used, reanalysis should be implemented based on the external standards. This action was taken immediately and completed by April 6. In addition,

the laboratory was asked to investigate the issue of data bias and data quality based on the use of internal standard calibration vs. external standard calibration and to also perform instrument detection limit studies. These studies were completed and the results reported to the auditor. The detection limits obtained during these studies were used as the detection limits for the analytical reports submitted for the Data Report on May 10, 1989.

Of minor concern was the issue of laboratory security. The auditor recommended that the lab personnel continually update sign-out logbooks used for intra-laboratory custody documentation for all samples. The auditor also recommended that more stringent security measures be taken to ensure that non-laboratory employees had proper authorization for entry into the laboratory area. Corrective action was taken for these concerns formally as of March 13, 1989.

The auditor identified another minor problem in that the laboratory had not analyzed a QC check standard prepared from a source separate from the calibration standards. The laboratory's QC group instituted the use of the recommended QC check standard as of March 9, 1989. Also, the auditor questioned whether it was prudent to allow the refrigerated samples to equilibrate to ambient temperature prior to analysis. The laboratory explained that allowing equilibration to ambient temperature was normal laboratory procedure, and not allowing equilibration to ambient temperature was an abnormality. Proper laboratory procedures were reemphasized to all laboratory staff to ensure that faulty procedures would not be repeated.

The auditor also expressed concerns involving extractions, the use of broken laboratory apparatus, the lack of updated extract documentation, and incorrect methods documented in the logbooks. Corrective action as recommended by the auditor was taken on March 13, 1989.

The auditor also identified two minor concerns involving the NIOSH analytical procedures for VOCs in the off-gases. The auditor recommended that the sampling tube lot number be recorded with each desorption efficiency study batch. Corrective action was implemented by making the lot numbers a part of the desorption efficiency studies documentation. The auditor also questioned the prudence of preparing vinyl chloride spiking and calibration solutions from the same stock solution. Corrective action was taken to verify that the analysis of fresh solution prepared from another source (EPA) would agree within 10 percent of the concentration of the original stock solution. This was validated on March 15, 1989.

## **HEALTH AND SAFETY CONSIDERATIONS**

A site health and safety plan (HSP) was prepared for use at the LB&D site during the Ultrox technology demonstration. This HSP consists of site and facility descriptions, hazardous and toxic materials identification, hazardous chemical evaluations, monitoring procedures, personnel responsibilities, decontamination and disposal procedures, emergency procedures, and emergency resources. Prior to initiation of the demonstration, a health and safety meeting with Ultrox staff and the SITE team members was held. For those not present during this initial meeting, health and safety procedures and requirements were discussed on an individual basis. The following subsections discuss site health and safety activities, wastewater staging, and contaminated debris disposal.

### **Health and Safety Activities**

The health hazards associated with the demonstration included exposure to groundwater contaminated primarily with VOCs. Groundwater used for the demonstration was pumped from on-site extraction wells and stored in two 7,500-gallon bladder tanks connected to the influent feed line of the Ultrox system. Although the system was entirely closed, the potential routes of exposure during the demonstration were inhalation, ingestion, and skin and eye contact from possible splashes or spills during sample collection.

During the site preparation, PRC established and set up work zones to minimize the transfer of hazardous materials and contaminated debris from potentially contaminated areas to "clean" areas. In conducting this demonstration, the contaminant reduction zone was combined with the exclusion zone. The work zone contained the Ultrox system and associated equipment, power connections, 55-gallon drums used to separately store wastewater and contaminated debris, two 7,500-gallon bladder tanks, and a 21,000-gallon steel storage tank used for effluent wastewater storage.

All personnel working in this area had, at a minimum, 40 hours of health and safety training and were under routine medical surveillance. Personnel were required to wear protective equipment appropriate for the activity being performed. Steel-toed safety boots were required in the exclusion zone. Personnel working in direct contact with contaminated groundwater wore modified Level D protective equipment, including safety shoes, latex inner gloves, nitrile or Viton outer gloves, and safety glasses.

VOCs were routinely monitored with equipment that included an HNu photoionization detector containing an 11.7 eV lamp and a Dräger hand pump used in conjunction with Dräger

tubes for benzene, chloroform, and vinyl chloride. The HNu was used to monitor the breathing zone at the influent sample collection location. The influent sample location, where the highest contaminant concentration would be expected, was monitored more closely. Daily readings taken during sample collection indicated contaminant levels at normal background levels. Due to the potential for benzene, chloroform, and vinyl chloride exposure, and because of their relatively low threshold limit values, these compounds were monitored every two days. Their presence was not indicated in the breathing zone at the influent sample location.

### **Wastewater Staging**

Wastewater was generated from sample collection activities, laboratory analyses, equipment and personnel decontamination, and effluent discharge from the Ultrox system. Several 55-gallon, open-top drums were used to store the wastewater generated during the sample collection activities, laboratory analyses, and decontamination procedures. The 55-gallon drums were placed adjacent to the Ultrox system for accessibility. Additional drums held the groundwater produced during well development which was collected prior to filling the bladder tanks. Following the test runs, the wastewater contained in the 55-gallon drums was pumped to the Ultrox system, treated, and discharged to the 21,000-gallon steel storage tank. All effluent was temporarily stored in the steel storage tank prior to testing for indicator parameters to meet regulatory criteria and ultimate discharge into the adjacent storm drain. All collected effluent was held for a minimum of two weeks before discharge.

### **Contaminated Debris Disposal**

Contaminated debris such as empty sample containers, laboratory wastes, and disposable protective equipment generated during the demonstration were placed in a 55-gallon, open-top drum. These materials contained only residual contamination. During the demobilization phase, the wastes were packaged and stored for ultimate off-site disposal by EPA Region IX.

## **COMMUNITY RELATIONS AND TECHNOLOGY TRANSFER**

The public had several opportunities to participate during the course of the SITE demonstration project. The remedial action alternatives were presented by EPA in the engineering evaluation/cost analysis report available to the public in September 1988. The proposed alternatives were summarized in a fact sheet distributed to community members in June 1988. EPA Region IX held a 30-day comment period (June 1 to 30, 1988) and a public meeting on June 15, 1988, on the proposed remedial action alternatives, including UV radiation/oxidation treatment.

In December 1988, EPA distributed a second fact sheet which included a discussion of the remedial action alternatives selected for the site cleanup and information about the SITE demonstration for testing the UV radiation/oxidation remedial action technology. EPA elected not to hold a separate public comment period for the SITE demonstration, because public comments on the UV radiation/oxidation technology had already been received during the June 1988 comment period.

A formal visitors day announcement was sent to approximately 1,300 individuals, including federal, state, and local officials and agencies, environmental professionals, interested community members and groups, and all nearby residents. About 130 people attended the visitors day, which included oral and slide presentations and a trip to the site. Of the people who attended, approximately 48 percent were federal, state, and local officials; 40 percent were environmental professionals and business representatives; and 12 percent were community members and representatives of interest groups.

All participants in the visitors day received information about the SITE program, the UV radiation/oxidation technology, the LB&D site, and the criteria and methods used to evaluate the technology. The information packet was also sent to about 25 individuals who were unable to attend the visitors day. The visitors day was covered by representatives from the local newspapers and television and radio stations. EPA distributed one of its periodic fact sheets in May 1989, that included information about the Ultrox SITE demonstration.

In addition, the field demonstration and the visitors day program were videotaped to produce a comprehensive record of all major field activities.

## SECTION 5

### PERFORMANCE DATA AND EVALUATION

This section summarizes the performance data of the Ultrox treatment system and also presents an evaluation of the Ultrox technology's effectiveness in removing the organic contaminants in the groundwater at the LB&D site. A summary of the results for critical parameters (VOC) is presented first, followed by the results for noncritical parameters. Field operational problems are presented at the end of this section.

#### SUMMARY OF RESULTS FOR VOCs

As outlined in the Demonstration Procedures (Section 4), 13 test runs were performed during the technology demonstration. The purpose of these runs was to evaluate the effectiveness of the Ultrox system in removing the 44 VOCs listed in Table 5-1 that were present in groundwater at the LB&D site. To ensure that the results of these test runs are presented in a clear and concise manner, the removal efficiencies and concentration profiles at each sampling location for each VOC in each run are not presented. Instead, a summary approach is used to present the results.

For each test run, the Ultrox system's performance was evaluated to determine its effectiveness at removing selected and total VOCs. The selected VOCs were three indicator VOCs used to determine the "preferred" operating conditions (see Section 4). The concentration of total VOCs was estimated by adding the concentration of each VOC. Since this study only uses the total VOC data for qualitative interpretation, this approach is considered practical and useful from an engineering perspective.

The removal efficiency (RE) at the effluent sampling port, expressed as percent removal, was calculated using the following relationship:

$$RE = \frac{(IC - EC)}{IC} \times 100$$

Where: IC = Mean influent concentration  
EC = Mean effluent concentration

**TABLE 5-1**  
**VOCs IDENTIFIED IN THE LB&D SITE GROUNDWATER**

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Benzene  
 Benzyl chloride  
 Bis (2-chloroethoxy) methane  
 Bis (2-chloroisopropyl) ether  
 Bromobenzene  
 Bromodichloromethane  
 Bromoform  
 Bromoethane  
 Carbon tetrachloride  
 Chloroacetaldehyde  
 Chloral  
 Chlorobenzene  
 Chloroethane  
 Chloroform  
 1-Chlorohexane  
 2-Chloroethyl vinyl ether  
 Chloromethane  
 Chloromethyl methyl ether  
 Chlorotoluene  
 Dibromochloromethane  
 Dibromomethane  
 1,2-Dichlorobenzene  
 1,3-Dichlorobenzene  
 1,4-Dichlorobenzene  
 Dichlorodifluoromethane  
 1,1-Dichloroethane  
 1,2-Dichloroethane  
 1,1-Dichloroethylene  
 Trans-1,2-dichloroethylene  
 Dichloromethane  
 1,2-Dichloropropane  
 1,3-Dichloropropylene  
 Ethyl benzene  
 1,1,2,2-Tetrachloroethane  
 1,1,1,2-Tetrachloroethane  
 Tetrachloroethylene  
 Toluene  
 1,1,1-Trichloroethane  
 1,1,2-Trichloroethane  
 Trichloroethylene  
 Trichlorofluoromethane  
 Trichloropropane  
 Vinyl chloride  
 Xylenes

---

To calculate RE at the midpoint of the reactor, the mean concentration at the midpoint was used instead of EC in the preceding equation.

Since six replicates were collected at each water sampling location, the arithmetic mean of the concentrations of the six replicates was used as the mean concentration. Two alternate approaches were examined to use data reported as below the detection limit (BDL): (1) replace the BDL value with zero or (2) replace the BDL value with the detection limit (D). Using a value of zero for replicates that had BDL concentrations reported, particularly for effluent samples, would unduly favor the technology developer, while using a value equal to the detection limit in such cases would unduly penalize the technology developer. Therefore, one-half the detection limit (0.5 D) was chosen for the first replicate with a BDL concentration. Values of 0.4 D and 0.6 D were chosen alternately for other replicates to reduce the impact on the standard deviation. That is, if the 0.5 D value had been used for all the replicates, the standard deviation for the six replicates would be reduced. If detection limits were not available for an analyte, zero was used as the detection limit.

For VOCs in air, a simpler approach was followed since only duplicate samples were collected: for these samples, one-half of the detection limits were used for samples with concentrations below the detection limits. No standard deviation was calculated for air samples; only the average concentration was calculated.

In addition to calculating REs, the effluent VOC concentrations were compared to the applicable National Pollutant Discharge Elimination System (NPDES) standards at the site. To conclude if the effluent met the discharge standards, the upper confidence limit (UCL) was calculated using the following relationship:

$$UCL = \bar{x} + \frac{ts}{(n)^{1/2}}$$

Where:	$\frac{UCL}{\bar{x}}$	=	Upper confidence limit
	$\bar{x}$	=	Sample mean concentration
	t	=	Student's t-test statistic value at a specified confidence level
	s	=	Sample standard deviation
	n	=	Sample size (number of samples)

The UCL value was compared with the discharge standard. If the UCL value was higher than the discharge standard, it was concluded that the effluent did not meet the discharge standard for that particular VOC. Otherwise, the conclusion was that the effluent met the discharge standard.



Finally, since ozone gas was bubbled through the contaminated water in the Ultrox system, the extent of VOC stripping was estimated using the following relationship:

$$\text{Extent of VOC stripping} = \frac{\text{mass of VOC air emission/unit time}}{\text{mass of VOC removal/unit time}} \times 100$$

In the above equation, the mass of VOC air emissions per unit time was estimated by multiplying the average VOC concentration in the reactor off-gas by the gas flow rate. The mass of VOC removal per unit time is estimated as follows. First, the mass of VOC in the influent (groundwater) to the reactor per unit time was estimated by multiplying the mean VOC concentration in the influent by the influent flow rate. Then, the mass of VOC in the effluent (treated groundwater) per unit time was estimated by multiplying the mean VOC concentration in the effluent by the effluent flow rate. To obtain the mass of VOC removal per unit time, the mass of VOC in the effluent per unit time was subtracted from the mass of VOC in the influent per unit time.

#### **Individual VOC Removal**

The concentration and removal data for the indicator contaminants (TCE; 1,1-DCA; 1,1,1-TCA) are summarized in Tables 5-2, 5-3, and 5-4, by run number and sampling location. In addition to the mean, maximum, and minimum concentrations, standard deviations are also presented in the tables. A comparison of the data summarized in the tables shows that TCE was present in the groundwater at an approximate concentration of 100 µg/L, and there was a 30 to 50 percent decrease of VOC concentrations in the influent during the demonstration period.

The mean concentration profiles for TCE, 1,1-DCA, and 1,1,1-TCA in each run for each sampling location are plotted in Figures 5-1, 5-2, and 5-3. The VOC concentrations progressively decreased from the influent to the midpoint and from the midpoint to the effluent except for Run 3. (In Run 3, the concentration of 1, 1-DCA at the midpoint was higher than that in the influent. It is believed that either the midpoint concentration or the influent concentration is just an outlier.) This progressive decrease is due to the ozone and the UV radiation provided in the last three chambers (after the midpoint) in addition to the increase in the hydraulic retention time from the midpoint to the effluent port. Additionally, the effluent and midpoint VOC concentrations are comparatively high for Run 7, where the decreased ozone dose was used.

**TABLE 5-2**  
**SUMMARY OF TCE CONCENTRATION AND PERCENT REMOVAL DATA**

Run No	Max	Min	Influent (µg/L) Mean	SD	Max	Min	Midpoint (µg/L) Mean	SD	% Removed	Max	Min	Effluent (µg/L) Mean	SD	%Removed
1	100	69	86	16	22	14	16	3.1	82	5.0	4.3	4.6	0.29	95
2	92	26	55	29	36	25	29	4.8	47	4.6	1.4	2.4	1.6	96
3	90	41	64	20	69	35°	47	16	38	5.9	2.5	3.6	1.4	94
4	87	25	56	25	19	13	16	2.0	72	3.7	3.0	3.4	0.29	94
5	62	42	50	9.6	52	30	40	10	21	7.1	5.0	6.2	0.97	88
6	86	66	73	7.5	18	15	16	1.0	77	1.4	0.80	1.0	0.20	98
7	74	67	70	2.4	52	38	44	4.9	36	21	14	17	3.1	76
8	83	43°	59	16	6.1	3.0	4.7	1.5	92	1.0	0.00	0.69	0.35	99
9	82	56	65	9.3	11	6.9	9.3	1.4	86	1.5	1.1	1.2	0.16	98
10	100	35	57	23	8.6	5.8	7.7	1.0	86	2.1	0.79	1.6	0.47	97
11	65	45	57	7.3	23	17	20	2.3	66	1.6	1.0	1.3	0.23	98
12	58	42	52	5.8	8.7	6.9	8.0	0.67	85	0.70	0.35	0.55	0.12	99
13	57	41°	49	5.7	9.5	5.9	7.6	1.5	84	0.80	0.49	0.63	0.11	99

SD Standard deviation

° Among the six replicates analyzed, the minimum concentration was observed to be below the detection limit (BDL). However, based on a two-tailed t-test at the 95 percent confidence level, the BDL value was determined to be an outlier. Therefore, the data for the other five replicates was used in the statistical analysis.

TABLE 5-3  
SUMMARY OF 1,1-DCA CONCENTRATION AND PERCENT REMOVAL DATA

Run No.	Max	Min	Influent (µg/L) Mean	SD	Max	Min	Midpoint (µg/L) Mean	SD	% Removed	Max	Min	Effluent (µg/L) Mean	SD	% Removed
1	14	9.9	11.5	1.5	8.3	2.3	6.8	2.2	41	6.8	5.7	6.2	0.41	46
2	12	5.8	10.	2.3	9.6	7.2	8.2	1.0	21	6.2	1.8	3.2	2.2	69
3	13	8.3 <sup>a</sup>	10.	2.4	15	5.5	11	3.6	0.0	7.3	6.0	6.7	0.59	35
4	13	10.	12	1.0	10.	8.1	9.0	0.77	22	9.3	6.4	7.8	1.1	32
5	12	4.8	10.	2.7	9.6	1.9	7.9	3.0	21	7.0	6.0	6.4	0.34	36
6	13	10.	11	1.2	8.8	8.3	8.5	0.24	25	5.7	4.7	5.2	0.37	54
7	14	13	13	0.4	12	9.9	11	0.66	16	9.8	8.6	9.2	0.47	30.
8	12	5.3 <sup>b</sup>	9.8	2.6	8.0	5.0	6.6	1.4	33	5.3	4.3	4.7	0.42	52
9	14	8.7	11	2.2	8.3	6.0	7.3	0.82	36	5.6	4.9	5.3	0.25	54
10	11	8.9	10.	0.94	8.9	6.1	7.4	0.95	28	6.3	0.011	3.9	2.4	62
11	13	8.7	11	1.6	10.	2.3	7.6	2.8	30.	6.1	4.2	5.4	0.65	50.
12	11	10.	11	0.41	7.6	6.1	6.9	0.48	36	4.2	2.9	3.8	0.49	65
13	11	9.5	10.	0.73	7.3	5.1	6.4	0.81	39	4.7	3.8	4.2	0.39	60.

SD Standard deviation

<sup>a</sup> Among the six replicates analyzed, the minimum concentration was observed to be 0.650 µg/L. However, based on a two-tailed t-test at the 95 percent confidence level, 0.650 µg/L was determined to be an outlier. Therefore, the data for the other five replicates was used in the statistical analysis.

<sup>b</sup> Among the six replicates analyzed, the minimum concentration was observed to be 0.011 µg/L. However, based on a two-tailed t-test at the 95 percent confidence level, 0.011 µg/L was determined to be an outlier. Therefore, the data for the other five replicates was used in the statistical analysis.

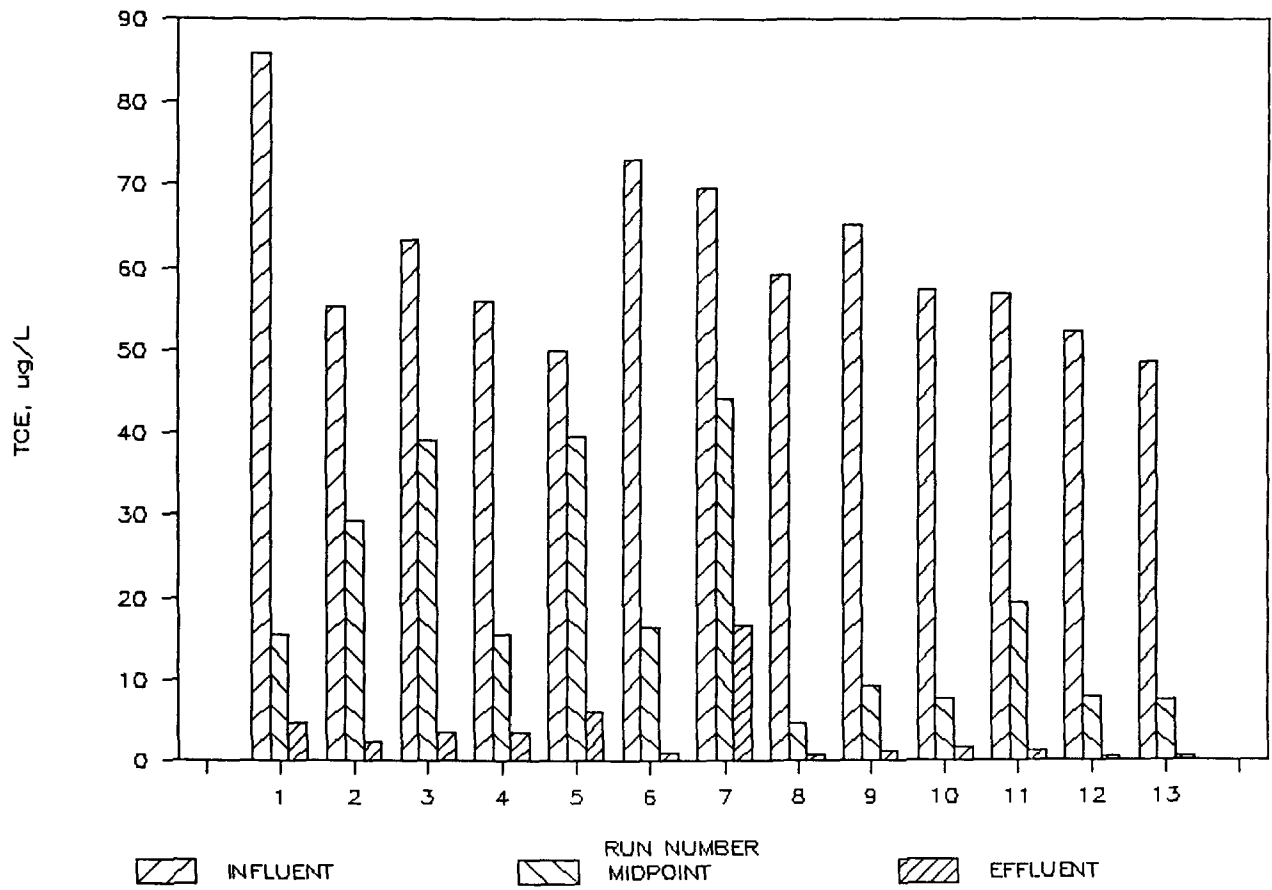
**TABLE 5-4**  
**SUMMARY OF 1,1,1-TCA CONCENTRATION AND PERCENT REMOVAL DATA**

Run No.	Max	Min	Influent (µg/L) Mean	SD	Max	Min	Midpoint (µg/L) Mean	SD	% Removed	Max	Min	Effluent (µg/L) Mean	SD	%Removed
1	5.1	3.2	4.0	0.68	2.0	0.016	1.4	0.83	66	1.3	1.1	1.2	0.08	70.
2	4.3	1.6	3.7	1.0	2.7	2.2	2.5	0.17	32	1.1	0.39	0.64	0.36	83
3	4.3	3.2	3.8	0.49	3.7	0.016	2.5	1.5	34	1.5	1.2	1.3	0.14	65
4	4.6	3.3	3.9	0.52	3.4	2.3	2.8	0.42	29	2.1	1.4	1.8	0.31	53
5	4.7	3.3	4.1	0.52	3.4	2.8	3.1	0.27	25	1.5	1.3	1.4	0.10	66
6	4.2	3.7	3.9	0.19	2.6	2.2	2.5	0.15	36	1.4	0.85	1.0	0.22	73
7	5.0	4.3	4.7	0.25	4.3	3.5	4.0	0.34	16	3.1	2.8	3.0	0.15	37
8	4.6	2.4*	3.5	0.80	2.0	1.4	1.7	0.23	51	1.0	0.02	0.70	0.35	80.
9	5.2	3.2	4.3	0.81	2.1	1.4	1.9	0.25	56	1.0	0.02	0.75	0.36	83
10	4.2	2.0	3.4	0.80	2.2	1.8	2.0	0.15	41	0.89	0.28	0.61	0.21	82
11	4.4	3.4	3.8	0.37	2.9	2.1	2.4	0.38	37	0.98	0.52	0.78	0.20	80.
12	3.4	3.2	3.3	0.098	2.5	1.2	1.6	0.47	52	0.48	0.31	0.43	0.06	87
13	3.4	2.7	3.2	0.29	1.4	0.90	1.2	0.18	63	0.59	0.39	0.49	0.07	85

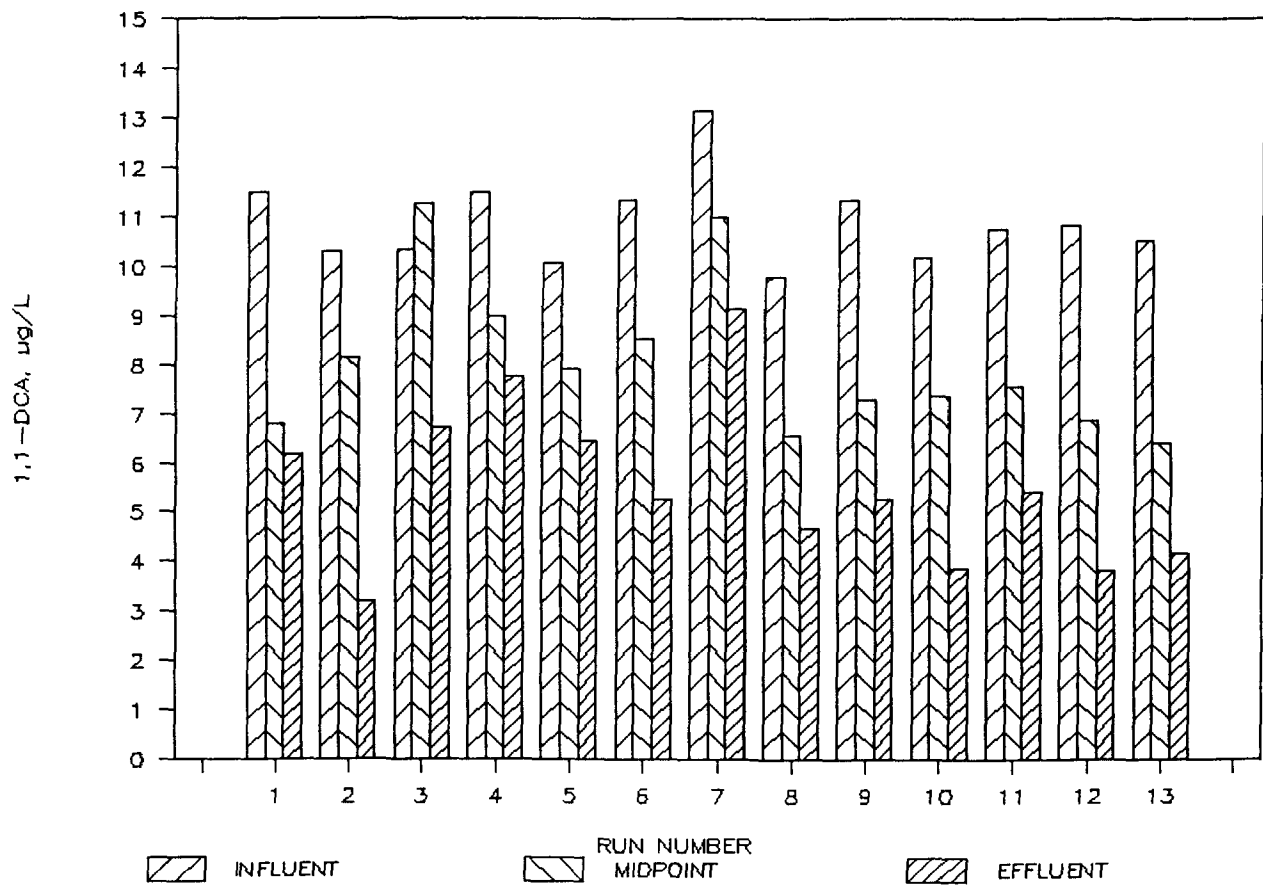
SD      Standard deviation

\*      Among the six replicates analyzed, the minimum concentration was observed to be 0.016 µg/L. However, based on a two-tailed t-test at the 95 percent confidence level, 0.016 µg/L was determined to be an outlier. Therefore, the data for the other five replicates was used in the statistical analysis.

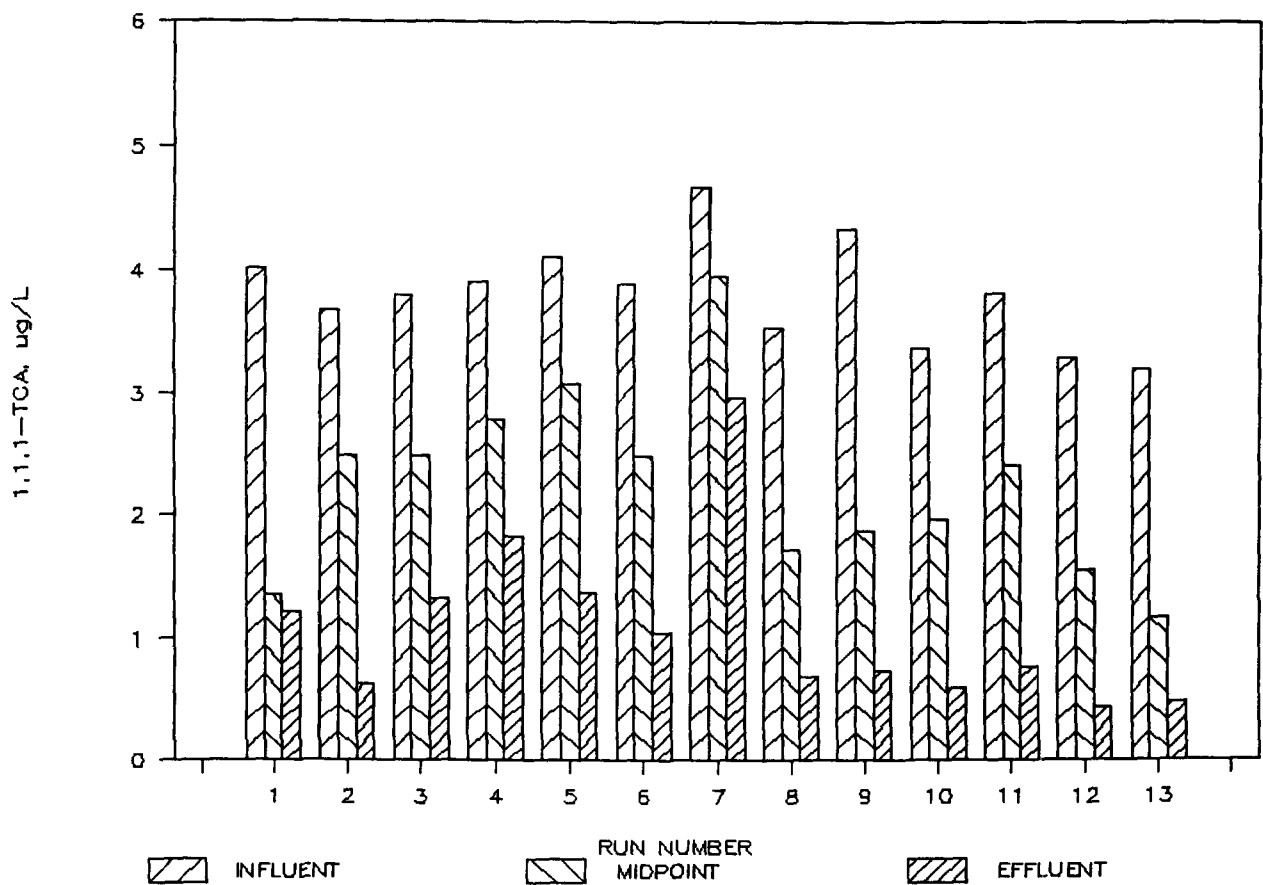
**FIGURE 5-1**  
**TCE CONCENTRATIONS IN DIFFERENT RUNS**



**FIGURE 5-2**  
**1,1-DCA CONCENTRATIONS IN DIFFERENT RUNS**



**FIGURE 5-3**  
**1,1,1-TCA CONCENTRATIONS IN DIFFERENT RUNS**



Comparison of the average effluent concentration (estimated using only two of the six replicates, as explained previously in Section 4) for each indicator VOC with the applicable discharge standards (NPDES) indicated that among the first 11 test runs, the effluent met the discharge limits in Runs 8 and 9. Since a lower hydrogen peroxide dose was used in Run 9 than in Run 8, Run 9 was chosen as the "preferred" operating run. However, based on a complete analysis of six replicates which could be done after the demonstration, the mean concentration of 1,1-DCA in the effluent was found to be slightly higher than 5 µg/L, the discharge standard for the compound. Since the "preferred" operating conditions were decided to be that of Run 9 (prior to the analysis of all replicates), the reproducibility runs (12 and 13) were performed at those conditions.

The REs of the indicator contaminants are presented in Figures 5-4, 5-5, and 5-6, and Tables 5-2, 5-3, and 5-4. These data indicate that the REs for the three indicator compounds were, in fact, dependent on the operating conditions. In general, the REs for the three VOCs decreased considerably in Run 7, probably due to the decreased ozone dose in that run.

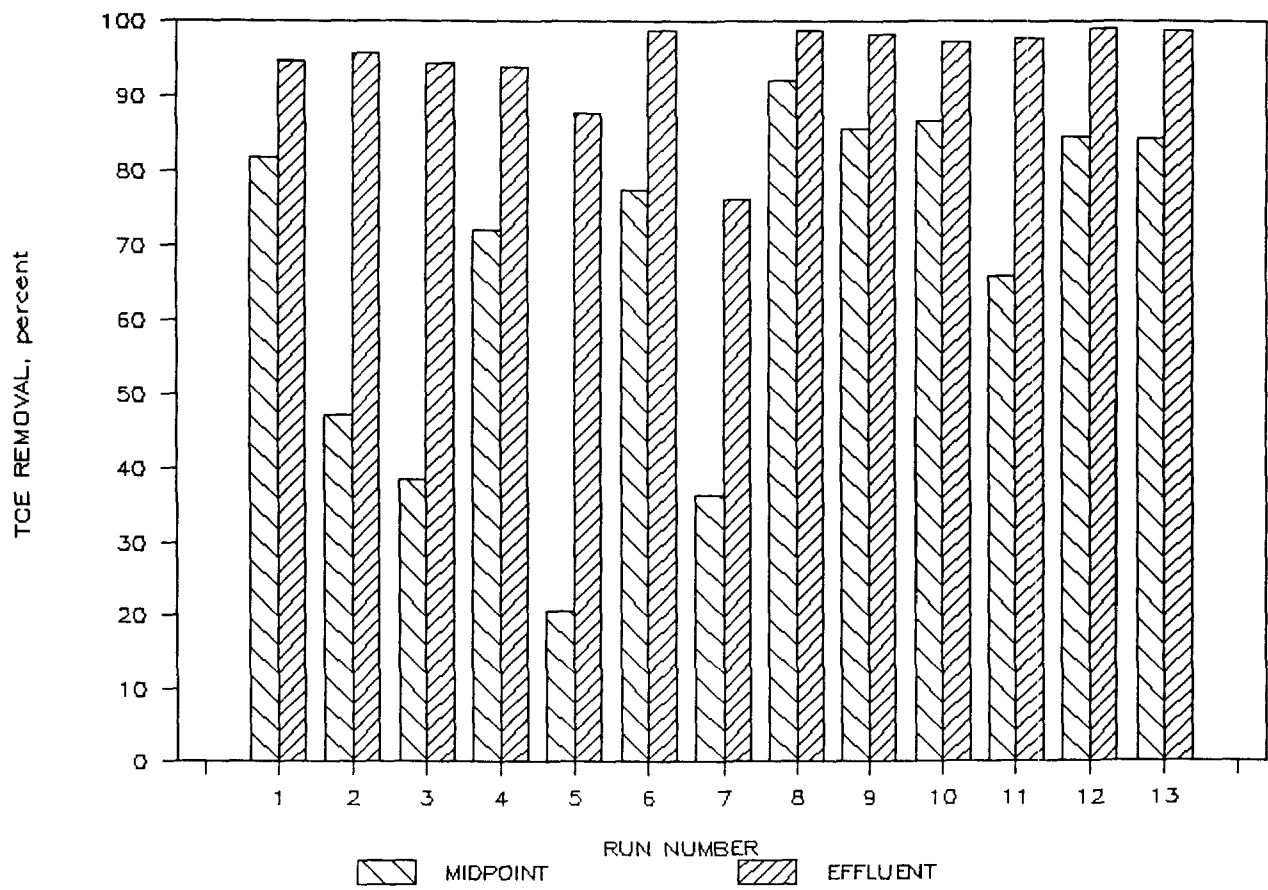
The REs for the indicator VOCs in the verification runs (9, 12, and 13) are highlighted in Figure 5-7. This figure indicates that the REs for each indicator VOC in the three runs were not different. That is, the technology performance levels are reproducible under the same operating conditions. The figures also show that the REs for TCE were higher than those for 1,1-DCA and 1,1,1-TCA, which is consistent with the rationale used in selecting the indicator VOCs.

A comparison of 95 percent UCL values for the effluent VOCs with the regulatory threshold is presented in Tables 5-5 through 5-10. These tables are grouped so that each table comprises the summary for the test runs in which one of the operating parameters was varied. For example, Table 5-5 presents data for the runs in which the pH was varied and Table 5-6 presents data for the runs in which the hydraulic retention time was varied.

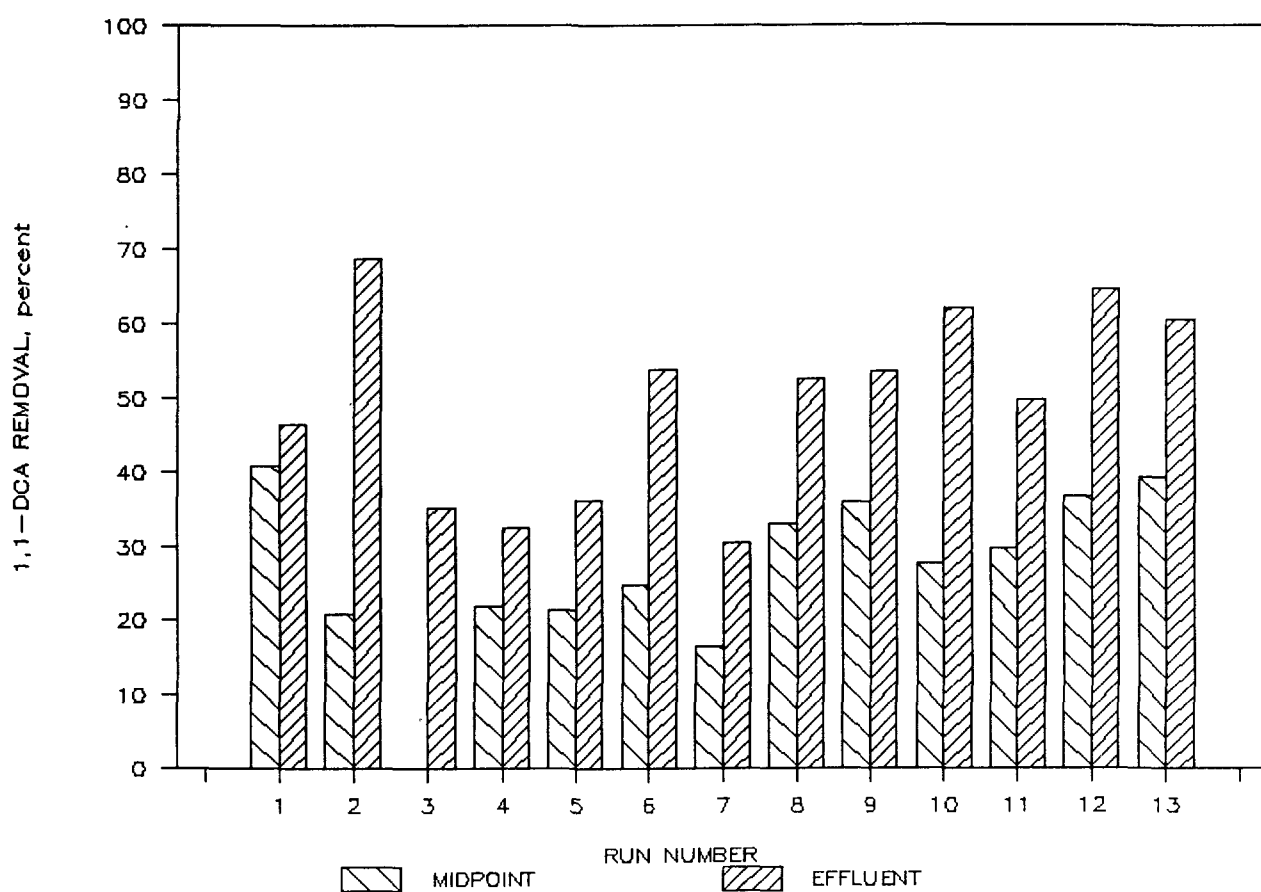
In this study, a cause and effect type of approach was not used to interpret the data because the experiments were not designed using a factorial design approach. The factorial design approach would have necessitated that approximately 250 experiments be performed, which would have substantially increased the cost of the technology demonstration. Also, the major purpose of the demonstration was to evaluate the effectiveness of the technology under varying operating conditions in treating VOCs present in the groundwater, rather than examine the developer's design.



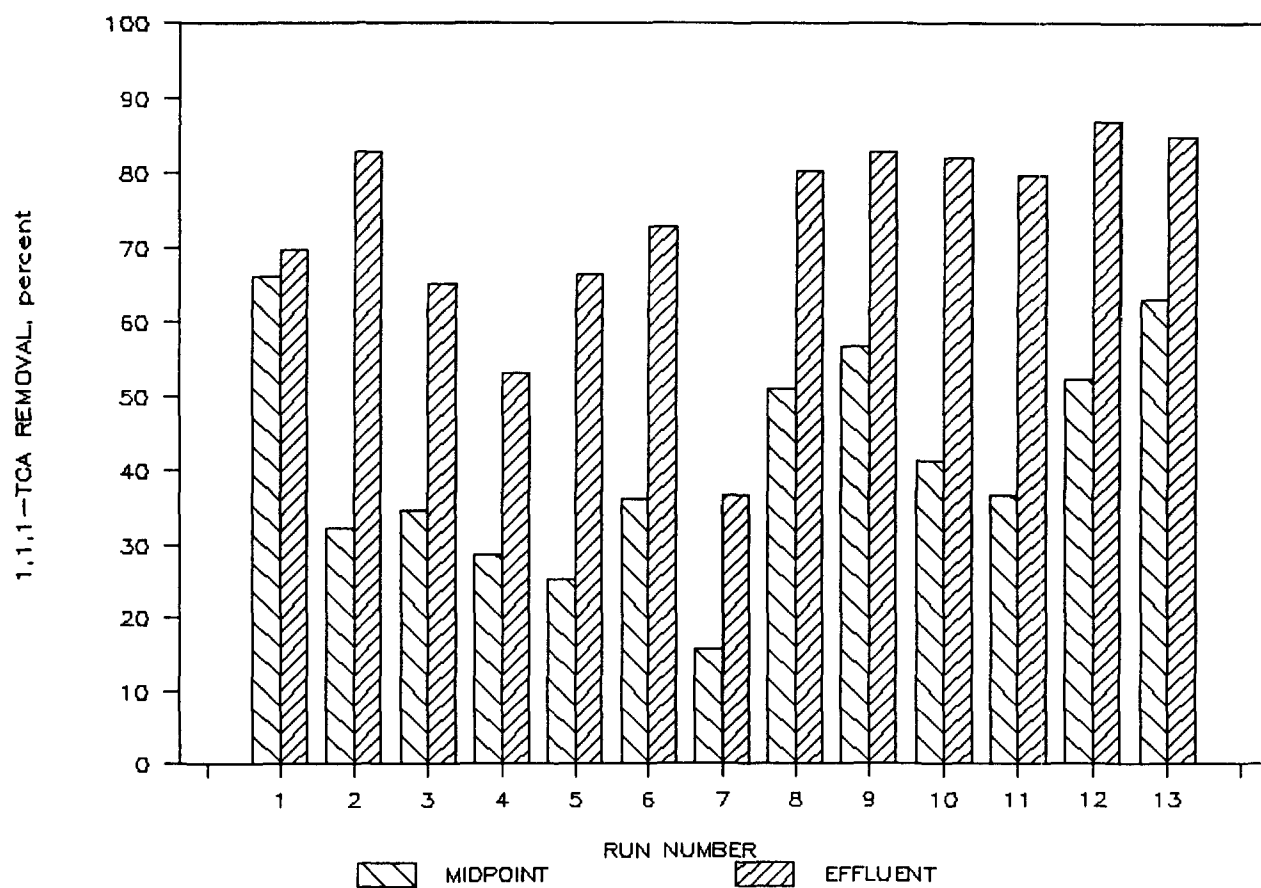
**FIGURE 5-4**  
**TCE REMOVAL IN DIFFERENT RUNS**



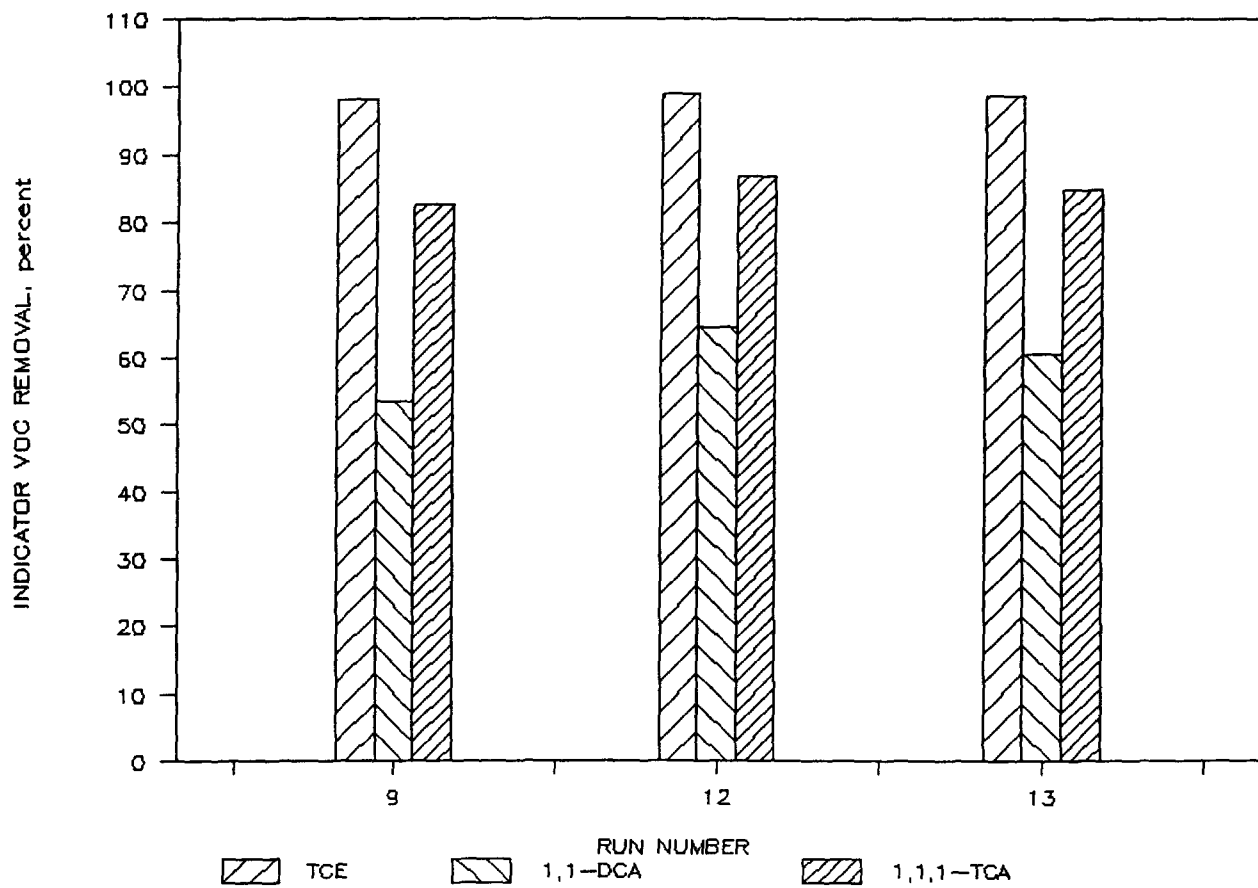
**FIGURE 5-5**  
**1,1-DCA REMOVAL IN DIFFERENT RUNS**



**FIGURE 5-6**  
**1,1,1-TCA REMOVAL IN DIFFERENT RUNS**



**FIGURE 5-7**  
**INDICATOR VOC REMOVALS**  
**IN VERIFICATION RUNS**



**TABLE 5-5**  
**COMPARISON OF EFFLUENT VOC CONCENTRATIONS**  
**IN RUNS 1, 2, AND 3**  
**(Parameter Varied: pH)**

	Mean, µg/L	95% UCL, µg/L	RT, µg/L	Conclusion
<b>Run 1 (pH = 7.2)*</b>				
1,1,1-TCA	1.2	1.3	5	OK
1,1,2,2-PCA	0.045	0.045	5	OK
1,1-DCA	6.2	6.5	5	N
1,1-DCE	0.00	0.00	5	OK
1,2-DCA	1.3	1.3	1	N
1,2-DCPA	4.3	4.5	5	OK
Benzene	0.023	0.026	5	OK
Chloroethane	0.00	0.00	5	OK
Chloroform	1.2	1.3	5	OK
PCE	0.042	0.045	5	OK
T-1,2-DCE	0.062	0.14	5	OK
TCE	4.6	4.8	5	OK
Vinyl Chloride	0.11	0.11	0.5	OK
<b>Run 2 (pH = 6.2)</b>				
1,1,1-TCA	0.64	0.93	5	OK
1,1,2,2-PCA	0.045	0.045	5	OK
1,1-DCA	3.2	5.0	5	OK
1,1-DCE	0.00	0.00	5	OK
1,2-DCA	0.44	0.99	1	OK
1,2-DCPA	2.8	3.8	5	OK
Benzene	0.14	0.29	5	OK
Chloroethane	0.00	0.00	5	OK
Chloroform	0.59	0.99	5	OK
PCE	0.041	0.041	5	OK
T-1,2-DCE	0.00	0.00	5	OK
TCE	2.4	3.7	5	OK
Vinyl Chloride	0.11	0.11	0.5	OK
<b>Run 3 (pH = 5.2)</b>				
1,1,1-TCA	1.3	1.4	5	OK
1,1,2,2-PCA	0.045	0.045	5	OK
1,1-DCA	6.7	7.2	5	N
1,1-DCE	0.00	0.00	5	OK
1,2-DCA	1.5	1.8	1	N
1,2-DCPA	5.2	6.1	5	N
Benzene	0.023	0.026	5	OK
Chloroethane	0.00	0.00	5	OK
Chloroform	1.2	1.3	5	OK
PCE	0.042	0.045	5	OK
T-1,2-DCE	0.067	0.15	5	OK
TCE	3.6	4.7	5	OK
Vinyl Chloride	0.12	0.12	0.5	OK

\* "Preferred" pH

95% UCL: Upper 95% Confidence Limit  
RT: Regulatory Threshold  
OK: Effluent met the regulatory threshold  
N: Effluent did not meet the regulatory threshold

Abbreviations: 1,1,1-TCA: 1,1,1-Trichloroethane; 1,1,2,2-PCA: 1,1,2,2-Tetrachloroethane;  
1,1-DCA: 1,1-Dichloroethane; 1,1-DCE: 1,1-Dichloroethylene; 1,2-DCA: 1,2-Dichloroethane;  
1,2-DCPA: 1,2-Dichloropropane; PCE: Tetrachloroethylene; T-1,2-DCE:  
Trans-1,2-Dichloroethylene; TCE: Trichloroethylene.

**TABLE 5-6**  
**COMPARISON OF EFFLUENT VOC CONCENTRATIONS**  
**IN RUNS 4 AND 5**

(Parameter Varied: Hydraulic Retention Time\*)

	Mean, µg/L	95% UCL, µg/L	RT, µg/L	Conclusion
<b>Run 4</b> (Hydraulic retention time = 60 min.)				
1,1,1-TCA	1.8	2.1	5	OK
1,1,2,2-PCA	0.045	0.045	5	OK
1,1-DCA	7.8	8.7	5	N
1,1-DCE	0.00	0.00	5	OK
1,2-DCA	0.99	1.6	1	N
1,2-DCPA	5.4	6.3	5	N
Benzene	0.050	0.11	5	OK
Chloroethane	0.00	0.00	5	OK
Chloroform	1.4	1.5	5	OK
PCE	0.042	0.045	5	OK
T-1,2-DCE	0.00	0.00	5	OK
TCE	3.4	3.6	5	OK
Vinyl Chloride	0.12	0.12	0.5	OK
<b>Run 5</b> (Hydraulic retention time = 20 min.)				
1,1,1-TCA	1.4	1.5	5	OK
1,1,2,2-PCA	0.045	0.045	5	OK
1,1-DCA	6.4	6.7	5	N
1,1-DCE	0.00	0.00	5	OK
1,2-DCA	0.013	0.013	1	OK
1,2-DCPA	5.3	5.9	5	N
Benzene	0.023	0.026	5	OK
Chloroethane	0.00	0.00	5	OK
Chloroform	1.2	1.3	5	OK
PCE	0.21	0.43	5	OK
T-1,2-DCE	0.00	0.00	5	OK
TCE	6.2	7.0	5	N
Vinyl Chloride	0.12	0.12	0.5	OK

\*"Preferred" hydraulic retention time = 40 minutes (Run 1)

95% UCL: Upper 95% Confidence Limit  
RT: Regulatory Threshold  
OK: Effluent met the regulatory threshold  
N: Effluent did not meet the regulatory threshold

Abbreviations: 1,1,1-TCA: 1,1,1-Trichloroethane; 1,1,2,2-PCA: 1,1,2,2-Tetrachloroethane;  
1,1-DCA: 1,1-Dichloroethane; 1,1-DCE: 1,1-Dichloroethylene; 1,2-DCA: 1,2-Dichloroethane;  
1,2-DCPA: 1,2-Dichloropropane; PCE: Tetrachloroethylene; T-1,2-DCE:  
Trans-1,2-Dichloroethylene; TCE: Trichloroethylene.

**TABLE 5-7**  
**COMPARISON OF EFFLUENT VOC CONCENTRATIONS**  
**IN RUNS 6 AND 7**

(Parameter Varied: Ozone Dose)

	Mean, µg/L	95% UCL, µg/L	RT, µg/L	Conclusion
<b>Run 6 (O<sub>3</sub> dose = 110 mg/L)*</b>				
1,1,1 -TCA	1.0	1.2	5	OK
1,1,2,2-PCA	0.045	0.045	5	OK
1,1-DCA	5.2	5.6	5	N
1,2-DCE	0.048	0.15	5	OK
1,2-DCA	1.2	1.3	1	N
1,2-DCPA	3.2	3.4	5	OK
Benzene	0.023	0.026	5	OK
Chloroethane	0.00	0.00	5	OK
Chloroform	1.0	1.5	5	OK
PCE	0.16	0.35	5	OK
T-1,2-DCE	0.00	0.00	5	OK
TCE	1.0	1.2	5	OK
Vinyl Chloride	1.12	0.12	0.5	OK
<b>Run 7 (O<sub>3</sub> dose = 38 mg/L)</b>				
1,1,1-TCA	3.0	3.1	5	OK
1,1,2,2-PCA	0.047	0.050	5	OK
1,1-DCA	9.2	9.5	5	N
1,1-DCE	0.33	0.55	5	OK
1,2-DCA	0.013	0.015	5	OK
1,2-DCPA	7.6	7.9	5	N
Benzene	0.49	0.58	5	OK
Chloroethane	0.00	0.00	5	OK
Chloroform	.17	1.7	5	OK
PCE	0.041	0.041	5	OK
T-1,2-DCE	2.8	3.4	5	OK
TCE	17	19	5	N
Vinyl Chloride	6.1	8.4	0.5	N

\* "Preferred" O<sub>3</sub> dose

95% UCL: Upper 95% Confidence Limit  
RT: Regulatory Threshold  
OK: Effluent met the regulatory threshold  
N: Effluent did not meet the regulatory threshold

Abbreviations: 1,1,1-TCA: 1,1,1-Trichloroethane; 1,1,2,2-PCA: 1,1,2,2-Tetrachloroethane;  
1,1-DCA: 1,1-Dichloroethane; 1,1-DCE: 1,1-Dichloroethylene; 1,2-DCA: 1,2-Dichloroethane;  
1,2-DCPA: 1,2-Dichloropropane; PCE: Tetrachloroethylene; T-1,2-DCE:  
Trans-1,2-Dichloroethylene; TCE: Trichloroethylene.

**TABLE 5-8**  
**COMPARISON OF EFFLUENT VOC CONCENTRATIONS**  
**IN RUNS 8 AND 9**

(Parameter Varied: Hydrogen Peroxide Dose)

	Mean, $\mu\text{g/L}$	95% UCL, $\mu\text{g/L}$	RT, $\mu\text{g/L}$	Conclusion
<b>Run 8 (<math>\text{H}_2\text{O}_2 = 38 \text{ mg/L}</math>)</b>				
1,1,1-TCA	0.70	0.99	5	OK
1,1,2,2-PCA	0.045	0.045	5	OK
1,1-DCA	4.7	5.0	5	OK
1,1-DCE	0.00	0.00	5	OK
1,2-DCA	3.3	0.74	1	OK
1,2-DCPA	3.8	4.2	5	OK
Benzene	0.023	0.026	5	OK
Chloroethane	0.00	0.00	5	OK
Chloroform	1.0	1.2	5	OK
PCE	0.042	0.045	5	OK
T-1,2-DCE	0.00	0.00	5	OK
TCE	0.69	.98	5	OK
Vinyl Chloride	0.12	0.12	0.5	OK
<b>Run 9 (<math>\text{H}_2\text{O}_2 = 13 \text{ mg/L}</math>)*</b>				
1,1,1-TCA	0.75	1.0	5	OK
1,1,2,2-PCA	0.045	0.045	5	OK
1,1-DCA	5.3	5.5	5	N
1,1-DCE	0.00	0.00	5	OK
1,2-DCA	1.3	1.4	1	N
1,2-DCPA	3.3	3.4	5	OK
Benzene	0.023	0.026	5	OK
Chloroethane	0.00	0.00	5	OK
Chloroform	1.1	1.2	5	OK
PCE	0.24	0.63	5	OK
T-1,2-DCE	0.00	0.00	5	OK
TCE	1.2	1.3	5	OK
Vinyl Chloride	0.11	0.11	0.5	OK

\* "Preferred"  $\text{H}_2\text{O}_2$  dose

95% UCL: Upper 95% Confidence Limit  
RT: Regulatory Threshold  
OK: Effluent met the regulatory threshold  
N: Effluent did not meet the regulatory threshold

Abbreviations: 1,1,1-TCA: 1,1,1-Trichloroethane; 1,1,2,2-PCA: 1,1,2,2-Tetrachloroethane;  
1,1-DCA: 1,1-Dichloroethane; 1,1-DCE: 1,1-Dichloroethylene; 1,2-DCA: 1,2-Dichloroethane;  
1,2-DCPA: 1,2-Dichloropropane; PCE: Tetrachloroethylene; T-1,2-DCE:  
Trans-1,2-Dichloroethylene; TCE: Trichloroethylene.



**TABLE 5-9**  
**COMPARISON OF EFFLUENT VOC CONCENTRATIONS**  
**IN RUNS 10 AND 11**

(Parameter Varied: UV Radiation Intensity\*)

	Mean, $\mu\text{g/L}$	95% UCL, $\mu\text{g/L}$	RT, $\mu\text{g/L}$	Conclusion
<b>Run 10</b> (UV in first 3 chambers)				
1,1,1-TCA	0.61	0.78	5	OK
1,1,2,2-PCA	0.045	0.045	5	OK
1,1-DCA	3.9	5.8	5	N
1,1-DCE	0.00	0.00	5	OK
1,2-DCA	0.42	0.95	1	OK
1,2-DCPA	4.6	5.4	5	N
Benzene	0.061	0.14	5	OK
Chloroethane	0.00	0.00	5	OK
Chloroform	0.83	1.0	5	OK
PCE	0.11	0.21	5	OK
T-1,2-DCE	0.00	0.00	5	OK
TCE	1.6	2.0	5	OK
Vinyl Chloride	0.11	0.11	0.5	OK
<b>Run 11</b> (UV in last 3 chambers)				
1,1,1-TCA	0.78	0.94	5	OK
1,1,2,2-PCA	0.045	0.045	5	OK
1,1-DCA	5.4	6.0	5	N
1,1-DCE	0.00	0.00	5	OK
1,2-DCA	0.62	1.2	1	N
1,2-DCPA	4.7	6.0	5	N
Benzene	0.023	0.026	5	OK
Chloroethane	0.00	0.00	5	OK
Chloroform	1.2	1.5	5	OK
PCE	0.042	0.045	5	OK
T-1,2-DCE	0.00	0.00	5	OK
TCE	1.3	1.5	5	OK
Vinyl Chloride	0.12	0.12	0.5	OK

\* "Preferred" UV radiation intensity = 24 lamps operating (Run 9)

95% UCL: Upper 95% Confidence Limit  
RT: Regulatory Threshold  
OK: Effluent met the regulatory threshold  
N: Effluent did not meet the regulatory threshold

Abbreviations: 1,1,1-TCA: 1,1,1-Trichloroethane; 1,1,2,2-PCA: 1,1,2,2-Tetrachloroethane;  
1,1-DCA: 1,1-Dichloroethane; 1,1-DCE: 1,1-Dichloroethylene; 1,2-DCA: 1,2-Dichloroethane;  
1,2-DCPA: 1,2-Dichloropropane; PCE: Tetrachloroethylene; T-1,2-DCE:  
Trans-1,2-Dichloroethylene; TCE: Trichloroethylene.

**TABLE 5-10**  
**COMPARISON OF EFFLUENT VOC CONCENTRATIONS**  
**IN RUNS 12 AND 13**

(Parameter Varied: None)

	Mean, $\mu\text{g/L}$	95% UCL, $\mu\text{g/L}$	RT, $\mu\text{g/L}$	Conclusion
<b>Run 12</b>				
1,1,1-TCA	0.43	0.48	5	OK
1,1,2,2-PCA	0.045	0.045	5	OK
1,1-DCA	3.8	4.2	5	OK
1,1-DCE	0.00	0.00	5	OK
1,2-DCA	0.92	1.0	1	OK
1,2-DCPA	2.6	2.9	5	OK
Benzene	0.023	0.026	5	OK
Chloroethane	0.00	0.00	5	OK
Chloroform	0.74	0.82	5	OK
PCE	0.19	0.38	5	OK
T-1,2-DCE	0.00	0.00	5	OK
TCE	0.55	0.65	5	OK
Vinyl Chloride	0.11	0.11	0.5	OK
<b>Run 13</b>				
1,1,1-TCA	0.49	0.54	5	OK
1,1,2,2-PCA	0.045	0.045	5	OK
1,1-DCA	4.2	4.5	5	OK
1,1-DCE	0.00	0.00	5	OK
1,2-DCA	1.0	1.0	1	OK
1,2-DCPA	2.9	3.1	5	OK
Benzene	0.45	0.52	5	OK
Chloroethane	0.00	0.00	5	OK
Chloroform	0.81	0.87	5	OK
PCE	0.091	0.17	5	OK
T-1,2-DCE	0.00	0.00	5	OK
TCE	0.63	0.73	5	OK
Vinyl Chloride	0.12	0.12	0.5	OK

95% UCL: Upper 95% Confidence Limit  
RT: Regulatory Threshold  
OK: Effluent met the regulatory threshold  
N: Effluent did not meet the regulatory threshold

Abbreviations: 1,1,1-TCA: 1,1,1-Trichloroethane; 1,1,2,2-PCA: 1,1,2,2-Tetrachloroethane;  
1,1-DCA: 1,1-Dichloroethane; 1,1-DCE: 1,1-Dichloroethylene; 1,2-DCA: 1,2-Dichloroethane;  
1,2-DCPA: 1,2-Dichloropropane; PCE: Tetrachloroethylene; T-1,2-DCE:  
Trans-1,2-Dichloroethylene; TCE: Trichloroethylene.

Table 5-5 shows that the 95 percent UCL values for 1,1-DCA are higher than the regulatory threshold values in Runs 1 and 3. This indicates that statistically, at the 95 percent confidence level, the effluent did not meet the discharge standards in these runs. In addition, effluent concentrations of 1,1-DCA and 1,2-DCA in Runs 1 and 3 and 1,2-DCPA in Run 3 did not meet the discharge standards. However, a general comparison of the three runs suggests that the effluent quality was better in Run 2.

In Run 2 (where the influent pH was lower by one pH unit), the effluent met the discharge standards for all VOCs (based on the analysis of six replicates). However, this information was not available at the time of demonstration; based on the two replicate samples analyzed overnight, 1,1-DCA did not meet the discharge standards. Therefore, Run 2 was not chosen as the "preferred" operating run. Instead, Run 1 was chosen because it required no pH adjustment (and, therefore, no additional cost).

Tables 5-6 through 5-9 present information similar to that in Table 5-5 for the other four test run parameters.

The information presented in Table 5-10 and Figure 5-7 can be used to verify the reproducibility of the performance levels. A comparison of the 95 percent UCL values for the effluent VOCs in Runs 12 and 13 with the discharge standards presented in Table 5-10 indicates that the effluent met the discharge standards for all regulated VOCs. However, in Run 9, the effluent did not meet the discharge standards for 1,1-DCA and 1,2-DCA. This difference in performance among the verifications Runs 9, 12 and 13 is negligible and attributed to the higher influent VOC concentrations in Run 9 than in Runs 12 and 13. Since the mean effluent VOC concentrations of 1,1-DCA and 1,2-DCA are higher than the discharge standard, statistical inferences at other confidence levels (such as 90 percent) will not be different, and, therefore, are not presented.

Since ozone gas is bubbled through the groundwater treated by the Ultrox system, the VOC removal could be attributed to stripping in addition to oxidation. To determine the extent of stripping within the treatment system, VOC samples were collected from the reactor off-gas. A total of 25 samples was collected during the demonstration. Although 1,1-DCE, 1,2-DCE, benzene, 1,1,2,2-tetrachloroethane, and acetone were present in two samples at concentrations close to the detection limits, TCE, vinyl chloride, 1,1,1-TCA, and 1,1-DCA were detected more frequently. To determine the extent of stripping, the emission rates in the reactor off-gas for these latter four VOCs were compared to the VOC removal rates (estimated by a difference between the VOC input rates at the influent and output rates at the effluent ports of the Ultrox system). The results are summarized in Table 5-11.

**TABLE 5-11**  
**EXTENT OF VOC STRIPPING IN THE ULTROX SYSTEM**

Run No.	<u>Air flow rate</u> Water flow rate	<u>Percent Stripping Contribution for</u>			
		1,1-DCA 0.0043 <sup>b</sup>	TCE 0.0091 <sup>b</sup>	1,1,1-TCA 0.014 <sup>b</sup>	VC <sup>a</sup> 0.082 <sup>b</sup>
1	2.1	7.4	2.0	43	0.013
2	2.3	9.1	3.4	34	0.95
3	2.1	9.9	2.7	31	0.013
4	2.0	7.4	3.0	29	0.010
5	2.1	17	3.5	29	1.7
6	4.5	16	1.2	65	0.072
7	1.0	4.9	1.2	12	3.1
8	4.5	23	7.5	85	1.2
9	4.5	16	6.6	58	0.040
10	4.3	27	9.4	73	1.1
11	4.6	44	24	>99	13
12	4.4	34	7.0	76	8.9
13	4.3	37	26	75	1.8

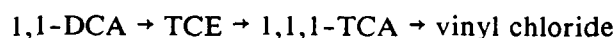
Notes:

a VC: Vinyl Chloride

b Henry's law constant of the VOC, atm-m<sup>3</sup>/mol.

Since the extent of stripping for any particular VOC is expected to be proportional to the ratio of air (ozone) flow rate to the water flow rate, this ratio is also presented in Table 5-11. The ratio for Runs 1 to 5 is approximately 2; for Run 6 and Runs 8 through 13, the ratio is about 4.5; and for Run 7, the ratio is 1. If stripping contributed to the total removal of the four VOCs, the extent of stripping should be the least in Run 7, and the most in Runs 6 and 8 through 13. The data presented in the table follow this trend for three of the four VOCs, but not for the vinyl chloride in Runs 6, 7, and 9. A quantitative correlation of the extent of stripping cannot be made because the operating conditions were different in each run. For example, at a given air (ozone) to water flow ratio, when oxidant doses varied, the extent of oxidation also varied. Therefore, the extent of stripping will be indirectly affected.

Table 5-11 also presents Henry's law constants for the four VOCs. By comparing these constants for the VOCs, their volatility is expected to increase from left to right, as follows:



However, a significant removal fraction for 1,1,1-TCA and 1,1-DCA was observed to be due to stripping. Conversely, the extent of stripping was low for vinyl chloride and TCE. This is because it is easier to oxidize vinyl chloride and TCE than 1,1-DCA and 1,1,1-TCA because of the double bonds between the carbon atoms in TCE and vinyl chloride. In other words, in the UV radiation/oxidation process, stripping is a significant removal pathway for compounds that are difficult to oxidize.

### **Total VOC Removal**

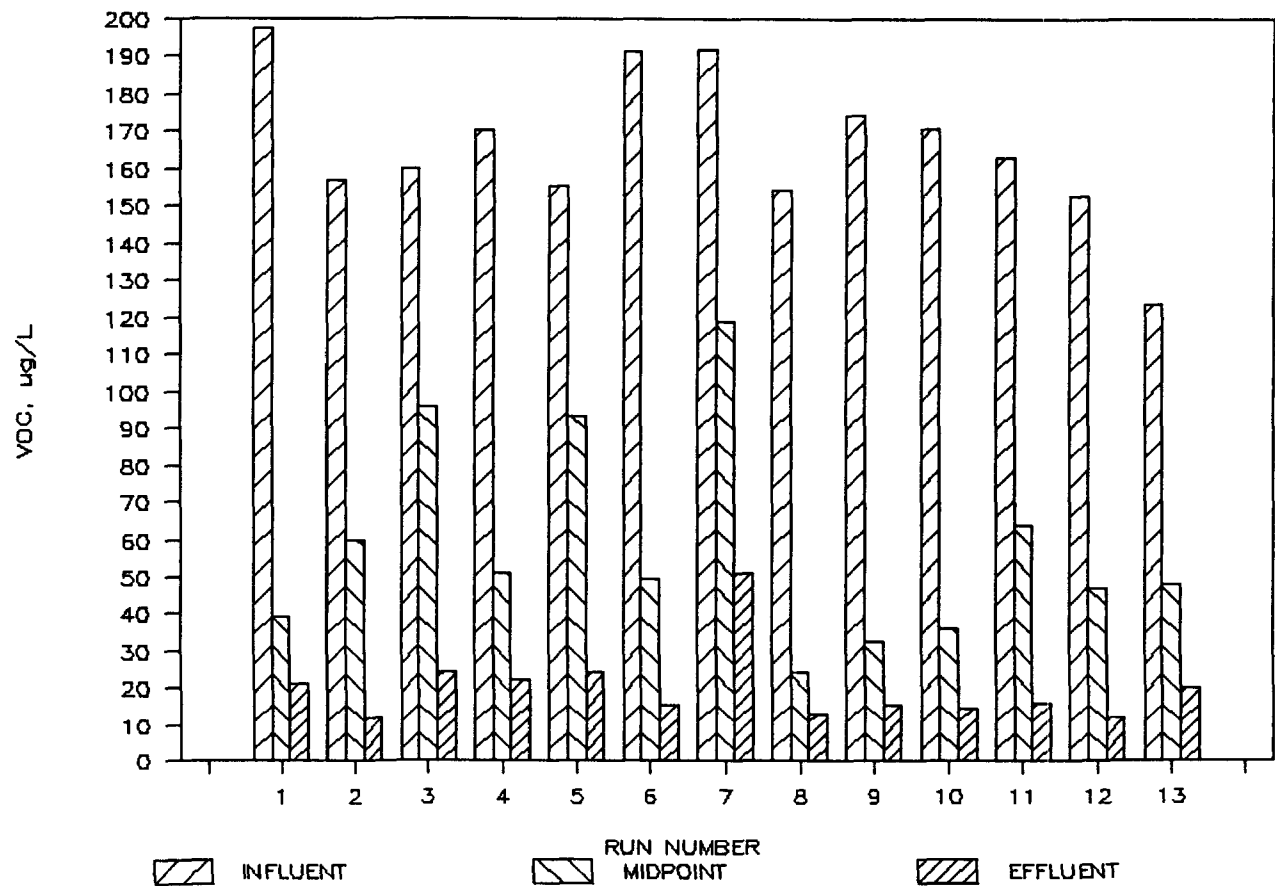
Total VOC concentration data are summarized in Table 5-12 by run number and sampling location. The mean total VOC concentrations at the influent, midpoint, and effluent are plotted in Figure 5-8. A comparison of Figure 5-8 with Figures 5-1, 5-2, and 5-3 indicates that the concentration profiles of total VOCs are similar to those of indicator VOCs. For example, the peaks seen at the midpoint and effluent for indicator VOCs are also seen in the total VOC concentration profiles. Similar observations can be made by comparing Figure 5-9 with Figures 5-4, 5-5, and 5-6.

The Ultrox process was successful in achieving removal efficiencies as high as 90 percent for the total VOCs present in the groundwater at the LB&D site. Based on the data for individual VOCs, removal efficiencies for TCE were greater than 99 percent, and the removal efficiencies for 1,1-DCA and 1,1,1-TCA were as high as 65 and 85 percent, respectively.

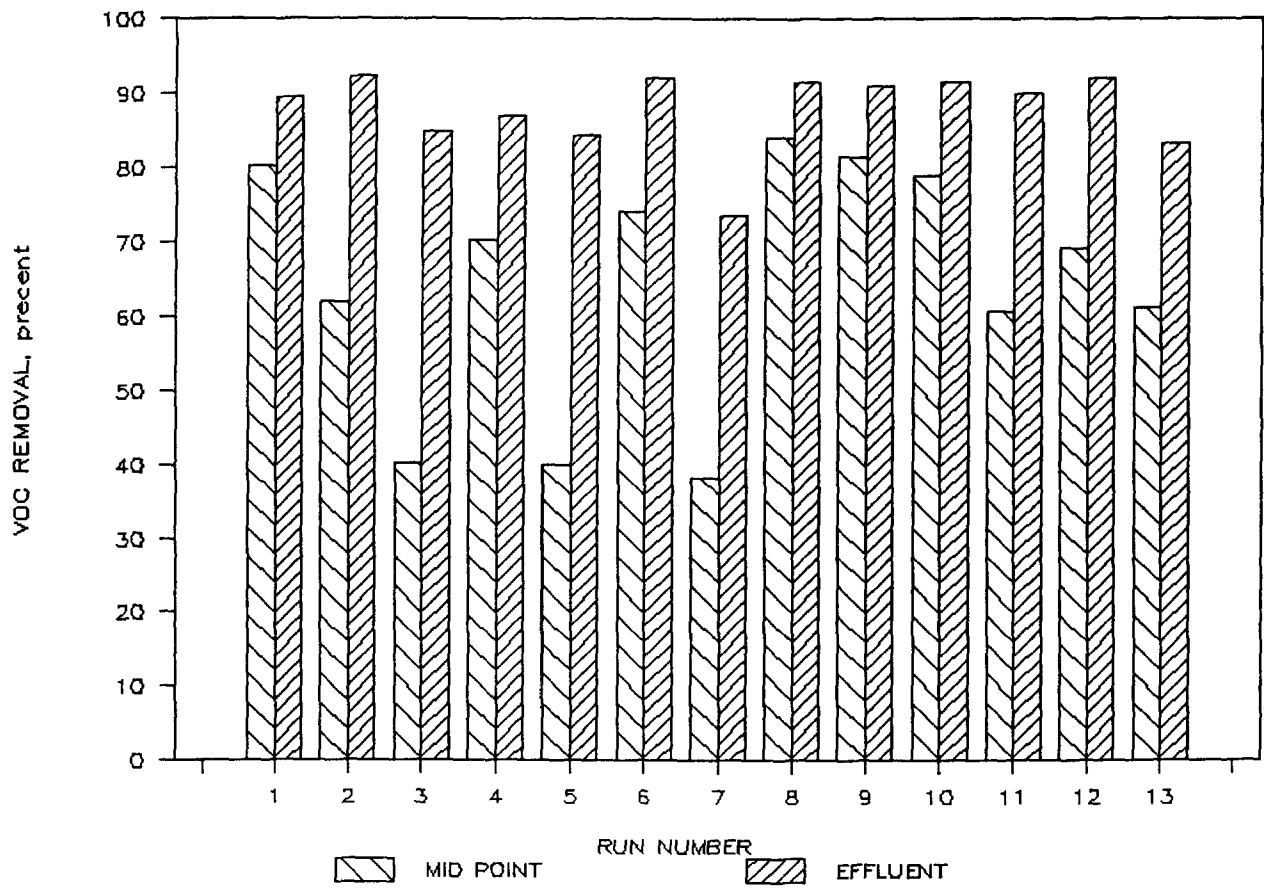
TABLE 5-12  
SUMMARY OF TOTAL VOC CONCENTRATION DATA

Run No.	Influent (µg/L)		Midpoint (µg/L)		% Removed		Effluent (µg/L)		SD		% Removed	
	Max	Min	Mean	Min	Max	SD	Max	Min	Max	Mean	SD	Mean
1	240	160	200	36	42	33	39	36	23	19	1.4	21
2	210	76	160	49	77	55	60.	49	22	6.6	7.9	12
3	220	130	160	19	150	36	96	19	28	19	3.2	24
4	230	130	170	45	60.	40.	51	45	26	19	3.1	22
5	180	130	160	81	110	20.	93	81	26	22	1.8	24
6	210	180	190	44	52	13	50.	44	19	13	2.0	15
7	210	180	190	100	130	11	120	100	61	46	6.5	51
8	190	120	150	18	29	27	24	18	14	12	1.1	13
9	210	140	170	26	35	29	32	26	29	0.082	9.3	16
10	240	120	170	28	41	38	36	28	19	7.8	4.4	14
11	180	140	160	50.	91	16	64	50.	18	12	2.1	16
12	160	130	150	36	55	14	47	36	14	9.0	1.9	12
13	150	63	120	38	61	31	48	38	33	14	6.7	20.
SD	Standard deviation											

**FIGURE 5-8**  
**VOC CONCENTRATIONS**  
**IN DIFFERENT RUNS**



**FIGURE 5-9**  
**VOC REMOVAL IN DIFFERENT RUNS**





At the 95 percent confidence level, the effluent had a few VOCs such as 1,1-DCA and 1,2-DCA that exceeded the discharge standards. However, at the 90 percent confidence level for Run 12, the effluent met the discharge standards. This was because for a few VOCs, the mean effluent concentrations were quite close to the discharge standards.

The VOC air sampling data gathered from air samples taken inside the treatment system indicated that stripping contributed significantly to the total removal (chemical oxidation plus stripping) of 1,1,1-TCA and 1,1-DCA. However, for compounds such as vinyl chloride and TCE, oxidation was found to be the major removal mechanism. For other VOCs such as 1,1-dichloroethene, 1,2-dichloroethene, benzene, acetone, and 1,1,2,2-tetrachloroethane, stripping was insignificant since only occasional traces of these compounds were detected in the off-gas.

All of the VOCs were reduced to below detection limits by the off-gas treatment unit before air was discharged to the atmosphere.

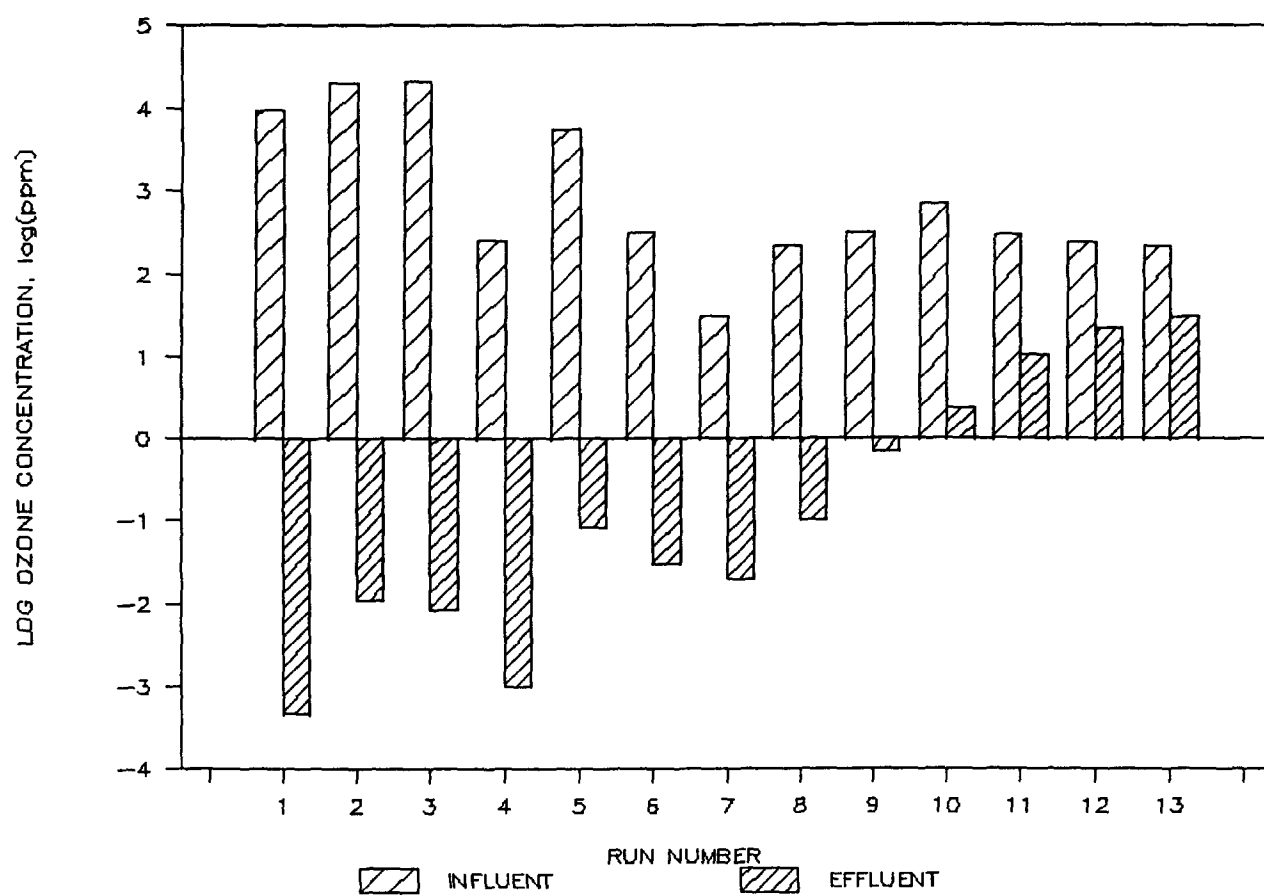
#### **PERFORMANCE OF THE DECOMPOZON UNIT**

The Ultrox system's ozone decomposer (Decompozon) unit, which is designed to destroy ozone in the reactor off-gas, was evaluated to assess destruction efficiency. The ozone concentrations in the influent to the Decompozon unit (reactor off-gas) and in the effluent from the Decompozon unit were analyzed on-site during the demonstration. These ozone concentrations are plotted in Figure 5-10 on a semi-log plot for each run.

Figure 5-10 indicates that the effluent ozone concentrations were quite low (<0.1 ppm) for Runs 1 to 8, approximately 1 ppm in Runs 9 and 10, and greater than 10 ppm in Runs 11, 12, and 13. The higher ozone levels in the effluent for Runs 11 to 13 may be attributable to the malfunctioning heater in the Decompozon unit. The temperature in the Decompozon unit should have been 140°F for the unit to function, whereas the temperature for Runs 11 to 13 was about 80°F. The removal efficiencies plotted in Figure 5-11 indicate that greater than 99.9 percent ozone destruction was achieved in Runs 1 to 10.

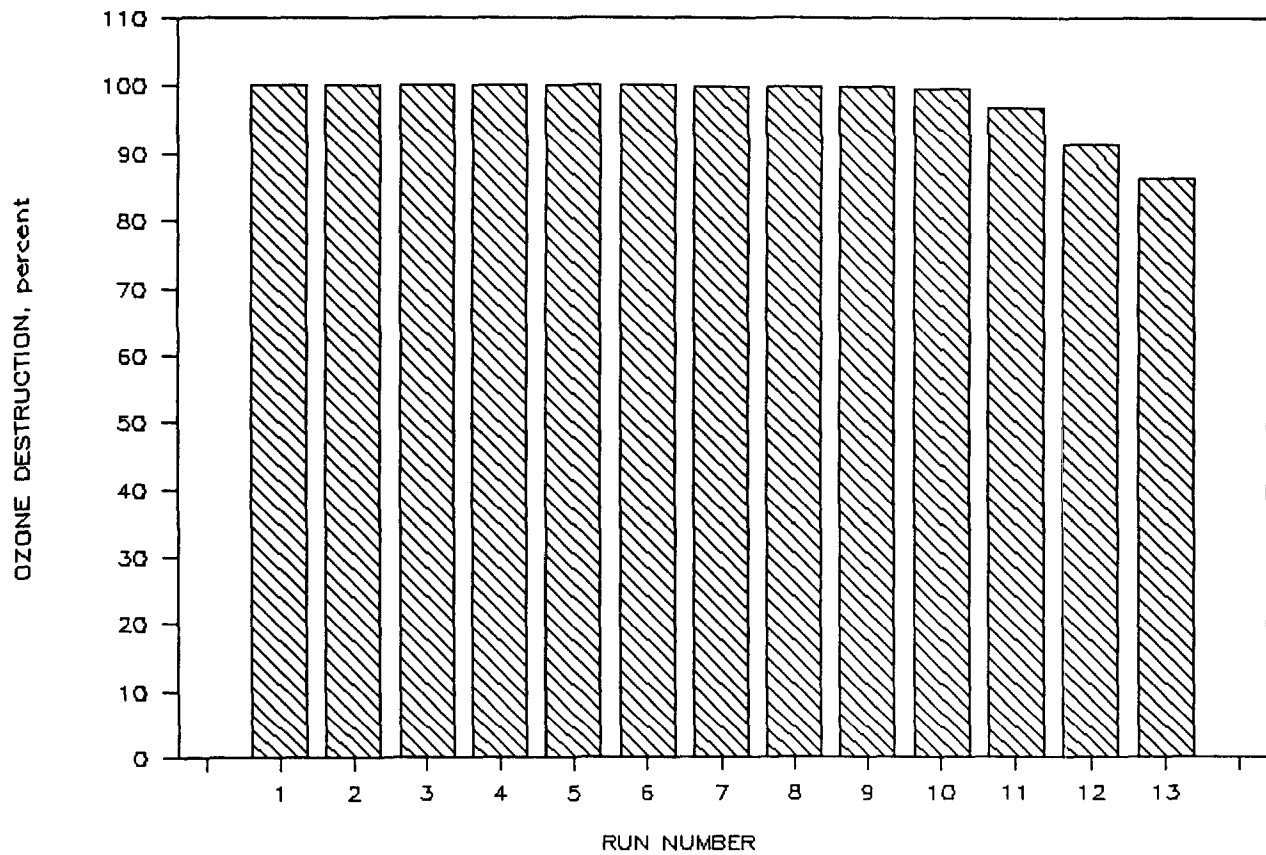
Although the primary function of the Decompozon unit is to remove ozone, the data presented in Figures 5-12 to 5-15 clearly indicates that significant VOC removals occurred in the Decompozon unit when it functioned as designed (Runs 1 to 8).

**FIGURE 5-10**  
**OZONE CONCENTRATIONS IN DIFFERENT RUNS**



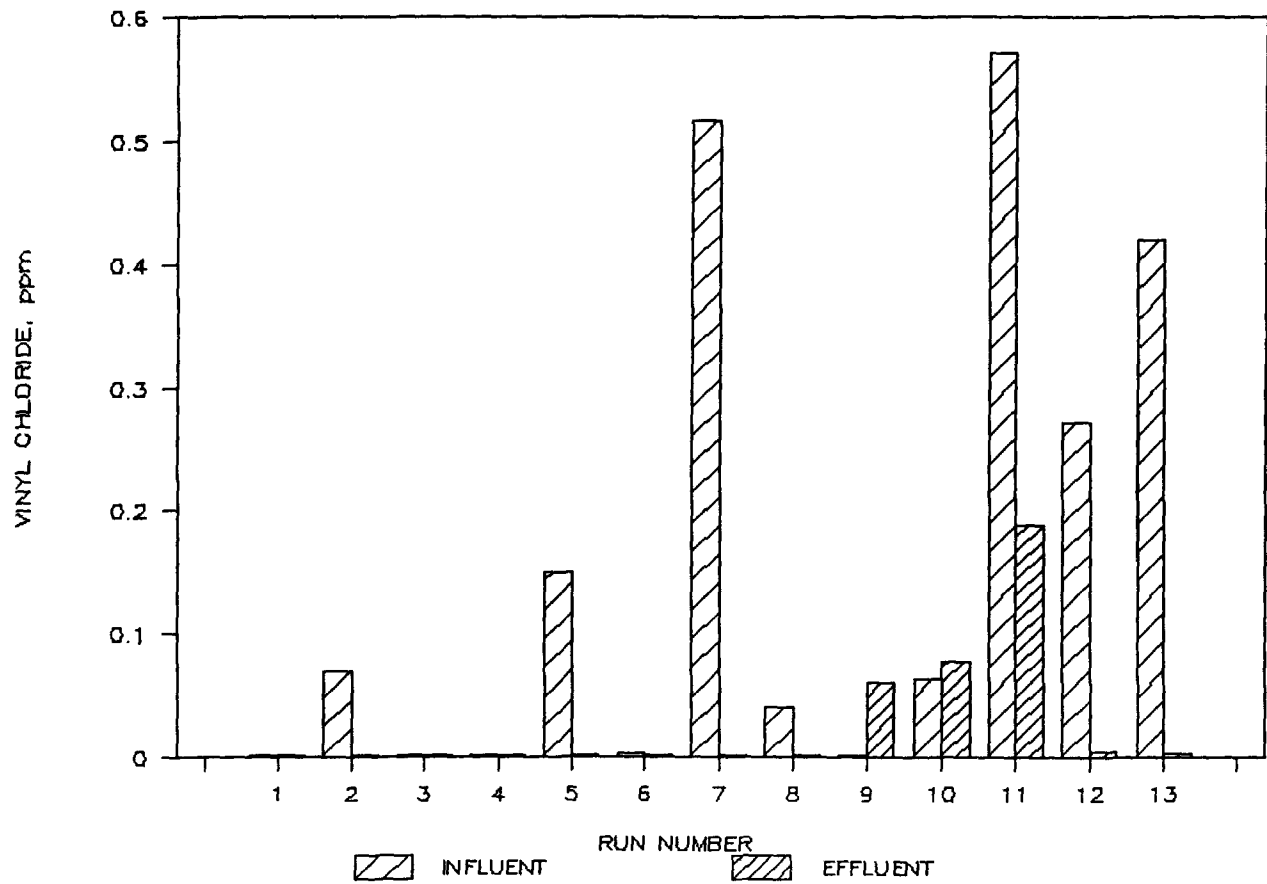
Note: The heater in the Decompozon unit failed after Run 8.

**FIGURE 5-11**  
**OZONE DESTRUCTION IN DIFFERENT RUNS**



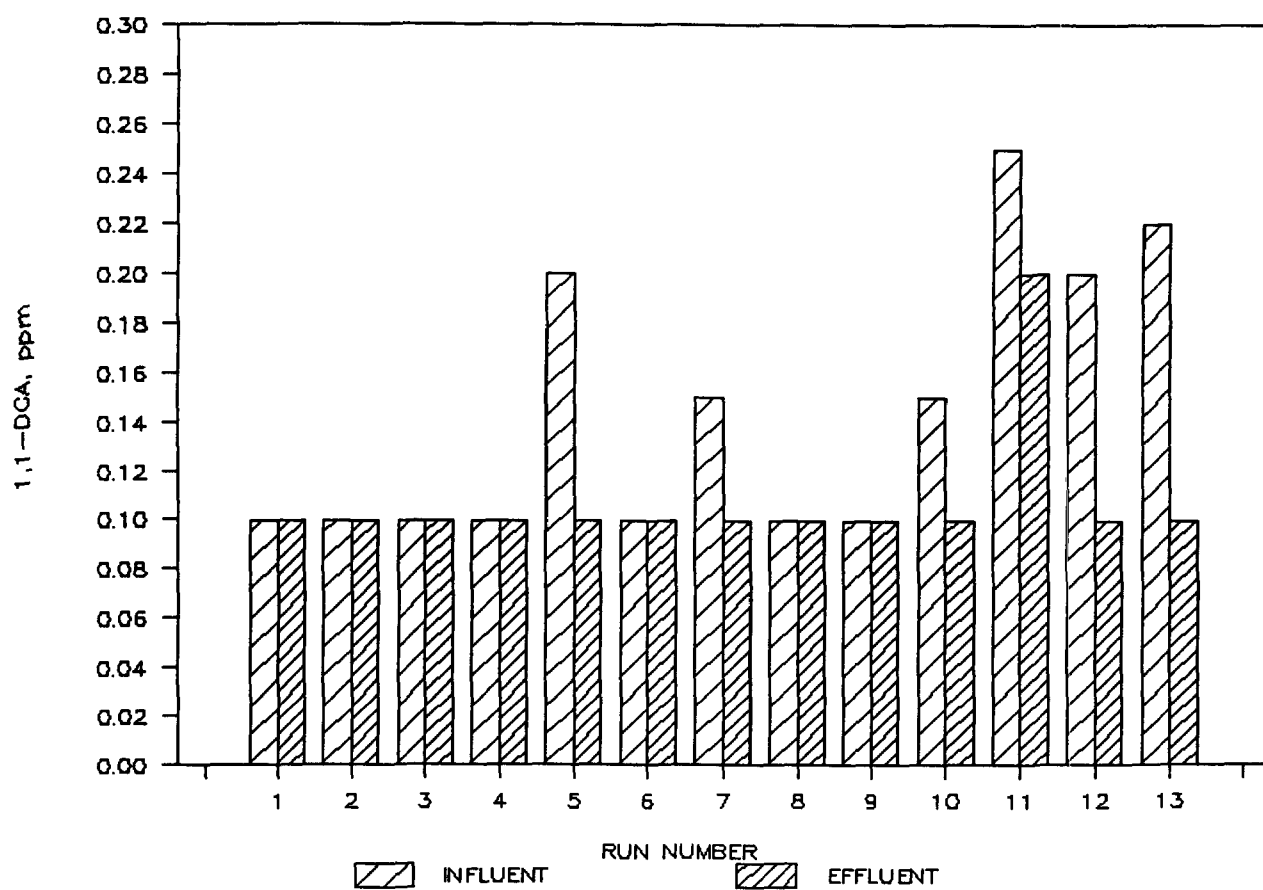
Note: The heater in the Decompozon unit failed after Run 8.

**FIGURE 5-12**  
**VINYL CHLORIDE CONCENTRATIONS IN AIR**



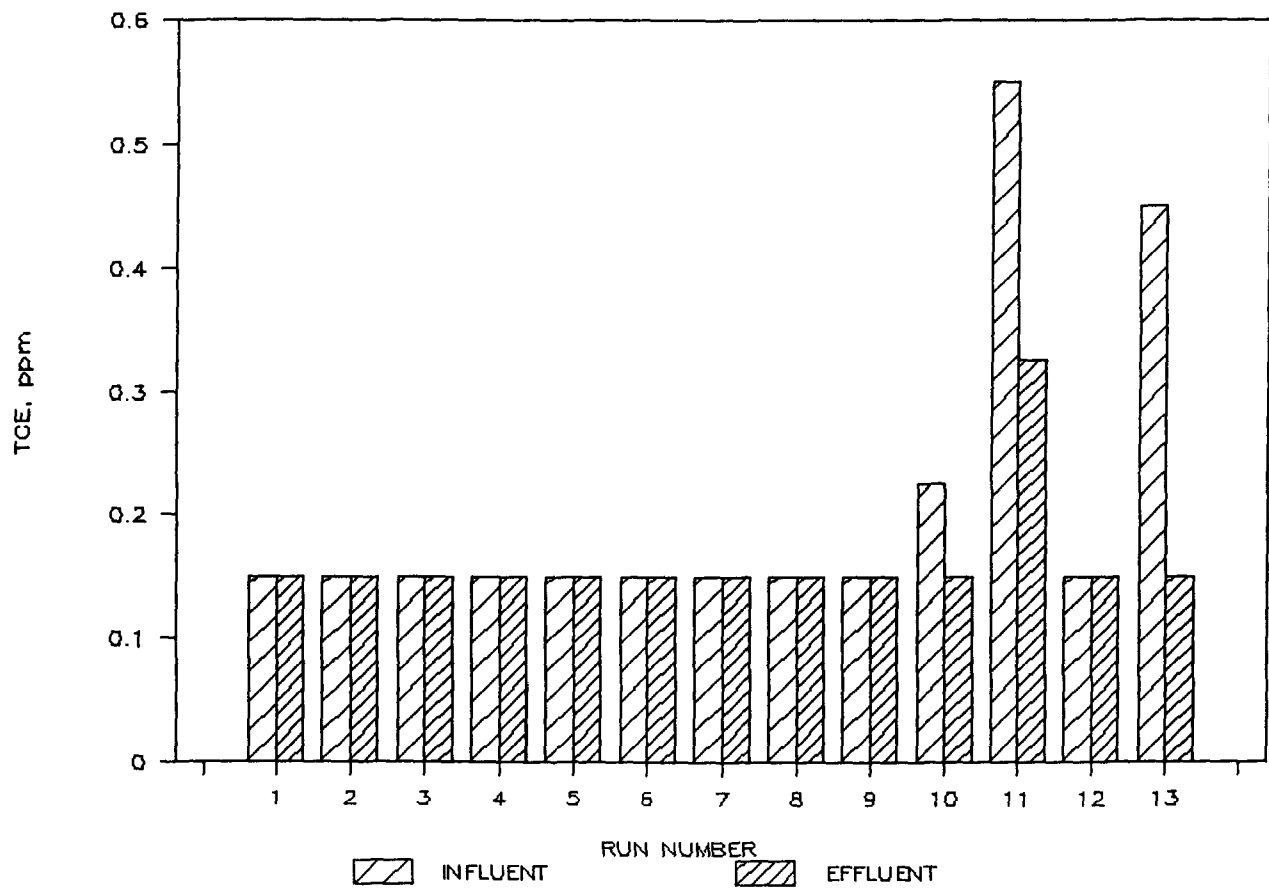
Note: The heater in the Decompozon unit failed after Run 8.

**FIGURE 5-13**  
**1,1-DCA CONCENTRATIONS IN AIR**



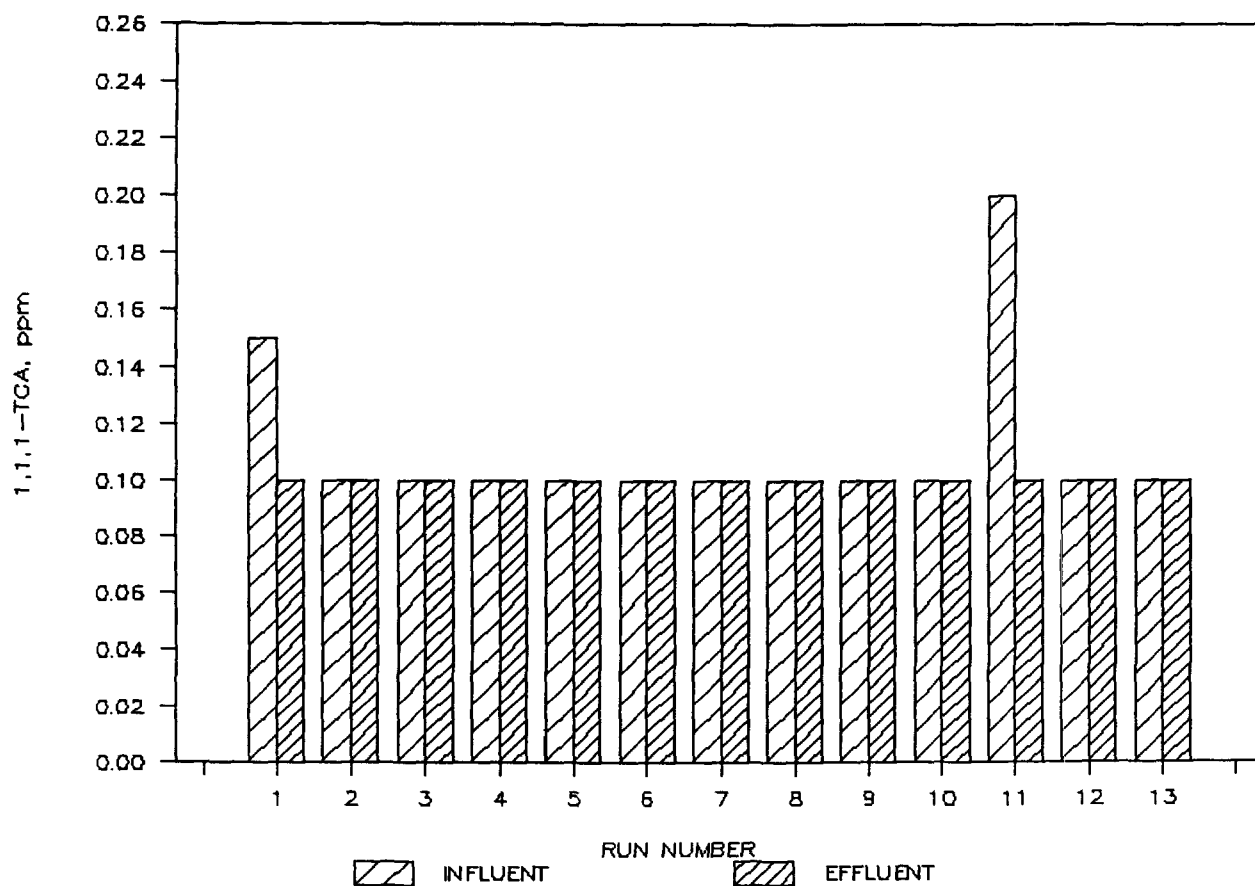
Note: The heater in the Decompozon unit failed after Run 8.

**FIGURE 5-14**  
**TCE CONCENTRATIONS IN AIR**



Note: The heater in the Decompozon unit failed after Run 8.

**FIGURE 5-15**  
**1,1,1-TCA CONCENTRATIONS IN AIR**



Note: The heater in the Decompozon unit failed after Run 8.

## SUMMARY OF RESULTS FOR NONCRITICAL PARAMETERS

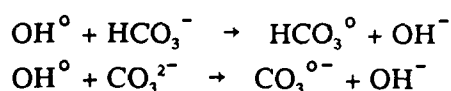
The noncritical parameters for organics included semivolatiles, PCBs/pesticides, and TOC, and the noncritical parameters for inorganics included pH, conductivity, and alkalinity. Additionally, temperature, turbidity, residual oxidants, and electricity consumption were also measured during the demonstration. The results for these noncritical parameters are briefly summarized below.

### Organics

No semivolatiles or PCBs/pesticides were found in the influent. In addition, semivolatiles or PCBs/pesticides were not found in the effluent, which indicates that the Ultrox unit did not generate these compounds. The TOC concentrations in the influent and effluent are plotted in Figure 5-16. Since the curves are close and intersect for all runs except Run 6, no significant TOC removals were achieved. From this data, it appears that the oxidation to carbon dioxide and water did not occur. That is, only partial oxidation was achieved during the treatment operating conditions. However, since no VOCs were found by GC/MS analysis and GC analysis of the effluent, the oxidation products do not appear to be new VOCs. The products may be organic acids, which were analyzed as TOC in the TOC analysis. Since the water had a high alkalinity (950 mg/L as CaCO<sub>3</sub>), the bicarbonate and carbonate ions appeared to have significantly competed with the organics for oxidants.

### Inorganics

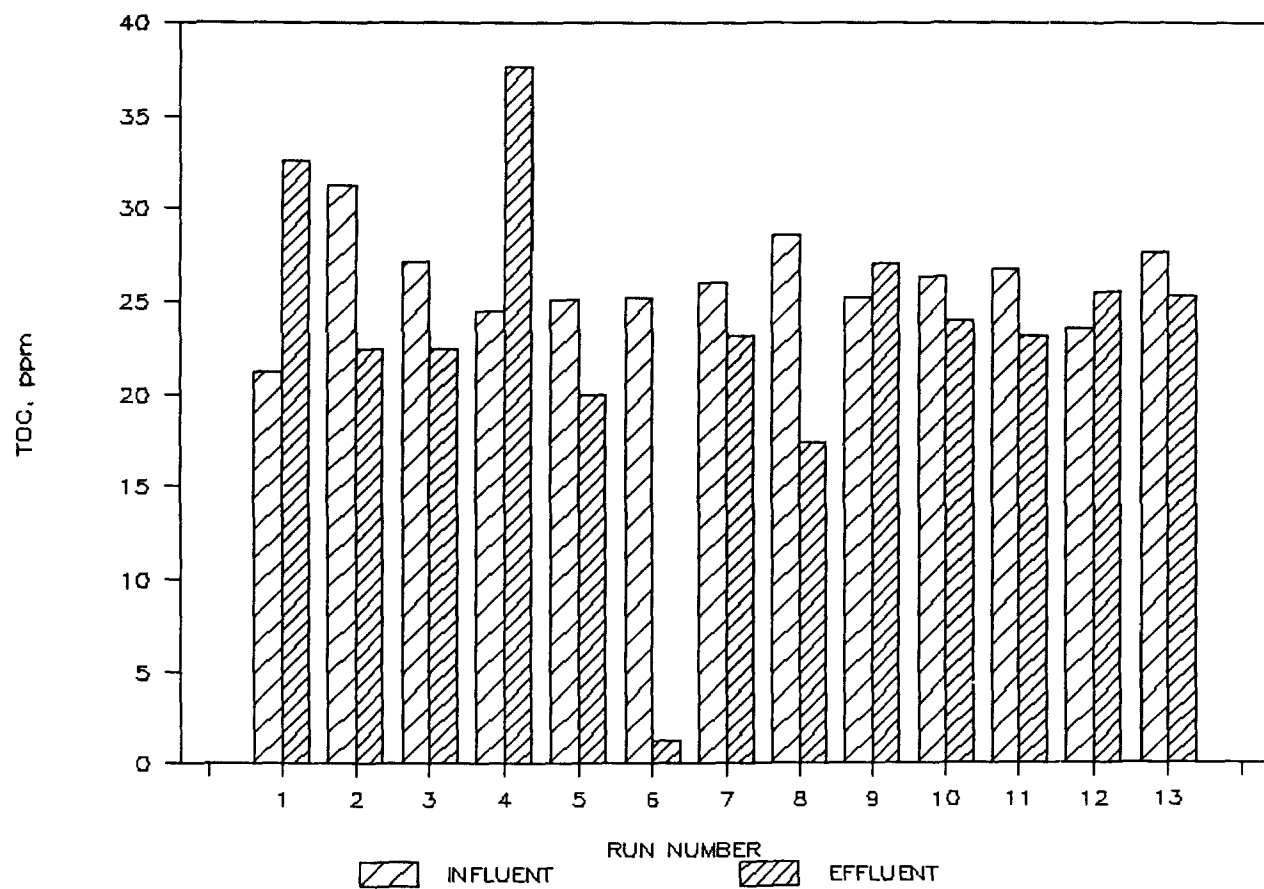
Metals such as iron and manganese were present at low concentrations, and no significant metal removal was observed. No changes in alkalinity and conductivity were observed after the treatment. However, the pH increased by 0.5 to 0.8 units after the treatment. The pH increase does not indicate that organics are being destroyed, since the partial oxidation products are organic acids and the complete oxidation product is CO<sub>2</sub>, which should result in a pH decrease. However, the pH increase is not surprising because the groundwater had high alkalinity and an initial pH of about 7.2, at which the predominant form of alkalinity is bicarbonate. The reaction of hydroxyl radicals (OH<sup>•</sup>) with bicarbonate or carbonate ions yields hydroxyl ions (Hoigne and Bader, 1975) as shown below:



The production of hydroxyl ions would have caused an increase in pH.



**FIGURE 5-16**  
**TOC CONCENTRATIONS IN DIFFERENT RUNS**



### **Miscellaneous Parameters**

Turbidity usually increased by 1 to 4 units (NTU) after the treatment (Figure 5-17). This slight increase in turbidity may be due to the insignificant metal removal by metal oxidation and precipitation.

The temperature increased by approximately 2 to 3 degrees Celsius after the treatment (Figure 5-18). This increase was mainly due to the heat from the UV lamps and was not due to the oxidation of organics. This is because (1) the temperature increase was higher than usual when the hydraulic retention time was increased from 40 minutes to 1 hour (Run 5), and (2) the increase was not observed in Runs 10 and 11 when the UV lamps were used in only three chambers.

Ozone gas transfer to groundwater was greater than 95 percent, with the remaining 5 percent present in the reactor off-gas. After the reaction, the concentrations of residual ozone and residual hydrogen peroxide in the effluent were usually less than 0.1 ppm.

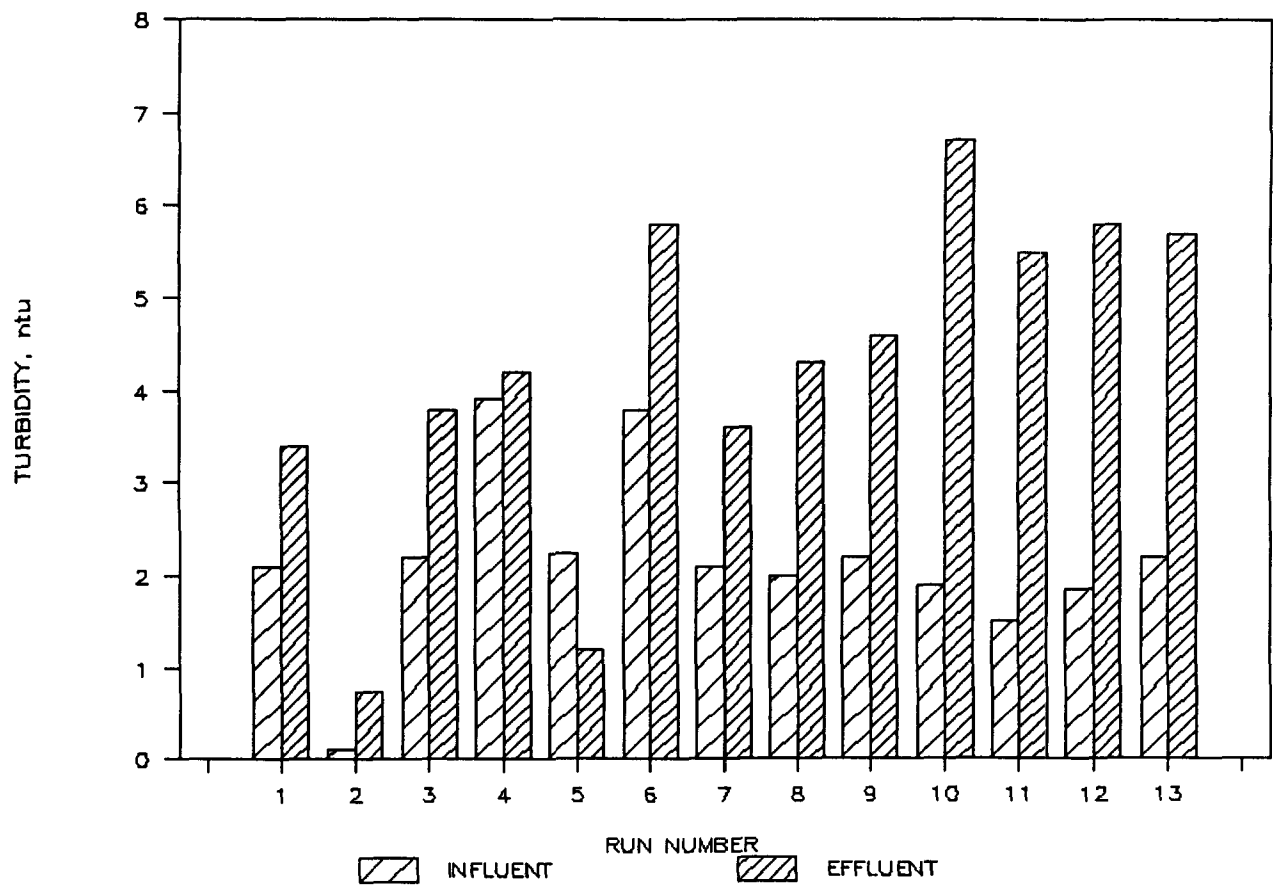
The electrical energy consumption to operate the Ultrox system is plotted as kilowatt hours of electrical energy consumed per unit hour of operation by run number (Figure 5-19). The figure indicates that the average electrical energy consumption was about 11 kWh/hour of operation. It should be noted that the electrical energy consumption was higher in Run 7 (38 mg/L ozone dose) than that in Run 6 (110 mg/L ozone dose), contrary to the prediction. This result cannot be explained.

## **FIELD OPERATIONAL PROBLEMS**

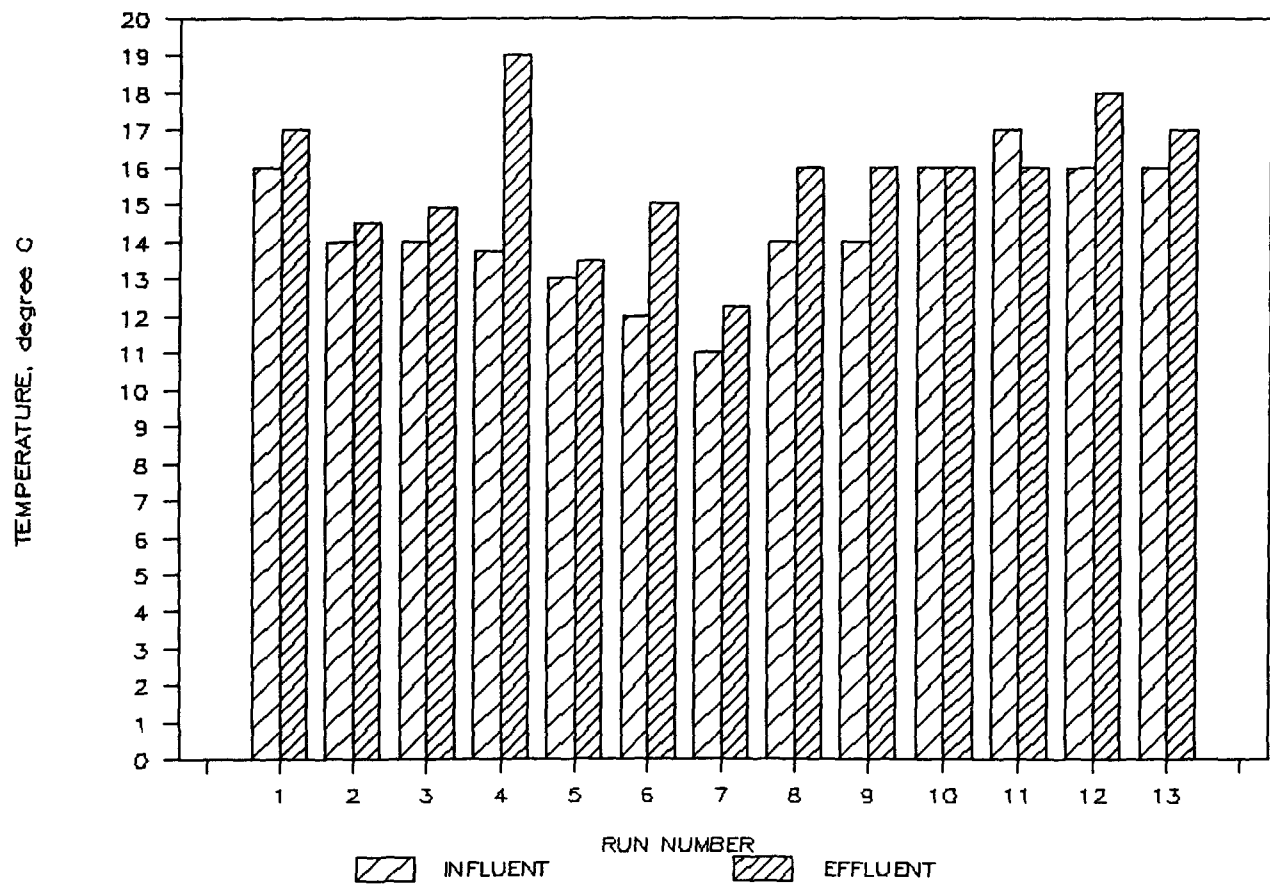
### **Air Sampling**

Sampling of air emissions and the various operating parameters was conducted as described in the QAPP with a few minor exceptions. No replicate sampling or measurement for Run 2 was performed due to the high moisture content in the reactor off-gas during the run, which caused problems with the VOC sampling equipment. In addition, ozone feed rate and concentration, as measured by Ultrox's process instruments, were recorded by field personnel during each test. The reactor off-gas and Decompozon unit exhaust gas temperature was measured using a thermocouple inserted into the gas stream. The reactor off-gas ozone concentration was recorded from an instrument provided by Ultrox. One recording was made every minute during VOC sampling.

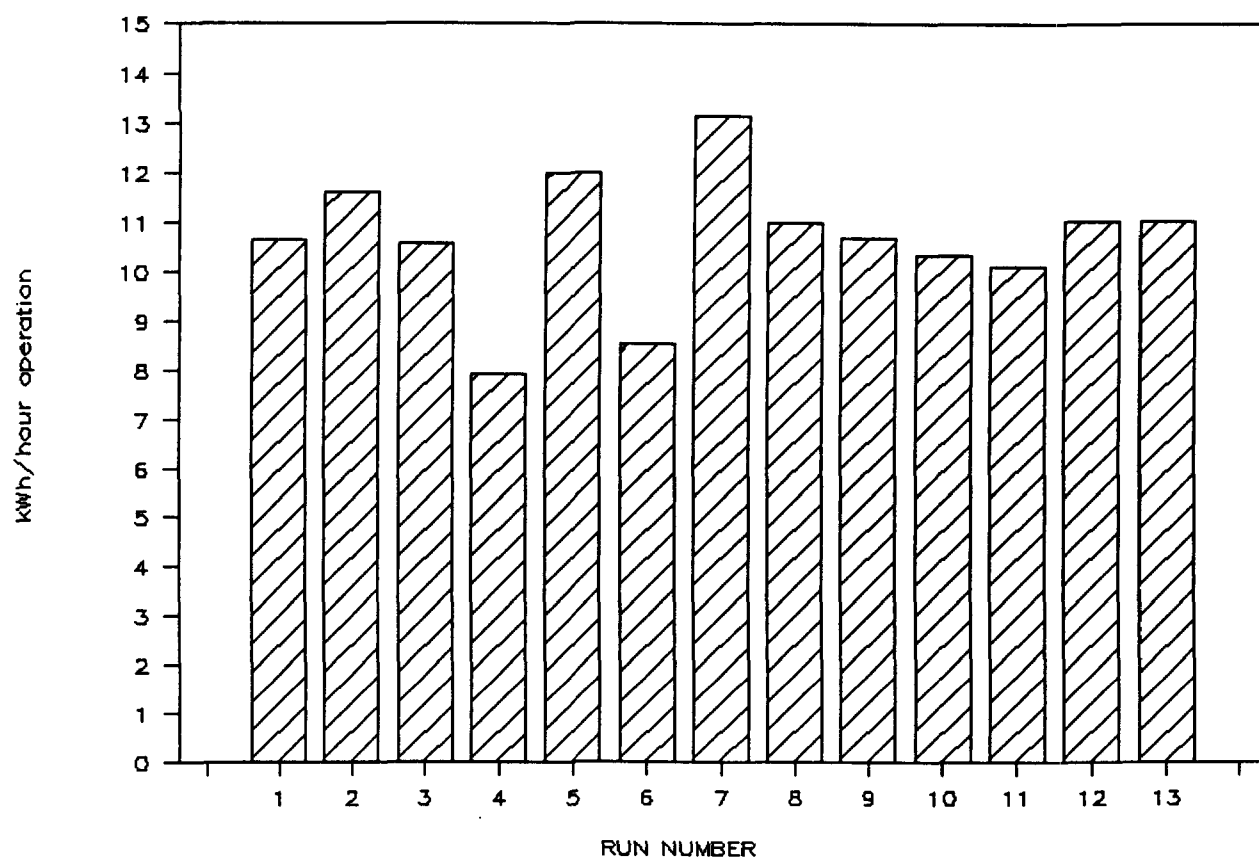
**FIGURE 5-17**  
**TURBIDITY IN DIFFERENT RUNS**



**FIGURE 5-18**  
**TEMPERATURE IN DIFFERENT RUNS**



**FIGURE 5-19**  
**ELECTRICITY CONSUMPTION IN DIFFERENT RUNS**



The Decompozon unit exhaust gas ozone concentration was to be measured using an Ultrox analyzer, calibrated against a primary reference. However, the Ultrox instrument calibration was determined to be incorrect and the photometer of the standard was then used as an ozone analyzer. This was not in accordance with the QAPP (40 CFR 50, Appendix D). A second analyzer was used for Runs 10 through 14. Both the reference standard and second analyzer calibrations were checked after testing. The reference was checked against an NBS traceable standard at the Virginia State Air Pollution Control Board, and the second analyzer was then checked against a reference standard. Both devices met the required linearity limits without adjustment.

### **Electrical Power Supply**

During the course of the field demonstration, two operational problems with the electrical power supply were encountered. These were: (1) a wiring problem affecting electricity measurements for two runs; and (2) an electrical power shutdown caused by a minor accident at the site.

Separate watt-hour meters and service panels were installed for the Ultrox system and the on-site trailer. During the second run, it was discovered that both the trailer and the Ultrox system were inadvertently wired to a common meter. An electrical subcontractor rewired and set each meter properly. Since Runs 1 and 2 were conducted with common metering for the trailer and the Ultrox system, the electrical energy consumption for these two runs could only be estimated. Although the trailer consumed varying amounts of electrical energy for heat, lights, instruments (including a water bath), and other miscellaneous uses, the electricity consumption for the first two runs can be estimated by analyzing the power consumed on subsequent runs. With two meters working during the remaining runs, the electrical energy consumption measurements could be easily made for Runs 3 to 13. However, based on the electrical energy consumption observed in Runs 3 to 13, the electrical energy consumption by the trailer appears to be negligible.

A 480-watt, 3-phase electrical service was provided at the site using a transformer to convert the available utility power to operate the Ultrox system. At the end of Run 9, a truck with a trailer entered the site premises and accidentally broke the wooden power pole that supported the electric power lines by catching the sagging lines with the trailer. Although the accident did not cause any injury to the people working on-site or damage any equipment, as a precautionary measure, the power was shut off, and the electrical subcontractor was contacted to install a new power pole. A stronger pole was installed, and power restored the following morning.

## SECTION 6 COST OF DEMONSTRATION

The cost of conducting the EPA SITE demonstration of Ultrox International's ultraviolet (UV) radiation/oxidation technology on the contaminated groundwater at the Lorentz Barrel and Drum site was approximately \$633,000. This cost includes site characterization and preparation, demonstration planning and field work, chemical analyses, and report preparation. The developer's portion of this cost was \$23,000 and the balance of \$610,000 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 \$100) 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 reports.

#### Phase I: Planning

Phase I activities included:

- UV radiation/oxidation technology review
- Protocol evaluation
- Site sampling and treatability testing
- Development of the demonstration plan
- Site subcontractor procurement

Costs for Phase I are summarized below by cost category:

Labor	\$ 74,700
Equipment and supplies	8,800
Travel	6,700
Chemical analyses	<u>10,800</u>
Total	\$ 101,000

## **Phase II: Demonstration**

Phase II activities included:

- Site preparation, mobilization, and demobilization
- Sample collection and field oversight
- Chemical analyses
- Report preparation

Costs for Phase II are summarized below by cost category:

Labor	\$ 175,200
Equipment and supplies	116,200
Travel/transportation	6,000
Chemical analyses	180,800
Subcontractors	<u>31,100</u>
Total	\$ 509,300

Labor costs include estimates through report preparation. Subcontractors costs include electrical, mechanical, piping, and security work.

## **DEVELOPER COSTS**

Ultrox provided the costs presented in this section. They are actual costs incurred by Ultrox in preparing for and conducting the SITE demonstration.

Labor	\$ 5,900
Laboratory	3,700
Travel	3,700
Equipment (using retail rate)	7,300
Freight	1,600
Raw material	100
Health & safety	<u>800</u>
Total	\$ 23,100

Equipment and parts were both rented and purchased. Hydrogen peroxide and acid were the purchased raw materials. Ultrox estimates the purchase price of the field unit at approximately \$140,000.



## SECTION 7

### CONCLUSIONS AND RECOMMENDATIONS

#### CONCLUSIONS

The groundwater treated by the Ultrox system met the applicable National Pollutant Discharge Elimination System (NPDES) standards for discharge into Coyote Creek, a nearby watercourse, at the 95 percent confidence level under certain operating conditions. Success was obtained by using a hydraulic retention time of 40 minutes; ozone dose of 110 mg/L; hydrogen peroxide dose of 13 mg/L; all 24 UV lamps operating; and influent pH of 7.2 (unadjusted).

There were no volatile organics detected in the exhaust from the ozone decomposer (Decompozon) unit.

The Decompozon unit destroyed ozone in the Ultrox reactor off-gas to levels less than 0.1 ppm (OSHA Standards). The ozone destruction efficiencies were observed to be greater than 99.99 percent.

The Ultrox system achieved removal efficiencies as high as 90 percent for the total VOCs present in the groundwater. The removal efficiencies for trichloroethylene (TCE) were greater than 99 percent. However, the maximum removal efficiencies for 1,1-dichloroethane (1,1-DCA) and 1,1,1-trichloroethane (1,1,1-TCA) under optimal operating conditions were about 65 and 85 percent, respectively.

Within the treatment system, the removals of 1,1-DCA and 1,1,1-TCA appear to be due to both chemical oxidation and stripping. Specifically, stripping accounted for 12 to 75 percent of the total removals for 1,1,1-TCA, and for 5 to 44 percent of the total removals for 1,1-DCA. However, stripping accounted for less than 10 percent of the total removals for TCE and vinyl chloride. For other VOCs such as 1,1-dichloroethene, benzene, acetone, and 1,1,2,2-tetrachloroethane, stripping was negligible. Volatile organics present in the gas phase within the reactor at levels of approximately 0.1 to 0.5 ppm were removed to below detection levels in the Decompozon unit.

Based on the gas chromatography (GC) and GC/mass spectrometry (MS) analyses performed for VOCs, semivolatile organics, and PCBs/pesticides, no new compounds were detected in the treated water. The organics analyzed by GC methods represent less than two percent of the total organic carbon (TOC) present in the water. Very low TOC removal occurred,

which implies that partial oxidation of organics (and not complete conversion to carbon dioxide and water) took place in the system.

The Ultrox system's average electrical energy consumption was about 11 kilowatt-hours/hour of operation.

## **RECOMMENDATIONS**

Based on the experience gained during the demonstration, the following recommendations are made:

Electrical lines (480 v) were found to be a potential source for danger due to possible vehicular accidents. Although adding to the cost of the demonstration, it would have been worthwhile to bury the electrical lines to provide a safer work atmosphere. Alternatively, the lines could have been placed clear of any possible transportation routes or elevated to a height necessary to accommodate truck clearance. Electrical portable generators, as a backup, could also have been provided.

Due to the heater failure in the Decompozon unit during the latter part of the demonstration period, levels of ozone exceeding safety standards were emitted to the atmosphere from the system. At its permanent installations, Ultrox incorporates interlocks for emergency automatic shut-off of the treatment unit if the heater fails so that operating personnel will not be exposed to ozone even for short periods. This feature should be used at similar type demonstrations.

The bladder tanks, made of synthetic materials suitable for potable water storage and used to store the influent, were helpful in minimizing the VOC losses over the two-week test period. Other demonstrations should consider this alternative if VOC losses need to be minimized. One limitation with regard to the use of bladders is the potential that they could be punctured through vandalism, if proper security is not present at the demonstration site. They are also difficult to handle and could be torn or punctured during normal operations unless care is exercised.

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