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**PROJECT TITLE: "Use of Sonication for In-Well Softening of Semivolatile Organic Compounds"**

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## ABSTRACT

This project investigates the *in-situ* degradation of semivolatile organic compounds (SVOCs) and volatile organic compounds (VOCs) using in-well sonication, in-well vapor stripping, and bioremediation. Pretreating groundwaters with sonication techniques *in-situ* would form VOCs that can be effectively removed by in-well vapor stripping and bioremediation. The mechanistic studies focus on the coupling of megasonics and ultrasonics to "soften" (i.e., partially degrade) the SVOCs; oxidative reaction mechanism studies; surface corrosion studies (on the reactor walls/well); enhancement due to addition of oxidants, quantification of the hydroxyl radical formation; identification/quantification of degradation products; volatility/degradability of the treated waters; development of a computer simulation model to describe combined in-well sonication/in-well vapor stripping/bioremediation; systems analysis/economic analysis; large laboratory-scale experiment verification; and field demonstration of the integrated technology. Benefits of this approach include: (1) Remediation is performed *in-situ;* (2) The treatment systems complement each other; their combination can drastically reduce or remove SVOCs and VOCs; (3) Ability to convert hard-to-degrade organics into more volatile organic compounds; (4) Ability to remove residual VOCs and "softened" SVOCs through the combined action of in-well vapor stripping and biodegradation; (5) Does not require handling or disposing of water at the ground surface; and (6) Cost-effective and improved efficiency, resulting in shortened clean-up times to remediate a site.

## 1 PROJECT OBJECTIVES

The specific objective of the proposed work is to investigate the *in-situ* degradation of semivolatile organic compounds (SVOCs) and to:

- Determine the system performance of the combined in-well sonication, vapor stripping, and biodegradation to destroy VOCs and change SVOCs into VOCs;
- Determine how the combined in-well vapor stripping, sonication, and *in-situ* biodegradation remedial system functions together at the laboratory-scale to remove SVOCs and VOCs;
- Determine the chemical reaction mechanisms for destroying VOCs and changing the SVOCs into

VOCs, and improve the overall system performance;

- Quantify the roles of the individual treatment components (sonication, in-well vapor stripping, and biodegradation) on the overall effectiveness of the remediation, and acceleration. It deals with novel bioremediation reactions, alternative electron acceptor conditions, and modeling the overall system;
- After water is treated in the well with sonication and VOCs are partially removed through in-well vapor stripping, determine the role of volatilization and microbial activity on water containing VOCs that is forced to infiltrate through the unsaturated zone;
- Determine the effect of sonication/megasonics on well corrosion, and
- Identify the appropriate system design for scale-up of the remedial system for demonstration in the field and deployment.

This project has as its goal the softening of the more recalcitrant organic compounds (e.g., SVOCs and nonvolatile organic compounds) in order to convert them into compounds that are more amenable to both vapor stripping and biological treatment. The SVOCs are not effectively removed from solution using air sparging techniques. Conversion of SVOCs to VOCs could allow effective removal of the organics with vacuum extraction techniques or *in-situ* biotreatment. This project investigates the combined treatment using in-well sonication. in-well vapor stripping, and biodegradation. The proposed work will examine the use of sound-wave energies (e.g., ultrasonics and megasonics) to transform the SVOCs to VOCs. Performing the softening in-well would permit the treated organics to be reinjected and percolated through the subsurface, thereby enhancing biodegradation rates by generating organics that are more easily biodegraded. Successful implementation of such an approach would considerably reduce both the time and cost of *in-situ* biotreatment. Pretreating groundwaters with sonication techniques would form VOCs that could be removed effectively by either bioremediation technologies or a dual vapor extraction technique (being developed by Stanford University under the VOC-Arid Program, now part of the Plumes Focus Area). Sonication could also be coupled with technologies aimed at mobilizing dense non-aqueous phase liquids (DNAPLs) in the subsurface, such as surfactant flooding.

## 2 INTRODUCTION/DESCRIPTION OF TECHNOLOGY

An extensive discussion of the principles behind sonication was provided in the original research proposal for this program. The concept behind using sonication to “soften” halogenated organic compounds and polyaromatic hydrocarbons is relatively simple. By “softening”, we mean partial degradation of VOCs and SVOCs. Previous biodegradation studies have demonstrated relatively long periods of time are required to biologically remediate many aquifers contaminated with halogenated compounds. However, many of the corresponding non-halogenated organic compounds are relatively easily microbially degraded to innocuous products such as carbon dioxide ($CO_2$). By using the sonication step to quickly remove the bound Cl from a molecule. the by-product or remaining organic compound can be easily degraded under anaerobic or aerobic conditions.

This approach eliminates the costly proposition of using in-well sonication for a relatively long detention time to render the halogenated compounds innocuous to HCI and $CO_2$. Using sonication to enhance the relatively slow step in microbial degradation (i.e., dehalogenation) will allow remediation to occur at a much faster rate. This technology can be used at sites where natural attenuation is not a realistic option. At facilities where the contamination is moving “beyond the fence”. a line of treatment wells could be set-up to prevent halogenated compounds from moving off-site. The “by-products” can be degraded by natural attenuation.

The in-well sonication process utilizes *in-situ* ultrasonics/acoustics in a down-hole well for destruction/conversion of organic contaminants from groundwater, described in an Invention Disclosure filed

by Peters and Wu [ 1995]. Treatment is accomplished by circulating groundwater through the ultrasonic reactor and reinjecting the treated water into the unsaturated (vadose) zone rather than lifting the treated water to the ground surface. The ultrasonically treated water, partially or completely free of contaminant concentrations, infiltrates back to the water table. This process is continued until the contaminant concentrations are sufficiently reduced. Addition of oxidants/catalysts into the process may further enhance the process efficiency and reduce the required sonication period. Use of an in-well ultrasonic reactor. potentially coupled with megasonics, which is more one-directional in nature, may be required for more recalcitrant organic contaminants [Peters and Wu. 1995].

The in-well vapor stripping component of this combined sonication and stripping remedial technology is based on a special well design (See Figure 1) developed by Stanford University [Gorelick and Gvirtzman. 1993, 1995] that removes VOCs from groundwater without bringing the water to the surface for treatment. The well itself is screened at depth below the water table and allows groundwater contaminated with VOCs to enter the well. An upper screened interval is located above the water table and allows water depleted in VOCs to be returned to the aquifer. An eductor pipe is installed inside the well casing, creating a “well-within-a-well”. Inside the inner well, an air line is introduced into which air is injected. The air is released beneath the water table, creating bubbles that rise. A simple separator plate (or well packer) is located within the inner well at an elevation above the water table. As the water/bubble mixture hits this separator plate, the water is forced laterally into the outer well and exits into the vadose zone through the upper screened interval. From there, the water freely infiltrates back to the water table. The air bubbles, enriched in VOCs, are released into the outer well and are extracted to the ground surface under a vacuum.

In-well vapor stripping operates on two basic principles: groundwater recirculation and volatilization. Groundwater recirculation is accomplished using a dual-screened recirculation well. Air-lift pumping occurs when air is injected into the well. The density difference between the water outside the well and the water/bubble mixture within the inner well causes a lift to be created [François et al., 1996]. Water and air rise within the inner well, forcing additional water to flow from the aquifer into the well through the lower screened interval. The water and bubble mixture flows upward in the annular space around the air line. Because the water enters the well as the lower screened interval and returned to the water table, a groundwater circulation cell is developed in the vicinity of the well. The second operating principle is that of volatilization [Gvirtzman and Gorelick, 1992, 1993; Pinto, 1996]. When contaminated water enters the well at the lower screened interval, it encounters the injected air which has formed bubbles. The VOCs will volatilize and mass is transferred from the water to the gas phase. Given approximately 20 feet of contact distance between the contaminated water and the air bubbles, equilibrium partitioning occurs. The air within the well strips out the VOCs. During a demonstration conducted at Edwards Air Force Base demonstration, approximately 90% of the TCE was stripped from the water with each pass through the well. This air is separated from water using the separator plate located above the upper screened interval and the VOC-enriched vapor is vacuumed off and treated by sorption onto granular activated carbon. The water exiting the well at the upper screened interval has then been depleted of VOCs and is returned to the aquifer where microbial degradation can occur. depending upon the type of compound, and during sequential passes through the treatment well, additional VOCs are stripped and removed. In-well vapor stripping has efficacy at any level of contaminant concentration and can be particularly effective when VOC concentrations are high.

The combined remedial system will take contaminated water and remove a significant portion of the SVOCs and VOCs in the well (the treatment well). The system operates by employing groundwater recirculation as described previously. Contaminated water enters the well and with each pass through the well contaminants are removed by both sonication and volatilization. As seen in Figure 2, a radial clean-up zone is created around the well. The figure shows “snap shots” of the clean zone for different times and indicates the expected growth of the zone. Previous work on recirculation wells [Philip and Walter. 1992; Kabala, 1993;

Herrling et al., I99 I ; Gvirtzman and Gorelick, 1992] has shown that a single well can achieve a zone of cleanup that extends radially 2 to 3 times the aquifer thickness. Groundwater entering this zone under regional flow conditions will be recycled and cleaned. It is expected that with each pass through the well, in-well vapor stripping will remove approximately 90 to 99% of the VOCs, and sonication will remove 9O+%. Any residual VOCs may be biodegraded as the water enters the unsaturated zone. In addition, the VOC vapors that are produced by the in-well vapor stripping system may be treated at the ground surface or may be degraded *in-situ* in the unsaturated zone through microbial activity.

## 3 RELEVANCE TO EMSP GOALS

This research work is consistent with the mission of providing the scientific understanding needed to develop methods for accelerating biodegradation processes for remediation of contaminated soils, sediments, and groundwater at DOE facilities. This project relates to *in-situ* chemical transformation, volatilization, and biodegradation; it deals with novel bioremediation reactions, alternative electron acceptor conditions, and modeling. Once sufficiently developed, the technique could be demonstrated at sites such as Hanford's 200 Area, Savannah River's A/M Area, the Paducah Gaseous Diffusion Plant's NE and NW Plumes, Argonne's 317/319 Area, and Lawrence Liver-more's Main Site.

## 4 ADVANTAGES OF THE IN-WELL SONICATION/IN-WELL VAPOR STRIPPING/IN-SITU BIODEGRADATION APPROACH

The research work is consistent with the mission of providing the scientific understanding needed to develop methods for accelerating biodegradation processes for remediation of contaminated soils, sediments, and groundwater at DOE facilities. This project relates to *in-situ* chemical transformation (e.g., softening of SVOCs), in-well vapor stripping, and biodegradation. The proposed technology couples in-well sonication, in-well vapor stripping, and biodegradation into an integrated process. By partially destroying the SVOCs (e.g., opening up the benzene-ring structures), the ability to remove the resultant VOCs and biotreatment of the resultant organics is enhanced (over the case of biotreatment alone). Advantages of this technique include:

- Remediation is performed *in-situ* (i.e., does not require handling or disposing of water at the ground surface);
- Treatment systems complement each other and their combination has the potential to drastically reduce or remove SVOCs and VOCs;
- System has the potential to add other innovative components (such as *in-situ* chemical treatments or surfactants);
- Ability to convert hard-to-degrade organics such as chlorinated organics and heavy organics (e.g., polyaromatic hydrocarbons) into more volatile organic compounds;
- Ability to destroy chlorinated organic compounds;
- Ability to remove residual VOCs and softened SVOCs through the combined action of in-well vapor stripping and biodegradation;
- Improved *in-situ* biotreatment of contaminated soils and groundwater;
- Cost-effective and improved efficiency thereby shortening the time required to clean-up a contaminated site.

## 5 TECHNICAL ISSUES

A number of issues need to be addressed to develop and demonstrate the in-well softening technology, as summarized below:

- Design of in-well system/couple with ultrasonics/megasonics;
- Identification of breakdown/daughter products and their volatilities;
- Biodegradability of parent and breakdown/daughter products;
- Measurement of OH•, H•, and other radicals, and investigation of their roles in the chemical reactions;
- Mass balance closure;
- Investigation of key parameters affecting process (e.g., dissolved gases, salt concentration, etc.);
- Fouling/scaling of process under hard water environments;
- Zone of influence, treatment zone, and time requirements in subsurface (modeling); and
- Enhancements afforded with $H_2O_2$ or Fenton's Reagent

These issues are addressed in the various tasks described in this proposal, in order to develop the technology for deployment.

The proposed technology couples in-well sonication, in-well vapor stripping, and biodegradation into an integrated process. By partially destroying the SVOCs (e.g., opening up the benzene-ring structures), the ability to remove the resultant VOCs and biotreatment of the resultant organics is enhanced (over the case of biotreatment alone).

## 6 APPROACH

This research is a collaborative effort among applied and basic research groups at Argonne, the California Institute of Technology (Caltech), and Stanford University. In addition to the overall management of the project, Argonne's responsibility will include investigations on the decomposition of SVOCs and VOCs using a laboratory-scale reactor, model simulation of the reaction mechanisms (with information obtained from Argonne and Caltech) and optimization of the operating conditions, validation of the theoretical model and the optimized operating conditions using a small-scale laboratory well unit, identification and quantification of corrosion and scale potential, and engineering design and testing of a pilot-scale in-well ultrasonic/megasonic reactor. The mechanistic studies proposed will address the following areas:

- Coupling of megasonics and ultrasonics for softening of more recalcitrant organics
- Studies of oxidative reaction mechanisms
- Investigations of surface corrosion mechanism studies (on the reactor walls/well)
- Studies of salt formation mechanisms in the field of ultrasonics
- Characterization of the catalytic effects associated with addition of oxidizing/reducing agents (e.g., hydrogen peroxide, ozone)
- Quantification of hydroxyl radical formation
- Molecular modeling of SVOC softening reactions

Tasks to be performed in this study (over the three year period) include the following:

*Task 1. Quantify representative VOC und SVOC contaminants at DOE facilities*

In consultation with DOE and the Plumes Focus Area. representative target VOCs and SVOCs will be

determined. Potential VOCs and SVOCs present at various DOE facilities include: trichloroethylene (TCE), trichloroethane (TCA), 1 ,2-ethylene dibromide (EDB), carbon tetrachloride (Ccl,), chloroform ($CHCl_3$), vinyl chloride (VC), 1, 1 -dichloroethylene (DCE), 1,1,2,2-tetrachloroethylene (PCE), and polychlorinated biphenyls ( PCBs). The contaminants $CCl_4$, TCE, TCA. PCE, and EDB were selected for this study. Physical properties of these contaminants are listed in Table A. I in the Appendix.

*Task 2. Conduct batch sonication experiments to determine preliminary optimal conditions for subsequent continuous-flow experiments*

Batch laboratory experiments will be conducted to identify key process parameters such as solution pH values. steady-stated operating temperature, ultrasonic power intensities, and oxidant concentrations. This task is a collaborative effort between Argonne and the California Institute of Technology (Caltech).

*Task 3. Perform batch experiments for measuring hydroxyl/hydrogen radicals in solution*

Hydroxyl radicals can be trapped by direct reaction with terephthalic acid and will be measured using a fluorimeter (the emission is measured at 425 nm). Measurement of the radical intermediates will be conducted at Caltech. The quantification of hydroxyl and hydrogen radicals will be quantified for various operating conditions (e.g., solution pH values, steady-stated operating temperature, ultrasonic power intensities, and oxidant concentrations). Caltech has the major responsibility for this task.

*Task 4 Conduct continuous-flow experiments for degradation of SVOCs and identfiication or quantification of by-products*

The degradation products will be determined by GC (or GUMS) analysis for various sonication operating conditions. This task is a collaborative effort between Argonne and Caltech. The resulting degradation products are being identified and characterized in terms of their volatility and biodegradability.

*Task 5. Investigate the chemical reaction mechanism to improve system performance*

Model simulations of the chemical reactions will be performed using the data obtained in Tasks 2 and 3. This model will describe in detail the chemical mechanisms being followed in the overall reaction. The model includes all of the identified organic by-products (from Argonne and Caltech) and radical intermediates (from Caltech) generated during the sonication. Since the purpose of conducting model simulation is further understanding of the chemical mechanisms behind the reactions and to identify the optimal operating conditions resulting in an improvement of the decomposition efficiency of target contaminants, the model simulation will be closely linked to the laboratory research. The laboratory research and the model simulation are highly iterative, so that the results from the laboratory research is fed into the theory/model development, and vice versa. This task is a collaborative effort between Argonne and Caltech.

*Task 6. Perform batch or continuous-flow experiments to determine the effects of oxidants ($H_2O_2$, Fenton's Reagent, etc.) on SVOC degradation and the biodegradability of the resultant product*

Potential enhancements of the destruction of the parent SVOCs and VOCs by addition of oxidants (such as $H_2O_2$, Fenton's Reagent. etc.) are being investigated in batch and/or continuous flow sonication experiments. The influence of these oxidants will be addressed in terms of the radical intermediates (See Task 3) and organic degradation products (see Task 4). This information will be used in conjunction with the reaction mechanism model being developed in Task 5. Argonne has the primary responsibility for this task.

*Task 7. Identify and quantify corrosion potential and salt formation*

Using metal coupons placed in the sonication reactors, the coupons will be analyzed for potential corrosion and scale formation (e.g., calcium carbonate, magnesium hydroxide, and metal salts). This information will be used in conjunction with the reaction mechanism model being developed in Task 5. Argonne will have the primary responsibility for this task.

*Task 8. Determine the volatility and biodegradability of the treated waters (and compare to untreated waters)*

The untreated water and the sonicated-treated water (containing degradation products, identified in Task 4) will be determined compared in terms of the degradation products. The volatility and biodegradability of the resultant organic compounds are being determined. The volatility of the target organic contaminants can be determined by measuring the residual contaminant concentrations using a laboratory-scale air stripping unit. Argonne has the primary responsibility for this task.

For the biodegradability of the resultant organic compounds, triplicate samples of untreated water and sonicated treated material will be subjected to shake flask biodegradation studies. Initially, soil inoculum from sites contaminated with the parent compound(s) will be needed to determine the biodegradability of the untreated and treated material. Comparisons will be made using GC/MS and HPLC of material before and after biotreatment. It is possible that an acclimation period may be required to provide for sufficient degradation to occur. These studies will be conducted aerobically and anaerobically.

As the sonication system generates sufficient volumes of material continuously, soil columns will be operated to determine the long-term degradation of the material under simulated *in-situ* conditions.

It is critical to determine the long-term operability of the system over a significant period of time to verify that the sonicated treatment material can be degraded under dynamic soil column operation.

*Task 9. Develop computer simulation model to describe combined in-well sonication/in-well vapor stripping, and biodegradation*

***Technical Objectives:***

The technical objectives of the laboratory and modeling components of this proposal are to develop:

1) An understanding of the behavior of the combined sonication and in-well vapor stripping process, and

2) A predictive simulation mode1 of the system that is tested ("validated") on the lab-scale system, used to design the field pilot system, and later used to interpret the operation of the field pilot system.

The physical model will consist of an instrumented sand-box approximately 3 meters long by 1 meters wide by 2 meters high. The physical model will include a central recirculation well and will be instrumented with multi-level piezometers and sampling ports. The system can be run as a closed flow system which simulates the case of no (or low) regional groundwater flow or as an open system which can be used to simulated regional flow of the effects of nearby pumping. Flow through the system will be carefully monitored. The central recirculation well can be run under conditions of in-well vapor stripping or conditions of combined in-well sonication and vapor stripping; in-well vapor stripping will employ a small blower. Air (or gas) injection rates will be monitored as will temperature and pressure. VOC-enriched vapor will be vacuum extracted from the recirculation well and the vapor phase concentrations will be measured. The recirculation

well water will be sampled for VOCs and other chemicals of interest at the lower inflow elevation and the upper outflow elevation. The tank will be filled with natural porous media to an elevation of 70% leaving the upper portion (30%) water unsaturated. At the beginning of an experiment a VOC or SVOC will be fed into the system by replacing the pore waters with the contaminant solution. Initial conditions will be carefully measured via the sampling ports. Additional sampling ports will be placed in the unsaturated zone to measure VOC vapor. Experiments will run for approximately 1 to 2 weeks each depending upon the removal rate of the contaminants. Once the system has been run under conditions representing sonication and in-well vapor stripping, additional experiments will include biodegradation which may involve the addition of nutrients and a carbon source to the lab system, all of which will be monitored.

The simulation model will be developed initially to represent the behavior of the physical model. The simulator will consist of a 3-D finite-difference code to simulate variably saturated flow and transport. The underlying model will account for advection, dispersion, as well as equilibrium and kinetically controlled sorption. The model will be developed as a series of modules with capabilities to represent the in-well SVOC and VOC removal processes, volatilization and diffusion of VOCs in the unsaturated zone, and biodegradation. The model will build upon the simulator developed by Professor Gorelick at Stanford University and used to simulate lab and field in-well vapor stripping systems. Initial model development will be aimed at design of the lab-scale system to help identify the best locations for sampling ports and to target optimal sampling intervals at each multilevel sampler. Once the lab system is constructed, the simulator will be refined as we collect data and re-evaluate the model's performance. Finally, the simulator will be used to scale up to the pilot field system.

The laboratory integrated prototype system and modeling should provide information that can be used directly in the simulation model. Given known boundary conditions, initial conditions, physical parameters, media properties, and system stresses (flow rates and VOC removal rates), the simulation model can be used to predict the behavior of the laboratory system. Measured parameters needed for incorporation into the simulation model are listed in the table below. Concentrations and hydraulic heads are the dependent variables in the simulation model and are the variables that will be measured during each experiment. The physical and chemical processes in the model will be constructed so as to best represent the key observed changes observed in heads (flow) and concentration (transport). The data measured in the laboratory system will be compared with the simulation results. During different experiments, various physical processes will be "turned on or turned off' and the model results will be compared to measured values. For example experiments with and without air injection, with and without in-well sonication, and with and without biodegradation (sterile or inoculated conditions) will be performed.

| Porous Media Properties | Water Properties | Vapor Properties |
|---|---|---|
| -Hydraulic conductivity<br>-Porosity<br>-Bulk density<br>-Grain size distribution<br>-Mineralogy (including organic carbon content)<br>-Distribution coefficient<br>-Unsaturated media properties (conductivity vs. saturation) | -Temperature<br>-Chemical composition including dissolved oxygen and pH | -Temperature<br>-Chemical composition |

*Task IO. Perform large-.scale experiments with a laboratory in-well sonicationlbioremediation system*

Using the laboratory prototype system described in Task 9 above, large-scale laboratory experiments will be performed. Laboratory prototype experiments will be performed to test the technology prior to conducting pilot-scale field demonstrations. The prototype system will be constructed in the laboratory to simulate field conditions. The prototype system will involve a large reservoir tank (which will hold soil containing sand and silt/clay along with water simulating groundwater flow. A small laboratory "well" (i.e., a pump system) will be installed to which the ultrasonics apparatus will be attached. The system will be used at a larger scale for the use of in-well sonicator(s) for decomposition of SVOCs and VOCs. Particular attention will be focused on reactor design (i.e., placement of the sonicator(s) -- in series, orthogonally, etc.), changing/alternating power intensity, and addition of oxidants, in a effort to reduce the time requirements for ultrasonic decomposition of organic contaminants, thereby optimizing the in-well system performance. This laboratory prototype system will be used to test and verify the simulation model (described in Task 9 above) for various treatment combinations that will be "turned on or turned off'. For example experiments with and without air injection, with and without in-well sonication, and with and without biodegradation (sterile or inoculated conditions) will be performed. Argonne will have the primary responsibility for this task. This latter effort will be tied closely to the work of Stanford University in which a computer simulation model will be developed to describe combined in-well sonication/in-well vapor stripping, and biodegradation.

*Task 12. Perform systems analysis and economic analysis for system scale-up for afield demonstration*

A systems analysis and an economic analysis will be performed on this integrated in-well sonication system, based upon the data collected in the above tasks. A comparison will be made between this in-well sonication process and conventional pump-and-treat techniques, addressing wattage input and economics. The systems analysis approach will be used to identify any major operational problems that require attention, potential intermediate degradation/emission products formed during the process, effect of co-contaminants (such as hardness (calcium and magnesium salts), chromium, etc.), etc. This information will be used in the design of the field equipment. Argonne will have the primary responsibility for this task.

*Task 12. Fabricate field equipment*

An industrial partner will be sought during FY 1998 to fabricate the integrated in-well sonication system, coupled with in-well vapor stripping and biodegradation. The industrial partner will work with the project work team (Argonne, Caltech, and Stanford) to design and fabricate the pilot-scale field system.

*Task 13. Demonstrate the in-well sonication technology in the field at selected* ***DOE site(s)***

This task will be a joint effort of the industrial partner working with the project work team (Argonne. Caltech. and Stanford) to take the technology to the field. In consultation with DOE and the Plumes Focus Area, a DOE site will be selected for performing the pilot demonstration. Following the shakedown tests, the integrated treatment system will be operated by a qualified industrial operator for a minimum period of three months. On-site pilot-study oversight will be provided by the project team. Data collected during the pilot study will be used to determine and refine the economics of the system. and to estimate the capitol and operating costs of a full-scale system. System performance and process economics will be determined during the field demonstration. Detailed chemical analysis of the samples. before and after treatment, will be performed to ensure that a good mass balance is achieved and that adequate organics destruction is achieved. Prior to performing the pilot demonstration of the technology at a selected DOE site, the projects technical progress will be peer reviewed. The peer review will be coordinated with the Energy Research Program of DOE.

## 7 PREPARATION OF RESEARCH PLANS

During FY 1997. research plans related to this project were prepared. as appropriate. These plans included:

- Environmental Evaluation Notification Form for Project on "Use of Sonication for In-Well Softening of Semivolatile Organic Compounds"
- Safety Plan for Project on "Use of Sonicatibn for In-Well Softening of Semivolatile Organic Compounds"
- Standard Operating Procedure -- Chemical Carcinogen Use for Project on "Use of Sonication for In-Well Softening of Semivolatile Organic Compounds" (to classify the experimental laboratories at designated carcinogen areas)

Copies of these plans are available on request. Additionally, subcontracts have been established with Caltech, Stanford University, and the Illinois Institute of Technology (IIT).

## 8 RESEARCH PROGRESS

The progress for the various tasks worked on during this past year is summarized below:

### 8.1 Task 1. Quantify representative VOC and SVOC contaminants at DOE facilities

From the list of candidate contaminant, the contaminants $CCl_4$, TCE, TCA, PCE, and EDB were selected for this study. Physical properties of these contaminants are listed in Table A. 1 in the Appendix.

### 8.2 Task 2. Conduct batch sonication experiments to determine preliminary optimal conditions for subsequent continuous-flow experiments

#### 8.2.1 Experimental Apparatus

The batch-sonication apparatus includes a constant-temperature controlled bath. an ultrasonic power supply with a generator/converter and a probe, and one-liter glass reactors. The experimental apparatus was used inside a ventilated hood with an air flow rate of greater than 38.1 m/min (125 ft/min) for safety and environmental concerns. Figure 3 shows the overall experimental sonication apparatus, and Figure 4 shows the sonication apparatus contained in the constant-temperature controlled bath.

##### 8.2.1.1 Constant Temperature Controlled Bath

The temperature-controlling bath system (see Figure 5) consisted of a Haake D 1 water circulator/heater, a 12-liter capacity stainless water bath. a thermometer, a cooling water supply system (including a Poly Science KR-80A immersion chillier, a 50-liter water tank, a copper coil with tap water flowing inside and located in the water tank, and a flowmeter), and a tank set to maintain the constant temperature bath water level. The Haake D 1 water circulator/heater maintains constant temperatures (± 0.2° C) by a built-in temperature sensor when tap water was used as a coolant. It also provided good circulation in the water bath because of its circulating pump. The Poly Science KR-80A immersion chiller maintains the temperature of the coolant inside the water tank below 10°C. Tap water flowing through the copper coil in the water tank maintains its temperature lower than the required temperature.

8.2.1.2 Ultrasonic Power Supply

The 600 watt air-cooled ultrasonic power supply (Sonics & Materials VibraCell, Model VC 600) (see Figure 6) converts 50/60 kHz line voltage to electrical energy with a 20 kHz frequency. This 20 kHz frequency energy is transmitted to the piezoelectric transducer within the converter and be changed to mechanical vibrations. The mechanical vibrations are intensified by the probe and produced acoustic pressure in the liquid when the probe is located in a liquid. The output energy, from 0 to 600 watts, is adjusted by an output controller and monitored by a power monitor on the control pane!. Larger volumes of liquid can be treated with the use of a larger titanium probe tips with a flat 1.9 cm (0.75 inch) diameter surface are used. However, lesser intensities are obtained if larger tips are used. A standard horn with a 19-mm diameter titanium tip was used on the probe. This probe is immersed into the liquid about 2.54 cm to 3.81 cm (1 to 1.5 inches) to cause acoustic cavitation and avoid forming aerosols or foams. Aerosols and foams reduce the cavitation efficiency. Formation of aerosols can be reduced by using a sealed treatment chamber. Aerosols and foams also can be avoided by decreasing the power intensity and increasing the processing time, using a narrower reactor, or lowering the liquid temperature. Anti-foaming reagents such as surfactants should be avoided because that they decrease power intensity, although they also lower the power required. Theoretically, higher temperatures reduce cavitation; lower temperatures are chosen to enhance sonication. Contacting the probe with the wall of the reactor decreases the output power and damages the surface of the glass reactor. Lower surface tension liquids (compared to water) are problematical because they penetrate the probe/tip interface. Liquids with high viscosity or concentration are also problematic because they are too viscous to pour or circulate.

8.2.1.3 Sonication Reactor

The sonication reactor (see Figure 6) used is a one-liter glass cell with a sealed cover, which contains a l-in. center port for the ultrasonic probe, and two side ports for sampling and head space purging. A 500-mL sample is the maximum volume that the 1.9 cm (0.75 inch) diameter standard processing probe is suggested for operation. The center port of the reactor is connected with the ultrasonic probe by a metal collar with three o-rings on different positions to avoid an unexpected loss of vapor of target compounds. A Nupro pressure relief valve (10 atm upper limit) was included on the sampling port; higher pressure may be generated inside the air-tight reactor during ultrasonic irradiation at high temperature. A Teflon-faced silicon septum was used to sea! the sampling port and to permit the penetration of the 20-cm needles for the 5-mL air-tight sampling syringe (mode!: 1005, luer tip, Hamilton) to sample the solution, and spike the contaminants or oxidants. An inlet and an outlet line were configured on the sampling port and another side arm to permit air-flow through the space above the liquid level and allow the vapors of target chemicals to be purged from the headspace for sampling. The reactor is cooled by a constant-temperature coolant circulated in the constant-temperature controlled bath. A digital dual channel thermometer (model: 15-078-3A, Fisher Scientific) was placed in the reactor through the side arm to monitor the sample temperature.

**8.2.2 Experimental Materials**

Artificial ground water was generated by dissolving appropriate amounts of A.C.S. grade reagents in laboratory organics-free deionized water in 20-liter (5-gallon) containers. The procedure to prepare artificial groundwater involves addition of magnesium sulfate heptahydrate (certified A.C.S. grade. Fisher Scientific) -- 60 mg/L; potassium nitrate (certified A.C.S. grade. Mallinckrodt, Inc.) -- 20 mg/L; sodium bicarbonate (certified A.C.S. grade, Mallinckrodt, Inc.) -- 36 mg/L; calcium chloride (certified A.C.S. grade, Fisher Scientific) -- 35 mg/L; calcium nitrate (certified A.C.S. grade, Mallinckrodt. Inc.) -- 35 mg/L; calcium sulfate dihydrate (certified A.C.S. grade, G. Frederick Smith Chemical Co.) -- 25 mg/L; hydrochloric acid (certified A.C.S. grade, J. T. Baker Inc.) -- 0.35 mL/L; and monobasic sodium phosphate dihydrate (certified A.C.S. grade. J. T. Baker Inc.) -- 0.0312 mg/L. The estimated pH value of the solution in a closed system solution (immediately after

preparation of the solution) is 5.686. The measured pH value of artificial groundwater is typically in the range of 5.9 to 6.3. A digital pH/millivolt meter (model: 611, Orion Research) equipped with a pH electrode is used to measure the pH values of the artificial groundwater and samples. This pH meter is calibrated carefully at pH 4, pH 7, and pH 10, using standard buffer solutions (certified, Fisher Scientific). Nitric acid and sodium hydroxide (certified A.C.S. grade, J. T. Baker Inc.) were used to adjust the pH values of the artificial groundwater. The measured pH value of the artificial groundwater was higher than the value for a closed system calculated by MINTEQA2 Model, which was attributed to the loss of $CO_3^{-2}$ by the form of $CO_{2(g)}$ ($CO_3^{-2} + 2H^+ \rightleftarrows H_2CO_3 \rightleftarrows H_2O + CO_{,,,}$) in the open system. The concentration of H'was reduced when $CO_3^{-2}$ transfer to $H_2CO_3$. $H_2CO_3$ dissociates to water and carbon dioxide and $CO_{2(g)}$ may volatilize into the atmosphere. Because the concentration of carbon dioxide in ambient air is low (0.03% or 315 ppm), carbon dioxide in the liquid may escape into the atmosphere. The estimated pH value of the open system solution was 7.215. Measured pH values demonstrated that some carbonate was transformed into carbon dioxide and escaped into the atmosphere.

Carbon tetrachloride (certified A.C.S. grade, Mallinckrodt, Inc.), trichloroethylene (suitable for gas chromatography and spectrophotometry, Burdick & Jackson), l,l,l -trichloroethane (neat, Supelco, Inc.), tetrachloroethylene (certified A.C.S. grade, Mallinckrodt, inc.), and ethylene dibromide (Certificate of lot analysis, Acros, inc.) were chosen as the target compounds for the experiments. Saturated solutions were prepared by stirring the chemicals with prepared artificial groundwater. The solutions were stored in glass containers and put in refrigeration. The saturated solutions were used to spike the sample solutions for the experiments.

Additional chemicals used in this research included: hydrogen peroxide (30 Wt%, semiconductor grade, Aldrich, Inc.), nitric acid (reagent grade, Mallinckrodt, Inc.), ferrous sulfate (reagent grade, Mallinckrodt, Inc.), and potassium iodide neutral (reagent grade, Mallinckrodt, Inc.).

### 8.2.3 Experimental Procedure

A 500-mL artificial groundwater solution is placed in a one-liter glass reactor, that is partially immersed in the coolant of the constant temperature controlled bath for a period of time until the temperature inside the reactor reached the desired temperature. After the desired temperature has stabilized, the artificial groundwater solution is spiked by injecting the desired halogenated organic compound into the reactor with a syringe through a septum. Before any experiment, the ultrasonic power supply system is warmed up for -30 minutes. To get optima! performance, the transducer of this system is tuned before every experiment to adjust the reading on the monitor of power supply to the minimum value. This adjustment is minor, typically less than 1%. The probe is placed in the solution and activated for a few seconds to make sure no residue of prior run remains. The horn of the ultrasonic power supply is immersed in the sample (about 2.5 cm to 3.8 cm (1 inch to 1.5 inches) under the liquid surface) to inhibit possible interference (such as aerosoling or foaming). The solution in the reactor is irradiated at the intended intensity of the applied ultrasound (20 kHz, up to 600 Watts) for a given period of time (typically 10 minutes). The irradiating intensities are monitored from the power monitor and regulated by the output controller on the control panel. At each sampling interval, about l-2 mL irradiated sample is withdrawn from the reactor using a sampling syringe equipped with a 20-cm needle. One mL of every sample is placed in a headspace vial (10 mL volume. Hewlett Packard) which had been sealed with crimp aluminum caps with a 20 mm Teflon-faced silicon seal septum, and is immediately analyzed by gas chromatography.

### 8.2.4 Analytical Methods

Considerable effort went into development of appropriate analytical procedures and methods associated

with using volatile compounds. Analytical method development included selection and procurement of a Hewlett Packard 7694 Automatic Headspace Sampler for use with the Hewlett Packard 5890 Gas Chromatograph. Figure 7 shows the general lay-out of the gas chromatography system, while Figure 8 shows a schematic of the GC system configuration. Headspace analysis is well-suited for analysis of volatile and semivolatile organic compounds in water, and avoids the column degradation caused by liquid injection of water. The headspace sampling method includes ten minutes equilibration of samples at 70°C with shaking, programmed via! pressurization, venting, sample loop fill (1 mL loop volume), and 0.30 minute injection time. Equilibration time was selected by measuring area response for times ranging from 1 to 60 minutes. A 30 meter megabore fused capillary DB-624 column was selected based on its sensitivity and selectivity in analysis of chlorinated organic compounds. The HP 5890 chromatograph is equipped with both flame ionization and electron capture detectors. In the analytical range for this project (0.1 to 100 ppm), flame ionization provided adequate resolution and reproducible detection. The electron capture detector was found to be too sensitive for detection of major components, but is useful in examining sonicated samples for minor breakdown products. The GC temperature program was set for 1 minute at 9O°C, ramping 10°/minute to 140°, then 25°/minute to 200°, and held for 2 minutes at 200° C. Standards were initially prepared in volumetric flasks. Due to analyte volatility, this was changed to injection by syringe through the via! septum of the chlorinated compounds into measured water mass. Planned sample size was 5 mL in 10 mL vials, however this was reduced to 1 mL in 10 mL vials to avoid overloading the column with analyte. Response of carbon tetrachloride standards held in sealed vials over a 0.25 to 48 hour time range was evaluated to determine how long samples could be stored prior to GC analysis (see Figure 9). It was found that vials analyzed within three hours after sampling gave the most reproducible response (see Figure 10). Vials showed a drop in response to approximately 80% at 15 hours, and to 20-40% at 25 hours. Since the hydrolysis rate for $CCI_4$ in water is very low, there appears to be loss through the vial seal or septum. Therefore a!! subsequent samples and standards were analyzed as closely as possible to the actual sampling time, and all within three hours. Five analyte standards were prepared each day for the initial calibration curve, and check standards were performed late in the day, or when any questionable sample result was obtained.

### 8.2.5 Safety and Other Considerations

#### 8.2.5.1 Safety Considerations

To avoid the high exposure of noise, Moldex pura-fit ear plugs with cord are used during the sonicator operating time. Proper persona! equipment, such as safety eyeglass, laboratory coat, and gloves, are worn during the experiments. All experiments are conducted in a ventilated hood to avoid release into atmosphere and inadvertent inhalation of chlorinated compounds by project staff in the laboratory. The vent of GC is connected to a ventilated hood by copper tubing to avoid the leakage of halogenated compounds into the genera! laboratory.

#### 8.2.5.2 Tip Erosion

Because acoustic cavitation erodes the titanium tip on the probe of ultrasonic power supply, the output will decrease without indication on the power monitor. Therefore, the sonicator tip is routinely examined after 5 or 6 hours of operating time. When necessary, the tip may need to be polished with fine emery cloth or sand paper (No. 600) to keep the surface smooth. The interfaces of converter/horn/tip also need to be reconditioned to maintain clean, smooth surfaces. The sonicator tip should be replaced if the wear is excessive.

#### 8.2.5.3 Pressure inside the Reactor

Because the sonication experiments involve volatile chemicals ($P_{vap}$ ranges from ~ 17.4 mm Hg to I25

mm Hg) and water which have vapor pressures at room temperature, the headspace pressure in the closed reactor system may increase during sonication. The maximum possible pressures (assuming that all 100 ppm of the chemicals in the liquid completely evaporated into the headspace of reactor) were from 1.23 to 1.54 psi (calculated using the ideal gas law). A 3 psig pressure relief valve was used on the reactor to avoid any potential damage.

### 8.2.6 Research Progress

Under Task 2, the experiments were designed to investigate the degradation of halogenated organic compounds by ultrasonic irradiation of a solution. The compounds initially targeted for this study are carbon tetrachloride ($Ccl_4$), trichloroethylene (TCE), tetrachloroethylene (PCE), 1, 1,l -Trichloroethane (TCA), and Ethylenedibromide (EDB). For the sake of brevity of this report, the results from the batch sonication system testing only CC!, and TCE are included below. Results of these two compounds are representative of the general trends observed. The effects of varying sonication time, ultrasonic power intensities, initial concentrations of target compounds, pH, hydrogen peroxide, ferrous sulfate, and Fenton's Reagent were examined. The results of these tests will aid in the determination of the operation conditions for a continuous-flowing ultrasonic irradiation system planned for Task 4. Procedural effects were also examined to better understand potential interferences. These include temperature increase of the sample due to sonication, and potential loss of the target compound due to volatilization.

#### 8.2.6.1 Temperature Increase Due to Batch Sonication

Experiments performed to date were all started with an initial sample temperature of 20° C. The sample, in the closed-system reactor, was placed in a circulating constant temperature water bath to minimize temperature fluctuation during sonication. Despite the use of the water bath, the temperature of the sample increased over time with sonication. Temperature profiles were determined for samples of artificial ground water (AGW) at various power intensities (35.8, 25.3, and 12.6 $W/cm^2$). Figure 11 illustrates the results of sonicating for 10 minutes at 35.8 $W/cm^2$ at the different $CCl_4$ concentrations (0, 2.75, 9,49, 44.57, and 81.34 ppm). Sample temperatures increased 6° C to 8° C (from 20° C to 26° C - 28° C) over the 10 minute period of sonication. No pattern was observed due to the presence of or concentration of the CC!,. Unspiked AGW samples compared at different power intensities are illustrated in Figure 12. It is apparent from the figure that a higher power intensity used will increase the sample temperature more rapidly than a lower power intensity. Looking again at Figure 11, slight variations in these results are most likely due to the slight variation in the power output of the sonicator from run to run. Average temperature values for the samples over the 10 minutes sonication period were approximately 25° C, 24° C, and 22° C for 35.8, 25.3, and 12.6 $W/cm^2$, respectively.

A test was performed to determine the temperature increase without the use of the water bath. A sample with an initial temperature of 22° C was sonicated at 25.3 $W/cm^2$ outside the water bath for 10 minutes. The final temperature of the AGW was 32°C. With the water bath, the same test increased the sample temperature by slightly more than 5 degrees. To minimize fluctuation in sample temperature. the water bath was used for further experimentation.

#### 8.2.6.2 Evaporation of the Target Compound

Because of the volatility characteristics of the target compounds, the headspace in the closed-system reactor was analyzed before and during sonication to determine evaporative losses. A sample spiked to 8 ppm $CCl_4$ was subjected to IO minutes of sonication at 12.6 $W/cm^2$. An air-tight syringe was used to take a 1 mL headspace sample through the septum port for GC analysis. The sample was taken from the 500 mL headspace inside the reactor 8 minutes before sonication began and at time 0, 4, and 10 minutes during sonication. After

IO minutes of sonication the concentration of the $CCl_4$ in the headspace was less than 0.1 % of the concentration in the aqueous sample. Losses of $CCl_4$ due to volatilization in the closed-system reactor 8 minutes without sonication and over the time period of a IO minutes sonication run showed to be insignificant.

The headspace over a sample spiked with TCE was also tested. This test involved a higher ultrasonic intensity (35.8 $W/cm^2$) and at a higher concentration (68.4 ppm). Almost 2% of the TCE concentration of the spiked sample was recovered in the headspace after 10 minutes of sonication. High ultrasonic irradiation leads to a high mass transfer in liquid and the geyser phenomena near the air/water interface [Trabelsi et al., 1996]. These phenomena enhance volatility of the contaminant. This amount of loss (2%) of the contaminant is, however, within the margin of experimental error.

8.2.6.3 Sonication of Target Compounds at Different Initial Concentrations

Once potential procedural interferences were established to be minimal (described above in the previous two sections), samples spiked with the target compounds were sonicated to determine the effectiveness of ultrasonics on decreasing the concentration of the compound in the sample solution. As described in the methods section, 500 mL samples were sonicated for 10 minutes and sampled at certain intervals during sonication. Results from samples spiked with varying concentrations of $CCl_4$ or TCE at 35.8 $W/cm^2$ for 10 minutes are represented in Table 1, below. For $CCl_4$, the concentration decreased by 54%, 50%, and 45% for initial concentration of 1.4, 9.1, and 65.2 ppm, respectively. Similar results were obtained for TCE, resulting in between 23% and 40% reduction for initial concentrations of 1.6 and 72 ppm. This data indicates that the rate of reduction is greater with a lower initial concentration.

Table 1. Percent Reduction of $CCl_4$ and TCE After 10 Minutes Sonication at 35.8 $W/cm^2$.

| Sonication Time, (min) | Chlorinated Organic Compound Concentration, (ppm) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Carbon Tetrachloride ($CCl_4$) | | | Trichloroethylene (TCE) | | | | |
| 0 | 1.40 | 9.10 | 65.20 | 1.62 | 6.51 | 6.89 | 68.44 | 72.09 |
| 3 | 1.00 | 7.40 | 51.70 | 1.38 | 5.68 | 5.88 | 63.13 | 67.60 |
| 6 | 0.87 | 6.00 | 45.30 | 1.16 | 5.19 | 5.44 | 58.27 | 60.80 |
| 10 | 0.65 | 4.60 | 35.80 | 0.93 | 4.34 | 4.83 | 50.50 | 55.44 |
| Percent Reduction After 10 min. | 53.6 | 49.5 | 45.1 | 42.3 | 33.4 | 30.0 | 26.2 | 23.1 |

First-order plots of the natural logarithm of concentrations versus sonication time are shown in Figures 13 and 14. The experimental data fit the first-order reaction kinetic model. Degradation rate constants for the first-order model were obtained from the slopes of the linear regression of the plots according to the equation:

$$-\frac{d[CCl_4]}{dt} = k\,[CCl_4]$$

8.2.6.4 Varying Power Intensities of the Ultrasonic Irradiation

The effect of varying the wattage introduced per probe tip surface area to the sample was also investigated. Three power intensities were investigated; 12.6, 25.3, and 35.8 $W/cm^2$. Figure 15 represents the rate of reduction of $CCl_4$ represented in the natural logarithm at these three power intensities with an initial concentration of 65 ppm. The samples were sonicated for 10 minutes. This figure illustrates a clear effect of the power intensity on the rate of reduction. With an increase in the wattage introduced to the sample there is an increase in the rate in which the $CCl_4$ concentration is decreased. Figures 16 and 17 illustrate this same effect for an initial $CCl_4$ concentrations of 8 and 1.6 ppm, respectively. The same effect is observed for TCE (see Figures 18, 19 and 20).

Figures 21, 22, and 23 compare the different $CCl_4$ concentrations at the same power intensities; 35.8, 25.3, and 12.6 $W/cm^2$, respectively. After 10 minutes of sonication, each figure clearly illustrates a correlation between initial concentration and reduction rate, as was also discussed in the previous section. Again, TCE also shows this trend (see Figures 24,25, and 26). The combined effect of power intensity and initial contaminant concentration for $CCl_4$ and TCE are shown in Tables 2 and 3 where reduction rate constants of each combination of power intensity and concentration are compared for both contaminants. Clearly the highest power intensity has the highest reduction rates over a!! concentrations. The *lower* the power intensities, the broader the difference between concentrations becomes. This is more pronounced for $CCl_4$ where the span between the lowest and highest concentrations for 35.8 $W/cm^2$ is 28% (relative to results from the highest concentration), whereas the highest span, 79% occurs for the lowest power intensity, 12.6 $W/cm^2$. For TCE, the difference between 25.3 $W/cm^2$ and 35.8 $W/cm^2$ is not so great. Figures 27 and 28 further illustrate the relationships of power intensity and initial concentration with the degradation rate of the $CCl_4$ and TCE.

Table 2. Comparison of Reduction Rate at Different Power Intensities and Different Initial CC!, Concentrations

| Parameter | Power Intensity, ($W/cm^2$) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 12.6 | | | 25.3 | | | 35.8 | | |
| Concentration, (ppm) | 1.7 | 7.4 | 68.9 | 1.6 | 8.3 | 63.3 | 1.4 | 9.1 | 65.2 |
| $k_{expenmental}$ | 0.0345 | 0.0308 | 0.0193 | 0.0574 | 0.0480 | 0.0376 | 0.0746 | 0.0674 | 0.0584 |
| Relative Percent* | 179 | 160 | 100 | 153 | 128 | 100 | 128 | 115 | 100 |

*Relative percents are compared to the highest $CCl_4$ concentration tested.

Table 3. Comparison of Reduction Rate at Different Power Intensities and Different Initial TCE Concentrations

| Parameter | Power Intensity, ($W/cm^2$) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 12.6 | | | 25.3 | | | 35.8 | | |
| TCE Concentration, (ppm) | 1.63 | 6.73 | 74.1 | 1.32 | 6.57 | 63.1 | 1.61 | 6.51 | 72.1 |
| $k_{experimental}$, ($min^{-1}$) | 0.0347 | 0.0221 | 0.0130 | 0.0426 | 0.0311 | 0.0210 | 0.0551 | 0.0403 | 0.0265 |
| Relative Percent* | 267 | 170 | 100 | 203 | 148 | 100 | 208 | 152 | 100 |

*Relative percents are compared to the highest TCE concentration tested.

8.2.6.5 Effect of Initial pH values

The effect of the initial pH of the sample solution on the rate of contaminant reduction was investigated. Initial pH test values were between 3 and 10. Samples spiked at 8 ppm $CCl_4$ were sonicated for 10 minutes at 25.3 or 35.8 $W/cm^2$. Figure 29 plots the reduction rates verses the initial pH values for these tests. Initial pH values between 5 and 9 did not appear to influence the rate of reduction. However, an initial pH value of 3 showed a significant decrease in the reduction rate. This phenomenon agrees with results of other researchers' studies [Wu et al., 1992a,b; Kotronarou et al., 1991].

Results from performing similar tests spiking the sample with TCE also show no effect on the rate of reduction due to initial pH between 5 and 10 (see Figure 30). The data suggests that there may be a decrease in the rate of reduction with a low pH of -3, but it is not as apparent as with the case with CC!,. This test should be repeated for further verification.

8.2.6.6 Comparison of the Ultrasonic Degradation Efficiencies of $CCl_4$ and TCE

Comparing the reduction rates observed for $CCl_4$ and TCE for the same test conditions, sonication of $CCl_4$ appears to be more effective in enhancing the degradation of $CCl_4$ than that of TCE (see Figures 31, 32, and 33). The major degradation mechanism of volatile organic compounds under ultrasonic irradiation is considered to be direct pyrolysis within the cavitation bubbles [Hua and Hoffmann, 1996; Kotronarou et al., 1992]. TCE has a lower volatility, which will decrease the rate at which it enters the cavitation bubbles. and it is more thermally stable, which may effect its rate of pyrolysis within the bubble. The comparison of the degradation rate constants of $CCl_4$ and TCE is shown in Table 4. Greater differences between the reduction rates of $CCl_4$ and TCE are observed at the higher concentration and power intensity ranges tested.

Table 4. Comparison of the Degradation Rate Constants of $CCl_4$ and TCE

| Power Intensity, (Watts/cm$^2$) | Nominal Concentration, (mg/L) | $k_{CCl4}$, (min$^{-1}$) | $k_{TCE}$, (min$^{-1}$) | $k_{CCl4}/k_{TCE}$ |
|---|---|---|---|---|
| 35.8 | 1.6 | 0.0788 | 0.0551 | 1.43 |
| 35.8 | 8 | 0.0673 | 0.0403 | 1.67 |
| 35.8 | 70 | 0.0612 | 0.0265 | 2.31 |
| 25.3 | 1.6 | 0.0574 | 0.0426 | 1.34 |
| 25.3 | 8 | 0.0489 | 0.0304 | 1.61 |
| 25.3 | 63 | 0.0376 | 0.0210 | 1.79 |
| 12.6 | 1.8 | 0.0345 | 0.0347 | 1.00 |
| 12.6 | 8 | 0.0308 | 0.0221 | 1.39 |
| 12.6 | 70 | 0.0193 | 0.0130 | 1.48 |

8.2.6.7 Duplication of Experimental Results

Most of the data generated in this project so far are based on one experiment per set of experimental conditions. However, three different sets of experimental conditions were performed in duplicate. The data comparing these duplicate results are presented in Figures 34 and 35. The slopes representing the rate of $CCl_4$ decrease on the linear regression curves (of In $C/C_o$ vs. reaction time) for each of the experiments prove to be extremely reproducible. Table 5, below, presents the slopes, average slope for each set, standard deviation, and percent deviation from the average. In each case, the slopes were within ±3% to 10% of the average slope. This data also indicates that with an increase in power intensity, the rate of decrease of the $CCl_4$ kinetics increases. In addition, with a lower initial $CCl_4$ concentration, the rate of decrease of $CCl_4$ is greater.

Table 5. Comparison of Duplicated Experimental Results for Sonication using $CCl_4$.

| Sonication Time, (min) | $CCl_4$ Concentration, (ppm) | | | | | |
|---|---|---|---|---|---|---|
| | 12.6 W/cm$^2$ | | | | 25.3 W/cm$^2$ | |
| | Trial 1 | Replicate Trial 1 | Trial 2 | Replicate Trial 2 | Trial 3 | Replicate Trial 3 |
| 0 | 1.73 | 1.40 | 6.36 | 7.39 | 8.30 | 7.74 |
| 3 | --- | 1.15 | --- | 6.70 | --- | --- |

| | | | | | | |
|---|---|---|---|---|---|---|
| 5 | 1.58 | --- | 5.37 | --- | 6.46 | 6.04 |
| 6 | --- | 0.92 | --- | 6.14 | --- | --- |
| 10 | 1.22 | 0.78 | 4.59 | --- | 5.16 | 4.77 |
| Slope | -0.0510 | -0.0624 | -0.1770 | -0.2083 | -0.3140 | -0.2970 |
| Average Slope | -0.057 | | -0.193 | | -0.306 | |
| Standard Deviation | 0.008 | | 0.022 | | 0.012 | |
| Percent of Average Slope | 90% | 110% | 92% | 108% | 103% | 97% |

8.3 Task 3. Perform batch experiments for measuring hydroxyl/hydrogen radicals in solution

No progress has been made on this task; this task will be worked on during FY 1998.

8.4 Task 4. Conduct continuous-flow experiments for degradation of SVOCs and identification or quantification of by-products

No progress has been made on this task; this task will be worked on during FY 1998.

8.5 Task 5. Investigate the chemical reaction mechanism to improve system performance

8.5.1 Sonolysis of Chlorinated Organic Compounds

The sonolytic degradation of $CCl_4$ in water has been studied by several research groups [Hua and Hoffmann, 1996; Bhatnagar and Cheung, 1994; Wu et al., 1992a; and Francony and Petrier, 1996]. The initial steps in the mechanism can be written as [Hua and Hoffmann, 1996]:

$$CCl_4 \xrightarrow{)))} Cl\bullet + \bullet Cl_3 \qquad \{1\}$$

$$CCl_4 \xrightarrow{)))} Cl_2 + :CCl_2 \qquad \{2\}$$

$$\bullet CCl_3 \rightarrow Cl\bullet + :CCl_2 \qquad \{3\}$$

$$\bullet CCl_3 + \bullet CCl_3 \rightarrow CCl_4 + :CCl_2 \qquad \{4\}$$

$$\bullet CCl_3 + \bullet CCl_3 \rightarrow C_2Cl_6 \qquad \{5\}$$

where ))) indicates sonolysis. The trichloromethyl radical reacts further with hydroxyl radicals to produce trichloromethanol:

$$\bullet CCl_3 + \bullet OH \rightarrow HOCCl_3 \qquad \{6\}$$

Since HOCCl3 is unstable, it decomposes rapidly to yield HCl and phosgene:

$$HOCCl_3 \rightarrow HCl + COCl_2 \qquad \{7\}$$

Phosgene hydrolyzes readily to give the final products as follows:

$$COCl_2 + H_2O \rightarrow CO_2 + 2HCl \qquad \{8\}$$

Dichlorocarbene formed in Equation {3} self reacts to form tetrachloroethylene

$$:CCl_2 + :CCl_2 \rightarrow C_2Cl_4 \qquad \{9\}$$

or it reacts with water to form carbon monoxide and hydrochloric acid:

$$:CCl_2 + H_2O \rightarrow HCl + CO \qquad \{10\}$$

Chlorine atoms self-react to form molecular chlorine, which hydrolyzes readily to yield hypochlorous acid and HCl:

$$2\ Cl\bullet \rightarrow Cl_2 \xrightarrow{+H_2O} HOCl + HCl \qquad \{11\}$$

The sonolyses of $CCl_4$, $CHCl_3$, and $CH_2Cl_2$ in water were investigated. The output power was set at 50 W. In this set of experiments, $CCl_4$ degradation was the fastest, and dichloromethane was the slowest. Due to a higher Henry's Law constant, more $CCl_4$ should diffuse into the bubbles and undergo pyrolysis as the bubbles collapse, than well $CHCl_3$ and $CH_2Cl_2$. The degradation products, which were detected by GC-ECD and ion chromatography (IC), are listed in Table 6 below.

Table 6. Intermediates Produced from the Sonication of the Chlorinated Organic Compounds

| Sample | $CCl_4$ | $CHCl_3$ | $CH_2Cl_2$ |
|---|---|---|---|
| Intermediates | $C_2Cl_4$, $C_2Cl_6$ | $CCl_4$, $C_2Cl_4$, $C_2Cl_6$ | $CHCl_3$ |
| Final Products | $Cl^-$ | $Cl^-$ | $Cl^-$ |

The final product in each case was HCl and $CO_2$. The principal intermediates, $C_2Cl_4$ and $C_2Cl_6$ obtained during the degradation of $CCl_4$ and $CHCl_3$, are shown in Figure 36. The primary intermediate during sonolysis of $CHCl_3$ was $C_2Cl_2$ and for sonolysis of $CCl_4$ was $C_2Cl_6$. These intermediates are consistent with the slightly different mechanisms for these two compounds. $CHCl_3$ degradation proceeds primarily by molecular elimination for form dichlorocarbene [Henglein and Fischer, 1984]:

$$CHCl_3 \xrightarrow{))\!)} :CCl_2 + HCl \qquad \{12\}$$

Two dichlorocarbenes then react to give $C_2Cl_4$.

$$:CCl_2 + :CCl_2 \rightarrow C_2Cl_4 \qquad \{13\}$$

On the other hand, $CCl_4$ degradation yields the trichloromethyl radical via pyrolysis of a C-Cl bond. The trichloromethyl radical self-reacts to give $C_2Cl_6$.

$$CCl_4 \xrightarrow{))) k1} \bullet CCl_3 + \bullet Cl \qquad \{14\}$$

$$2\ \bullet CCl_3 \xrightarrow{k2} C_2Cl_6 \qquad \{15\}$$

$$C_2Cl_6 \xrightarrow{))) k3} \text{products} \qquad \{16\}$$

The rate constant for the self-reaction of the trichloromethyl radicals is reported to be about $10^{10}$ $M^{-1}$-$sec^{-1}$ [Matheson et al., 1974]. $C_2Cl_6$ sonolysis was also observed to be a first-order reaction.

8.5.2 Kinetic Analysis

A simple kinetic model is used to describe the production and degradation process for analyzing the production of $C_2Cl_6$ based on the degradation results from $CCl_4$ and $CHCl_3$. Since the degradation of $CCl_4$ is observed to be a pseudo first-order reaction, the recombination of $\bullet CCl_3$ and $\bullet Cl$ radicals is ignored. Furthermore, we assumed that all the $\bullet CCl_3$ radicals yield $C_2Cl_6$. The mechanism of Equations {14} through {16} gives the corresponding kinetic expressions:

$$\frac{d[CCl_4]}{dt} = -k_1 [CCl_4] \qquad \{17\}$$

$$\frac{d[\bullet CCl_3]}{dt} = k_1 [CCl_4] - 2\ k_2 [\bullet CCl_3] \qquad \{18\}$$

$$\frac{d[C_2Cl_6]}{dt} = 2k_2 [\bullet CCl_3] - k_3 [C_2Cl_6] \qquad \{19\}$$

Integration of Equation {17} yields:

$$[CCl_4] = [CCl_4]_o\ e^{-k_1 t} \qquad \{20\}$$

Assuming a steady state for $\bullet CCl_3$ [Eyring et al., 1980],

$$\frac{d[\bullet CCl_3]}{dt} = k_1 [CCl_4] - 2k_2 [\bullet CCl_3]^2 = 0 \qquad \{21\}$$

we obtain:

$$[\bullet CCl_3]_{ss} = \left[\frac{k1}{2k_2}\right]^{1/2} [CCl_4]^{1/2} \qquad \{22\}$$

Substitution of $[\bullet CCl_3]_{ss}$ into Equation {8} under the boundary condition of $[C_2Cl_6]_{t=0} = [C_2Cl_6]_{t=\infty}$ yields upon integration:

$$[C_2Cl_6] = \frac{k_1}{2\ (k_1 - k_3)}\ [CCl_4]_o\ (e^{-k_3 t} - e^{-k_1 t}) \qquad \{23\}$$

The concentration versus time data for $C_2Cl_6$ appearance and disappearance were compared to the calculation based on Equation {12}. The observed and normalized reaction rates (k, and $k_3$) for $C_2Cl_6$ at different frequencies used in the model are listed in Table 7. As expected, the rate constants, k,, for all frequencies are quite close to those listed in Table 8 (which lists the total degradation rate of $CCl_4$). These results are consistent with a pathway involving $CCl_4$ pyrolysis into $\bullet CCl_3$ and $\bullet Cl$ as the rate-limiting step in $CCl_4$ sonolysis. The degradation rate for $C_2Cl_6$, $k_3$, is also faster at the higher frequencies and decreases again at 1078 kHz. The calculated degradation rates for $C_2Cl_6$ in $CCl_4$ solutions are faster than in the absence of $CCl_4$. This may be due to the attack on $C_2Cl_6$ by the chlorine radicals produced during $CCl_4$ sonolysis other than by OH• only [Hua and Hoffmann, 1996].

Table 7. Reaction Rates Obtained from the $[C_2Cl_6]$ Kinetic Studies

| Kinetic Rate Constant, ($min^{-1}$) | Ultrasonic Frequency, (kHz) | | | | | |
|---|---|---|---|---|---|---|
| | 20 | 205 | 358 | 500 | 618 | 1078 |
| $k_{CCl4}$ | 0.025 | 0.044 | 0.049 | 0.070 | 0.055 | 0.039 |
| $k_1$ | 0.020 | 0.045 | 0.056 | 0.058 | 0.066 | 0.045 |
| $k_3$ | 0.017 | 0.042 | 0.052 | 0.057 | 0.060 | 0.042 |

Table 8. Corrected Rate Constants at 10°C and $pH_{initial} \sim 7$ ($k_{CCl4} = k_{corr}$)

| Corrected Rate Constant, ($min^{-1}$) | Ultrasonic Frequency, (kHz) | | | | | |
|---|---|---|---|---|---|---|
| | 20 | 205 | 358 | 500 | 618 | 1078 |
| $k_{CCl4}$ | 0.025 | 0.044 | 0.049 | 0.070 | 0.055 | 0.039 |

Because the final stable Cl-containing product of $CCl_4$ sonolysis is $Cl^-$, the overall reaction mechanism can be simplified in the following way:

$$CCl_4 \xrightarrow{)))\ k1} \bullet CCl_3 + \bullet Cl \qquad \{14\}$$

$$2\ \bullet CCl_3 \xrightarrow{k2} C_2Cl_6 \qquad \{15\}$$

$$C_2Cl_6 \xrightarrow{)))\ k3} aCl^- + \text{other products} \qquad \{16\}$$

$$\bullet Cl + H_2O \xrightarrow{k4} HCl + \bullet OH \qquad \{24\}$$

The mechanisms yields the following kinetic equations:

$$\frac{d[\bullet Cl]}{dt} = k_1 [CCl_4] - k_4 [\bullet Cl] \qquad \{25\}$$

$$\frac{d[Cl^-]}{dt} = k_4 [\bullet Cl] + a k_3 [C_2Cl_6] \qquad \{26\}$$

Assuming a steady state for •Cl:

$$\frac{d[\bullet Cl]}{dt} = k_1 [CCl_4] - k_4 [\bullet Cl] = 0 \qquad \{27\}$$

we obtain the following:

$$[\bullet Cl]_{ss} = \frac{k_1}{k_4} [CCl_4] \qquad \{28\}$$

Substitution of $[\bullet Cl]_{ss}$ along with Equations {20} and {23} into Equation {26} under the boundary condition of $[Cl^-]_{t=0} = 0$, yields:

$$[Cl^-] = [CCl_4]_o \left[1 - e^{-k_1 t} + \frac{a k_1}{2(k_1 - k_3)} (1 - e^{-k_3 t}) - \frac{a k_3}{2(k_1 - k_3)} (1 - e^{-k_1 t})\right] \qquad \{29\}$$

If it is further assumed that the effect of the second term is small, the following equation can be used to fit the data for the $[Cl^-]$ versus time:

$$[Cl^-] = [Cl^-]_\infty (1 - e^{-k_{Cl^-} t})$$

Based on the curve fitting of the data obtained, rate constants $k_{Cl^-}$ were obtained from $Cl^-$ formation (see Table 6 below) for all frequencies. As expected, $k_{Cl^-}$ is close to the rate constant $k_1$ (see Table 7). A comparison of $k_{Cl^-}$ and $k_{CCl_4}$ is also tabulated in Table 9.

Table 9. $k_{Cl^-}$ Values from $Cl^-$ Formation

| Rate Constant, ($min^{-1}$) | Ultrasonic Frequency, (kHz) | | | | | |
|---|---|---|---|---|---|---|
| | 20 | 205 | 358 | 500 | 618 | 1078 |
| $k_{CCl_4}$ | 0.025 | 0.044 | 0.049 | 0.070 | 0.055 | 0.039 |
| $k_{Cl^-}$ | 0.024 | 0.042 | 0.042 | 0.056 | 0.049 | 0.031 |

8.6 Task 6. Perform batch or continuous-flow experiments to determine the effects of oxidants ($H_2O_2$, Fenton's Reagent. etc.) on SVOC degradation and the biodegradability of the resultant product

8.6.1 Hydrogen Peroxide Addition

Hydrogen peroxide is an effective oxidant in many applications. With ultrasonic irradiation, $H_2O_2$ will dissociate to form OH• radicals which will cleave the chlorines from the chlorinated organic compounds [von Sonntag and Schuchmann, 1991; Sunder and Hempei, 1997]. For this study, tests were performed to determine

the effect of adding $H_2O_2$ at various concentrations. Results summarizing the $CCl_4$ and TCE data are presented in Figures 37 and 38. Compared to sonication alone, the addition of $H_2O_2$ did not effect the reduction rate of these compounds. Tests performed with the addition of $H_2O_2$ but with out sonication only showed a slight reduction in the contaminant concentration. This reduction may be due to factors other than the oxidation from $H_2O_2$. Hydrogen peroxide is more effective in oxidizing organics with an H-C bond and a C=C bond [von Sonntag and Schuchmann, 1991; Buxton et al., 1988; Bremner et al., 1996; Jennings and Townsend, 1961].

### 8.6.2 Ferrous Sulfate Addition

Zero-valent iron (Fe') has been shown to degrade $CCl_4$ [Lipszynska-Kochany et al., 1994] to chloroform ($CHCl_3$). Fe(II) salt, such as pyrite ($FeS_2$), has also been shown to transformed $CCl_4$ [Kriegman-King and Reinhard, 1994]. Sulfur compounds, such as sodium sulfide, were speculated to induce transformation of $CCl_4$ and yield the toxic intermediate, carbon disulfide ($CS_2$) [Lipszynska-Kochany et al., 1994]. Hydrolysis of $FeSO_4$ had been suggested to be the major initial reaction pathway to initiate the reaction [Lipszynska-Kochany et al., 1994]. Hydrolysis of $FeSO_4$ formed ferric hydroxide, sulfate, and an electron.

Tests were performed using 0.098 M ferrous sulfate to study the degradation phenomena of $CCl_4$ and TCE. After 10 minutes contact time, reduction of the target compound was less than 5%. The degradation rate of sonolysis (25.3 $W/cm^2$) was 5.6 times faster than the degradation rate of adding 0.098 M $FeSO_4$ (see Figures 39 and 40). Combination of $FeSO_4$ and sonication also did not enhance the contaminant reduction efficiency compared to sonication alone.

### 8.6.3 Fenton's Reagent

Combining hydrogen peroxide and ferrous sulfate at a 10 to 1 ratio (known as Fenton's Reagent) results in an accelerated reaction to form OH• radicals. Fe(II) salts react with $H_2O_2$ to produce [von Sonntag and Schuchmann, 1991; Bremner et al., 1996]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + CDOTOH$$

The effect of increasing the OH• radicals available to enhance the degradation of the target compounds with sonication was examined. Spiked samples were mixed with 0.98 M $H_2O_2$ and 0.098 M $FeSO_4$ and immediately sonicated for 10 minutes at 25.3 $W/cm^2$. Figures 41 and 42 illustrate the results of these tests with solutions of 7 ppm $CCl_4$ and TCE in terms of reaction rates verses time. The Fenton's reagent produces a violent reaction when its two constituents are added to form the hydroxyl radicals. This reaction was quite effective in removing the target compounds from the sample solution. Within the first two minutes of reaction time, the Fenton's reagent alone was effective in removing the contaminants 100 times faster than sonication. After 10 minutes. the target compounds were no longer detectable. A disadvantage for using Fenton's reagent is its by-product of an iron sludge. At the concentration used in the described test, the amount of sludge produced would make it impractical for application in a vapor extraction well. Lower concentrations, near iron concentrations in groundwater, will be investigated in further tests to determine the potential enhancement of sonication.

## 8.7 Task 7. Identify and quantify corrosion potential and salt formation

No progress has been made on this task; this task will be worked on during FY 1998.

8.8 Task 8. Determine the volatility and biodegradability of the treated waters (and compare to untreated waters)

Carbon tetrachloride ($CCl_4$) was selected as the model compound for this study. The objective of this experiment was to study the ability of common soil bacterial consortium to biodegrade the "softened" $CCl_4$ after sonication treatment. This first biodegradation experiment was conducted under aerobic conditions. The $CCl_4$ at an initial concentration of 30 mg/L was sonicated for 10 min. at 20 kHz. The sonicated and unsonicated $CCl_4$ were used for the biodegradation studies.

8.8.1 Microorganisms:

An aerobic bacterial consortium isolated from a garden soil was used in this experiment. The purpose of choosing this common soil bacteria was that the in-well sonication method will partially degrade (soften) the target compound, in this case $CCl_4$, which in turn will be easily amenable to bacterial degradation. We have specific chlorinated solvents degrading bacteria in our culture collection; however, this specific chlorinated solvent degraders were not used for this study because in this experiment., the effects of sonication on $CCl_4$ and its amenability to bacterial degradation are being tested. The soil bacterial consortium was pregrown and a late logarithmic culture was used as inoculum for the experiment.

8.8.2 Growth Conditions:

The bacterial consortium was grown in a basic mineral salt medium containing the following components:

| Components | (g/L) |
|---|---|
| $K_2HPO_4$ | 1.0 |
| $KH_2PO_4$ | 0.5 |
| $MgSO_4$ | 0.1 |
| NaCl | 0.1 |
| $(NH_4)_2SO_4$ | 0.2 |
| Yeast extract | 0.01 |

The bacterial medium was prepared and distributed in 10-mL quantities into 150-mL culture bottles with airtight seal. A 50-mL quantity of the sonicated or unsonicated $CCl_4$ was added to each culture bottle. A 1% pregrown inoculum was added to the culture bottles. The experiment was conducted in triplicates with triplicate abiotic controls. All culture bottles were incubated in a gyratory shaker kept at 100 rpm at ambient temperature (20-22°C). Samples were drawn periodically from the culture bottles to measure bacterial growth and for the analysis of $CCl_4$ and its breakdown products.

8.8.3 Analysis:

8.8.3.1 *Bacterial growth:* Bacterial growth was monitored by observing the turbidity of the culture with a Spectronic 20 spectrophotometer (Milton Roy, Rochester, NY) kept at the wavelength of 600 nm.

*8.8.3.2 GC Analysis:* Analytical method development included selection and procurement of a Hewlett Packard 7694 Automatic Headspace Sampler for use with the Hewlett Packard 5890 Gas Chromatograph. Headspace analysis is well-suited for analysis of volatile and semivolatile organic compounds

in water, and avoids the column degradation caused by liquid injection of water. The headspace sampling method includes ten minutes equilibration of samples at 70°C with shaking, programmed vial pressurization, venting, sample loop fill (1 mL loop volume), and 0.30 minute injection time. Equilibration time was selected by measuring area response for times ranging from 1 to 60 minutes. A 30 meter megabore fused capillary DB-624 column was selected based on its sensitivity and selectivity in analysis of chlorinated organic compounds. The HP 5890 chromatograph is equipped with both flame ionization and electron capture detectors. In the analytical range for this project (0.1 to 100 ppm), flame, ionization provided adequate resolution and reproducible detection. The electron capture detector was found to be too sensitive for detection of major components, but is useful in examining sonicated samples for minor breakdown products. The GC temperature program was set for 1 minute at 90°C, ramping 10°/minute to 140°, then 25°/minute to 200°, and held for 2 minutes at 200º C. Standards were initially prepared in volumetric flasks. Due to analyte volatility, this was changed to injection by syringe through the vial septum of the chlorinated compounds into measured water mass. Planned sample size was 5 mL in 10 mL vials, however this was reduced to 1 mL in 10 mL vials to avoid overloading the column with analyte. Response of carbon tetrachloride standards held in sealed vials over a 0.25 to 48 hour time range was evaluated to determine how long samples could be stored prior to GC analysis. It was found that vials analyzed within three hours after sampling gave the most reproducible response. Vials showed a drop in response to approximately 80% at 15 hours, and to 20-40% at 25 hours. Since the hydrolysis rate for $CCl_4$ in water is very low, there appears to be loss through the vial seal or septum. Therefore ail subsequent samples and standards were analyzed as closely as possible to the actual sampling time. and ail within three hours. Five analyte standards were prepared each day for the initial calibration curve, and check standards were performed late in the day, or when any questionable sample result was obtained.

8.8.4 Experimental Scheme:

```
Sonicated samples                    Unsonicated samples
        / \                                  / \
        / \                                  / \
Control    Experimental              Control    Experimental
(no bacteria)   (with bacteria)   (no bacteria)        (with bacteria)
3 culture bottles each               3 culture bottles each
```

8.8.5 Results:

8.8.5.1 *Bacterial Growth:* Figure 43 shows the growth of the bacteria in the sonicated and unsonicated $CCl_4$ samples. Data were the average of triplicate culture bottles. The bacterial growth was minimal at the beginning (first 4 days) as the bacterial culture gets adapted to the compound $CCl_4$, after day 4, the bacteria grew slowly. The bacterial growth was better in the sonicated samples compared to unsonicated samples. This indicates that there is some softening of $CCl_4$ due to sonication, which bacteria were able to use as carbon source and break it down further. In the abiotic controls, there was no growth.

This preliminary experiment showed that the sonicated sample supported bacterial growth compared to unsonicated sample and this indirectly shows that the "softened" $CCl_4$ is being degraded by the common soil bacteria. This experiment is still continuing and the results will be updated later.

*8.8.5.2 Concentration of $CCl_4$:* The first two analysis of the head space of the culture bottles did not show any difference between sonicated and unsonicated samples in terms of parent compound concentration and its breakdown products from day 0 to day 7. However, this experiment is still on going and the data from later time points will be analyzed and discussed later.

### 8.8.6 Future Work on Biodegradation Studies:

Our hypothesis is that a wide variety of electron acceptor conditions can and will provide a wide variety of enzyme activities and associated microbial activities to remove chlorinated solvents. Aerobic and anaerobic bacteria present in the contaminated site can affect the rate of degradation of contaminants depending on the local environment. Under appropriate conditions microorganisms can biotransform, dechlorinate, and eventually degrade the chlorinated organic solvents. The presence or absence of certain electron acceptors will determine the redox potential in the environment. The redox potential in turn will control the range and distribution of microorganisms. Aerobic and anaerobic metabolism of organic compounds usually requires electron acceptors like organic compounds (fermentation conditions), oxygen, sulfate, nitrate, iron, and carbon dioxide. The effects of various electron acceptor conditions on the metabolism of pre-treated (sonicated) chlorinated solvents will be investigated.

#### 8.8.6.1 Experimental Approach

##### 8.8.6.1.1 Collection of Samples and Analyses:

Samples from the SVOC-contaminated site will be collected and analyzed for physical and chemical characteristics of the sample such as pH, redox potential. total organic carbon, ammonia, and phosphorous. Initial experiments will be conducted in shake flasks and anaerobic bottles that will determine the effect of microbial metabolism on the metabolites produced from the in-well softening of SVOCs.

##### 8.8.6.1.2 Selection of Microbial System for the Study:

Samples from the SVOC-contaminated sites will be collected and screened for various microbial population viz., aerobic heterotrophic bacteria and the following anaerobic bacteria such as sulfate reducing, nitrate reducing, iron reducing and methanogenic bacteria under various electron accepting conditions. The best conditions will be selected in terms of maximum organic contaminants degradation.

Once the microbial system has been selected for the bioremediation of organic contaminants, further studies will be carried out on the influence environmental factors on the bacterial growth and the application value of these bacteria in terms of bioremediation of softened organic solvents. The system of electron acceptor conditions is important for the removal of organics present in anaerobic sites.

#### 8.8.6.2 Laboratory Enrichment Studies:

##### 8.8.6.2.1 *Aerobic bacteria*

The aerobic heterotrophic bacteria present in the contaminated site will be enriched as described before [Boopathy et al., 1994]. The heterotrophic medium consisting of the following components will be prepared: $K_2HPO_4$ (1.0 g/L), $KH_2PO_4$ (0.5 g/L), $MgSO_4$ (0.10 g/L), NaCl (0.1 g/L), (NH,), SO, (0.2 g/L), yeast extract (0.01 g/L), and sonicated and unsonicated sample (90 mL). The medium (100 mL) will be distributed in several 200 mL culture bottles with screw cap and mineret lock for periodic headspace sampling (gas phase). A portion of the contaminated soil (1 g) will be added to these culture bottles as bacterial source. The culture bottles will be incubated at room temperature (20-22° C) in a gyratory shaker kept at 150 rpm. The enrichment cultures will be transferred to fresh media periodically. After five transfers, the enrichment culture will be tested for its effectiveness in removing organic contaminants. Bacterial growth will be monitored by measuring the culture turbidity at 600 nm using a Spectronic 20 spectrophotometer. The dissolved oxygen (D.O.) will be monitored using a D.O probe available in our laboratory. Experiments will be conducted in triplicates with triplicate

abiotic controls to compare the results. A similar parallel experiment will be conducted without the media but only with sonicated and unsonicated samples.

*8.8.6.2.2* *Anaerobic bacteria:*

Under ail the anaerobic conditions described below, one set of experiment will be conducted with the enriched media to enrich the selective bacterial population and another set of experiment will be conducted only with sonicated and unsonicated samples.

*8.8.6.2.3* *Sulfate reducing bacteria (SRB):*

The anaerobic techniques described by Balch and Wolfe [ 1976] and Daniels et al. [1986] will be used throughout the study. Anaerobic culture bottles with butyl rubber stoppers and aluminum crimps will be used. The enrichment medium for the experiment was described earlier by Boopathy et al. [1993]. The medium consists of the following components (in mM): KC1 (4.l), $NH_4Cl$ (16.8), $CaCl_2$ (0.61), $K_2HPO_4$ (1.45), $KH_2PO_4$ (1.85), NaCl (O.60), $MgCl_2$ (0.l), $Na_2CO_3$ (1.5), $Na_2S$ (1.0), rasazurin (0.003), pyruvate (30.0), sodium sulfate (20.0), and sonicated and unsonicated sample (90 mL). The pH of the medium will be adjusted to 6.8. After preparation, medium will be distributed into anaerobic culture bottles and will be made anaerobic as described previously by Balch and Wolfe [1976] using a gassing manifold system available in our laboratory. The gas phase will be 100% $N_2$ and the culture bottles will be kept at the pressure of 20 psi $N_2$.

The soil samples will be collected from the intermittently anaerobic vadose zone (which has significant anaerobic bacterial populations) of the contaminated site. Samples will be kept in sterile containers and transported to the laboratory. A portion of the soil sample (1 g) will be added to the anaerobic culture bottles containing sulfate reducing media in 100 mL amounts. The culture bottles will be incubated at room temperature (20-22° C) in a gyratory shaker kept at 150 rpm. The cultures showing substantial growth will be transferred to fresh medium. After five more transfers, experiments will be conducted on the sixth transfer enrichment cultures. In this enrichment cultures, bacterial growth will be monitored by observing the culture turbidity. The experiment will be conducted in triplicate with abiotic controls.

*8.8.6.2.4* *Nitrate reducing bacteria:*

The culture conditions described for SRB enrichment study will be followed except for a few changes in the media composition. The nitrate reducing medium will contain all the components described in the SRB medium, but, in the place of pyruvate, sodium acetate (40 mM) will be added. Sodium nitrate (20 mM) will replace sodium sulfate as electron acceptor. In this experiment. we will monitor bacterial growth. The experiment will be conducted in triplicates with abiotic controls.

*8.8.6.2.5* *Iron reducing bacteria:*

The culture conditions for iron reducing conditions will be similar to that of nitrate reducing conditions described above except that 20 mM Fe (III) will serve as electron acceptor in place of nitrate. The soluble iron will be added to the medium as iron-citrate complex as described by Coates et al. [1996]. The study will be conducted in triplicates with abiotic controls.

*8.8.6.2.6* *Methanogenic bacteria:*

All the culture conditions and experimental procedure described for SRB enrichment study will be followed except that the medium will contain 40 mM sodium acetate instead of pyruvate as carbon source and

the medium will not contain sodium sulfate. The headspace will contain $H_2$-$CO_2$ (80:20) instead of N,. Bacterial growth will be monitored. The experiment will be conducted in triplicates with abiotic controls.

*8.8.6.2.7* *Fermenting Bacteria;*

The fermenting bacteria present in the contaminated site will be enriched by supplementing simple sugars such as molasses in the media. The mineral salts present in the SRB medium will be used without the addition of pyruvate and sulfate. The medium will be supplemented with 0.3% (v/v) molasses as carbon source and will be incubated under anaerobic conditions with 100% $N_2$ in the headspace. Similar experimental protocols described above for SRB will be followed.

8.8.6.3 Analyses

8.8.6.3.1 Bacterial growth

The bacterial growth in the culture samples will be monitored by measuring the culture turbidity at 600 nm using a Spectronic 20 spectrophotometer.

8.8.6.3.2 Dissolved oxygen (D.O.)

The D.O in the sample will be monitored by using an oxygen analyzer (Gilson Oxygraph model Oxy-5, Gilson Electronics, Middleton, WI). The instrument will be calibrated with deionized water saturated with oxygen.

8.8.6.3.3 pH

The pH in the sample wi1l be measured by using a pH meter (Accumet pH meter).

8.8.6.3.4 Nitrogen, ammonia and phosphorous

phosphorous will be analyzed by calorimetric methods using Hach water analysis reagent kits (Hach Company, Loveland, CO).

8.8.6.3.5 VOC and SVOC

The VOC and SVOC analyses will be analyzed using GC techniques.

8.8.6.4 Degradation Products

Table A.1 in Appendix A lists physical properties of the parent halogenated organic compounds and various potential degradation products. Included in that table is information on the vapor pressures of these compounds. The higher the vapor pressure, the more volatile the compound. Carbon tetrachloride ($CCl_4$) and trichloroethane (TCA) have vapor pressures of ~100 mm Hg at ambient temperatures; they are the most volatile of the parent halogenated organic compounds, the other parent compounds (TCE, PCE, and EDB) are much less volatile. Hexachloroethane is not very volatile (~1 mm Hg) for the potential degradation products, while phosgene (if formed) has a relatively high vapor pressure (~1200 mm Hg), indicating that phosgene could be quite readily stripped out of solution, whereas hexachloroethane, is not readily stripped from solution.

Degradation rates were obtained from Howard et al. [ 1991]. The data is summarized in Table 10 below.

This material indicates that unacclimated biodegradation half-lives can range from ~ 168 days up to 4.5 years. Similarly, the half-lives of the halogenated organic compounds in soil range from 168 days up to 1 year. This material indicates the need to make the organic contaminants both bioavailable, and potentially partially degraded so that biodegradation activities can be enhanced. During FY 1998, additional data will be sought from the technical literature, as well as biodegradation rates will be determined in our experimental work.

Table 10. Biodegradation and Kinetic Rates for the Halogenated Compounds of Concern [adapted from Howard et al., I991]

| Compound | Half-Lives, (h) | | | | Aqueous Biodegradation (unacclimated) | | | Photooxidation Half-Life, (h) | | Hydrolysis Half-Life |
|---|---|---|---|---|---|---|---|---|---|---|
| | Soil | Air | Surface Water | Ground Water | Aerobic Half-Life, (h) | Anaerobic Half-Life, (h) | Removal./ Secondary Treatment | Water | Air | |
| $CCl_4$ | 4320-8640 | $1.6x\ 10^4$-$1.6x10^5$ | 4032-8640 | 168-8640 | 4032-8640 | 168-672 | up to 99% | No data | $1.6x\ 10^4$-$1.6x10^5$ | 7000 yrs |
| $CHCl_3$ | 672-4320 | 623-6231 | 672-4320 | 1344-43,200 | 672-4320 | 168-672 | Up to 96% | $6.9x\ 10^5$-2.8x 10' | 623-6231 | 3500 yrs |
| TCE | 4320-8640 | 27-272 | 4320-8640 | 7704-39,672 | 4320-8640 | 2352-39,672 | No data | No data | 27-272 | 7704 h |
| TCA | 3360-6552 | 5393-53,929 | 3360-6552 | 3360-13,104 | 3360-6552 | 13,440-26,208 | No data | No data | 5393-53,929 | 0.73 yrs |
| PCE | 4320-8640 | 384-3843 | 4320-8640 | 8640-17,280 | 4320-8640 | 2352-39,672 | **up to 86%** | No data | 384-3843 | No hydrolyz-able groups |
| EDB | 672-4320 | 257-2567 | 672-4320 | 470-2880 | 672-4320 | 48-360 | No data | No data | 257-2567 | 19,272 h |
| $CH_3Cl$ | 168-672 | 1472-14,717 | 168-672 | 336-1344 | 168-672 | 672-2688 | No data | No data | 1472-14,717 | 7000 h @ PH 7 |
| $C_2Cl_6$ | 672-4320 | $>6x\ 10^4$-$>6x10^5$ | 672-4320 | 1344-8640 | 672-4320 | 2688-17,280 | No data | Not significant | $>6x\ 10^4$-$>6x\ 10^5$ | Not significant |

8.9 Task 9. Develop computer simulation model to describe combined in-well sonication/in-well vapor stripping, and biodegradation

A numerical model is being developed at Stanford University to simulate the influences of the processes of in-well sonication, in-well vapor stripping, and biodegradation on the groundwater as they occur in the subsurface. Given the complexity of the flow and multi-process treatment system, the representation of removal processes in the model will be represented as simply as possible. The model will be based on MT3D, an existing groundwater contaminant transport code, which will be modified. The model will account for flow induced by a single recirculating well and the changes to water as dissolved VOCs are removed by the selected *in-situ* treatment. In addition to the contaminant removal processes mentioned above, other important physical and chemical processes that will be accounted for in the model are advection, dispersion, molecular diffusion, and equilibrium adsorption-desorption of contaminants to and from aquifer solids.

The success of contaminant transport modeling effort is strongly dependent on the availability of adequate input data. The first phase of model use will be in association with the laboratory-scale aquifer system to be constructed at ANL. This brief statement refers only to the laboratory system and the measurements that are needed for successful modeling. For the laboratory-scale system, several key parameters and state variables must be measured. Assuming that the laboratory system consists of homogeneous sand, that the contaminant under study is a single dissolved VOC, and that all significant changes in concentration occur in the treatment well or in the aquifer (saturated zone), the model will require the following input parameters:

- For flow, the following measurements are needed: porosity, effective porosity, hydraulic conductivity, bulk density, particle density, particle grain-size distribution analysis, the location of the treatment well and the specifics of its design (screened intervals, diameter), flow rate of air through the well, flow rate of water through the well. Depending on the exact experiment, we will need boundary conditions (heads in feed tanks around the edge depending on whether there is an induced natural gradient or not). During the experiment the primary state variable that must be measured is hydraulic heads in three dimensions (3D). This should be done using multi-level mini-piezometers. Observation of the capillary fringe may also be important if it represents a relatively large volume of water in the laboratory system.

- For contaminant transport, the following measurements are needed: Contaminant properties such as sorption isotherms, kinetic isotherms, Henry's law constants, aqueous diffusion coefficients, and gas diffusion rate constants. A tracer test using a non-reactive substance, such as chloride, should be conducted prior to loading the tank with VOC. The analysis of this test will help us determine the dispersion coefficient needed for simulation of VOC transport through the aquifer. If possible, other non-reactive tracers should be introduced once the recirculating flow system is operational. These tracers should be introduced at various locations in the tank and measured at each monitoring well and at various locations and depths in the feed tanks. This will help us better understand the flow system mechanics and local flow velocities. The state variable of interest is concentration which must be measured in 3D over time using multi-level monitoring wells. Initial concentrations, boundary concentrations, and concentrations during the tracer test must be measured. Other laboratory measurements required to characterize the contaminant removal processes include: the biodegradation rate in the aquifer, the air-water flow ratio for vapor stripping, the single-pass stripping percentage (assuming that the laboratory system will be too small for the water-bubble mixture to reach equilibrium), the single pass removal percentage-for in-well sonication as a function of dissolved VOC concentration, and the degradation product function due to sonication. Each VOC will be modeled sequentially. That is, first the parent VOC will be considered over the entire time frame of the experiment. and then based on the degradation product function due to sonication, the daughter product(s) will be modeled over the entire time frame of the experiment. Concentrations in the

treatment well at the bottom well screen and the top well screen must be measured. VOC off-gas from the vapor-stripping well must be measured over time. Granular activated carbon (GAC) usage must be measured. Soil VOC gas concentrations, humidity of the injected and retrieved vapor, the temperature of the water, and the temperature of the injected and retrieved air must be measured as well. A suite of basic water quality measurements must be obtained (e.g. major anions, cations, pH, dissolved oxygen. etc.) before and after each laboratory experiment. Some of the above parameters will require column experimental work to be conducted. If there are any interference effects due to combining contaminants, these must be investigated.

The main output of the model will be predicted heads and contaminant concentrations throughout the aquifer over time. Using reasonable estimates of parameter values. the model can be used to gain a quantitative understanding of how the entire system works. Given preliminary estimates of parameters, the model can be used to assist in the design of laboratory experiments. For example, we can simulate the concentration removal over time in the system and thereby get some idea of where and when to monitor concentrations. Once the experiments have been conducted, the model will be used to analyze the resulting data, and the process components of the model will be modified to better represent the true system. This calibration stage will involve matching simulated to observed heads and concentrations. Once the laboratory-scale system is understood and can be modeled, a similar process will be followed to help design the field system. That is, the model can be used to design the field-scale system, calibrate it to field data, and analyze system performance in 3D over time. In the field, this will be particularly valuable as measurements will be relatively sparse.

Tasks 10 through 13 will be performed during FY 1998 and 1999. Those tasks were not worked on during FY 1997.

## 9 ANNUAL SONICATION WORKSHOP

Argonne National Laboratory has taken the lead to hold an annual workshop for projects in the field of sonication which are funded by DOE's EMSP Program. The first annual workshop was held at Argonne on October 25, 1996. These workshops brings together researchers to discuss results from their research projects, from the following organizations: University of Illinois, Purdue University, University of Washington, Syracuse University, and the University of California at Davis, in addition to Argonne. Another workshop is tentatively planned during the latter part of October 1997. There are six sonication projects funded by EMSP:

(1) *Argonne National Laboratory:* "Use of Sonication for In-Well Softening of Semivolatile Organic Compounds"; PIs: Robert W. Peters and John Manning

(2) *Purdue University:* "An Investigation of Homogeneous and Heterogeneous Sonochemistry for Destruction of Hazardous Waste"; PI: Inez Hua

(3) *Syracuse University:* "Acoustic Probe for Solid-Gas-Liquid Suspensions"; PI: Lawrence L. Tavarides

(4) *University of California at Davis:* "On-Line Slurry Viscosity and Concentration Measurement as a Real-Time Waste Stream Characterization Tool"; PIs: Robert L. Powell (U.C. Davis) and Reza Shekarriz (Pacific Northwest Laboratory)

(5) *University of Illinois:* "Cavitational Hydrothermal Oxidation: A New Remediation Process"; PI: Kenneth Suslick

(6) *University of Washington:* "The Sonophysics and Sonochemistry of Liquid Waste Quantification and Remediation"; PI: Thomas J. Matula

Representatives of DOE's EMSP Program have been invited to attend these workshops: Drs. Robert Price and Gordon Roesler have indicated that they will attend this years workshop.

## 10 TECHNOLOGY TRANSFER ACTIVITIES

The integrated technology involving in-well sonication, in-well vapor striping, and in-situ biodegradation has been described in an article published in Argonne's **Tech Transfer Highlights** [1997]. In that article, Argonne is seeking industrial collaborators with technical strengths in megasonics to help develop a prototype down-well reactor.

A small potato processing firm (Idaho Supreme Potatoes, Inc.) has expressed an interest in the technology to treat wastewaters that contain a myriad of odorous compounds, including acetic acid, phenylacetic acid, indole, skatole, n-butyric acid, and iso-butyric acid. Work is being pursued through Argonne's Industrial Technology Development (IT'D) Center under a Technical Services Request to examine the applicability of this integrated treatment system involving sonication, vapor stripping, and microbial degradation, to minimize odors from their process waters.

Additionally, the results from this research are being shared (on an annual basis) with other sonication researchers (funded through DOE's EMSP Program) in the annual sonication workshop held at Argonne each year.

## 11 RECOMMENDATIONS FOR NEXT YEARS RESEARCH (FY 1998)

Several recommendations are suggested for performing the in-well sonication/in-well vapor stripping/in-*situ* biodegradation research, as listed below:

- To address the process performance using in-well vapor stripping alone, separate experiments will be performed employing air sparging of each of the halogenated organic compound-contaminated groundwaters. The performance results will be compared to that involving sonication alone, and the overall integrated system.
- Once the basic mechanisms of the various treatment subcomponents are identified, attempts will be made to optimize the overall effectiveness of the system by varying each of the subsystems.
- Biodegradation studies will be performed on various halogenated solvents (e.g., $CCl_4$, TCE, TCA, PCE, and EDB) using aerobic bacteria in the culture collection, mainly *Pseudomonas spp.* Biodegradation studies will also be performed under anaerobic conditions using sulfate reducing bacteria, specifically by *Desulfovibrio spp.*
- Experiments will be performed investigating the effect of adding micronutrients (e.g., nitrogen and phosphorus containing compounds) into the groundwater being sonicated to determine whether the addition of the micronutrients will enhance and facilitate biodegradation of the partially degraded halogenated organic compounds.
- Issues of corrosion on the sonication equipment and reactor walls will be addressed.
- Discussions will begin during FY 1998 to identify potential EM users for potential site demonstration and technology implementation. Potential DOE facilities include: Hanford's 200 Area, Savannah River's A/M Area, the Paducah Gaseous Diffusion Plant's NE and NW Plumes, Argonne's 317/319 Area, and

Lawrence Livermore's Main Site, among others. Hanford will have representatives at this year's Sonication Workshop to discuss their problems with the K-Basin sludge which contains PCBs.

- Technology transfer efforts will be continued and followed-up. As an example, this may include an invitation for Idaho Supreme Potatoes, Inc. to attend next years annual sonication workshop.

## 12 TECHNICAL PUBLICATIONS/PRESENTATIONS

Two technical presentations are planned that result from the research activities of this past year. The research presentations are listed below:

(1) "Formation of Degradation Products of Chlorinated Organic Compounds in Sonication Operations", by Robert W. Peters, Linda Shem, Po-Yao Kuo, Mary Quinn, Michael R. Hoffmann, and Hui-Ming Hung; Paper to be presented at the Fourth International Conference on Advanced Oxidation Technologies for Water and Air Remediation, Orlando, Florida, September 23-26, 1997.

(2) "Kinetics of Carbon Tetrachloride and Trichloroethylene Degradation Using Sonication Techniques", by Robert W. Peters, Po-Yao Kuo, Mary Quinn, Linda Shem, Michael R. Hoffmann, and Hui-Ming Hung; Paper to be presented at the 1998 Spring National AIChE Meeting, New Orleans, Louisiana, (March 8-12, 1998).

## 13 DISCLAIMER

The viewpoints expressed here are not necessarily those of Argonne National Laboratory or its sponsors.

## 14 ACKNOWLEDGMENT

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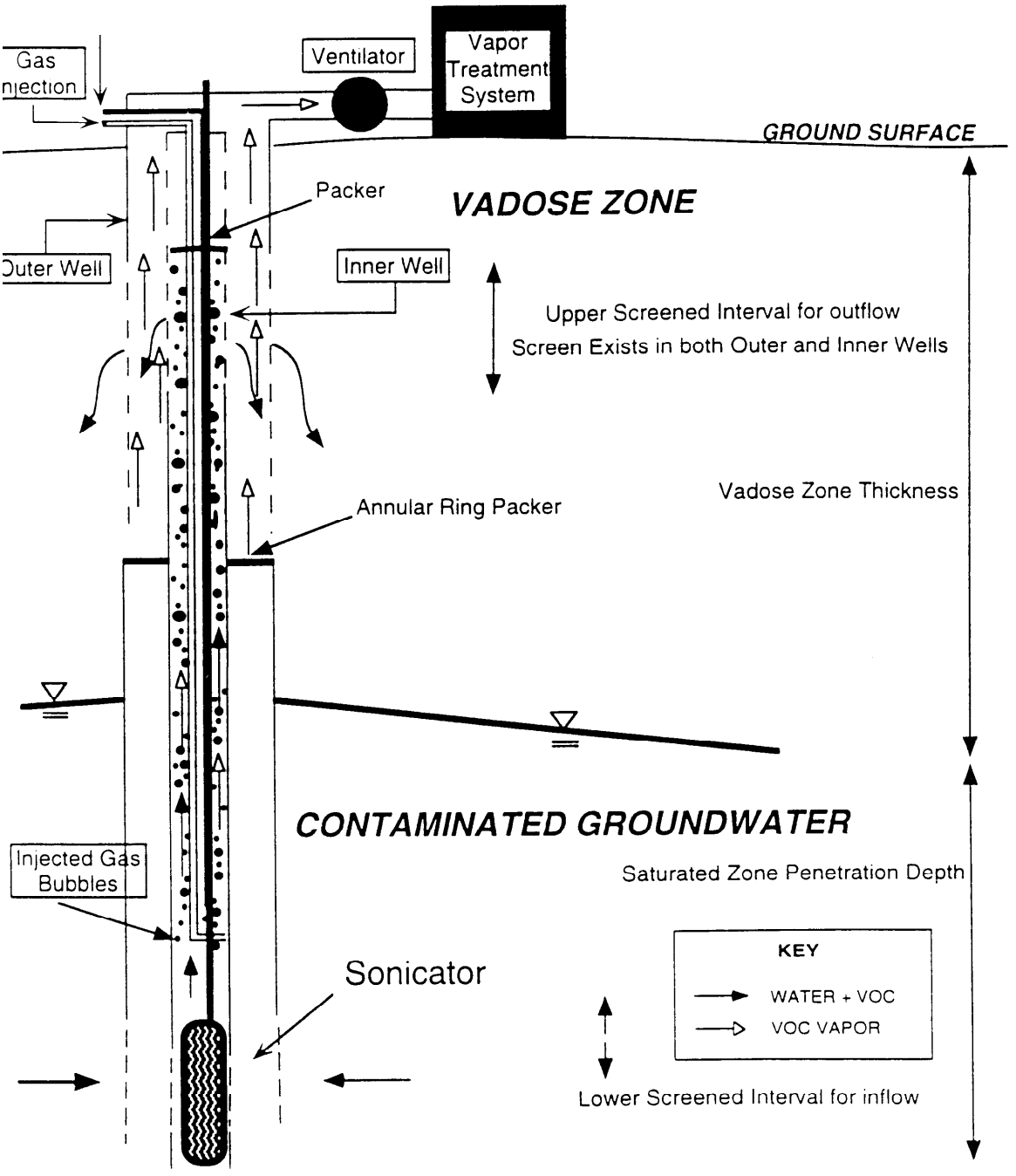


Figure 1. Diagram of a Single Treatment Well in Which In-Well Sonication Softens and Partially Destroys VOCs and Semi-VOCs, and In-Well Vapor Stripping is Used to Remove the VOCs as a Vapor. The treatment process is performed completely *in-situ* wherein no water is brought to the surface

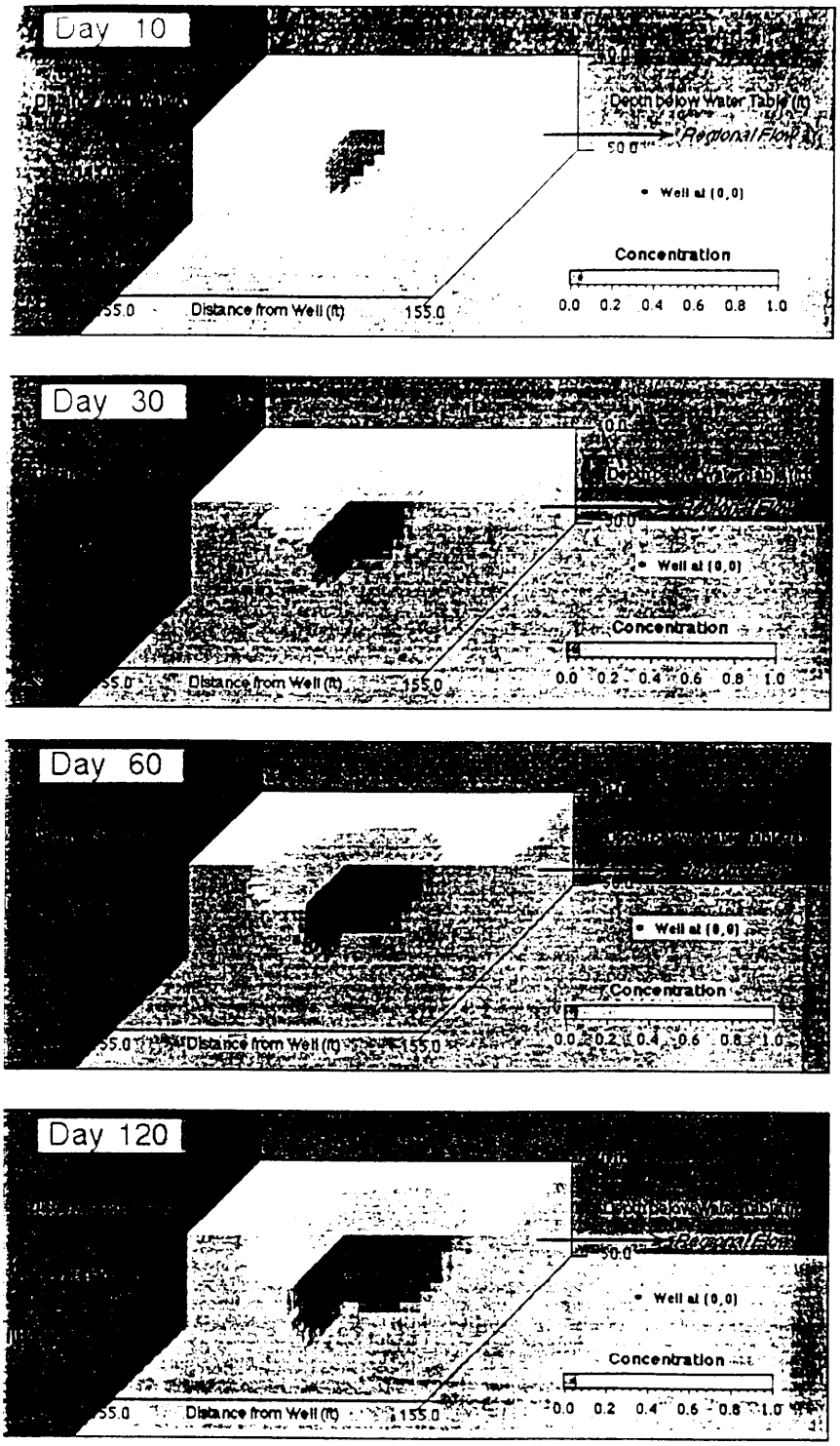


Figure 2. Sequence of Four "Snapshots" Showing the Zone of Influence and Removal of VOCs for a Hypothetical Combined In-Well Sonication and In-Well Vapor Stripping for Contaminants Within the Saturated Zone. Very conservative estimates for degradation and removal were used in the simulation

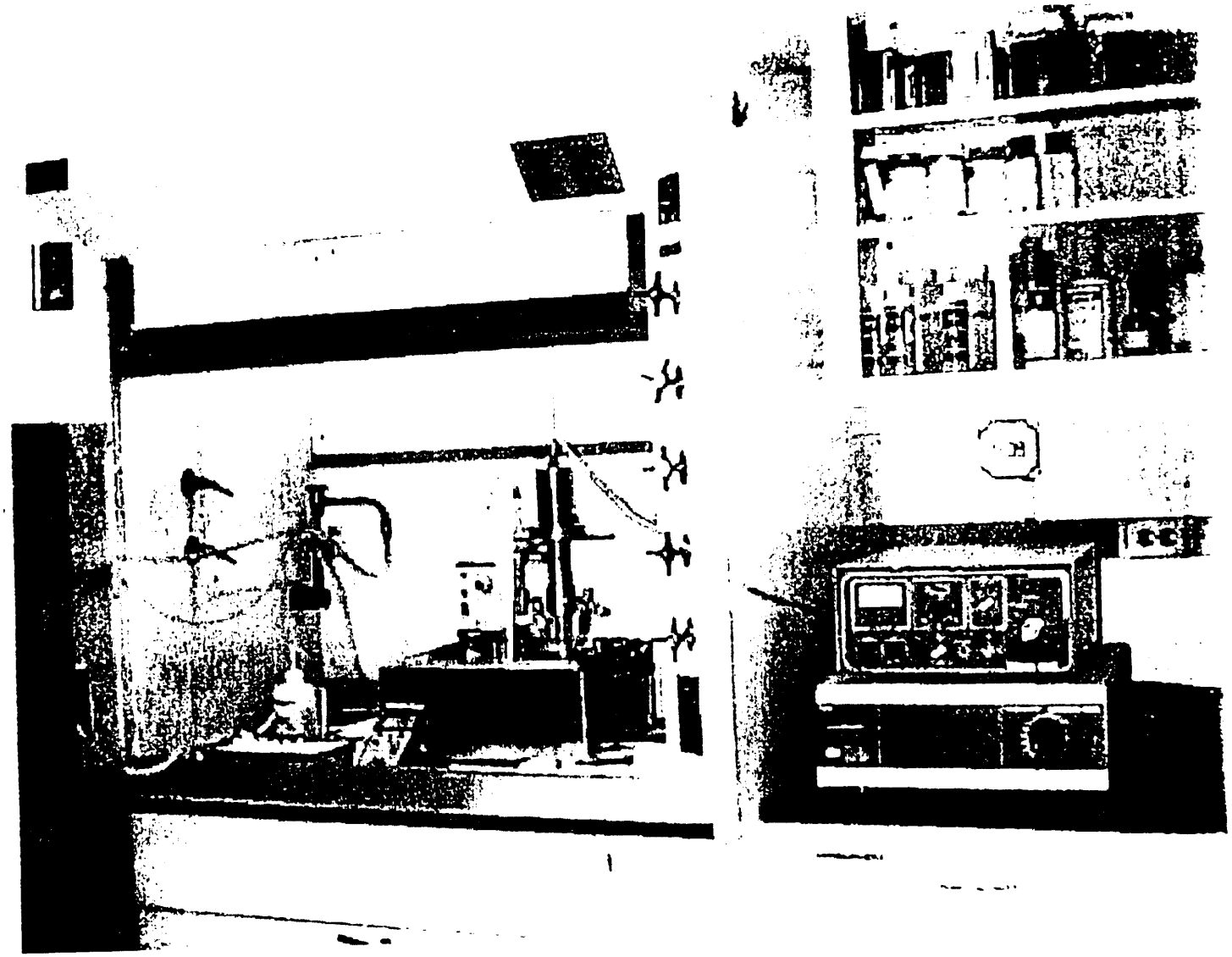

Figure 3.Experimental Batch Sonication System

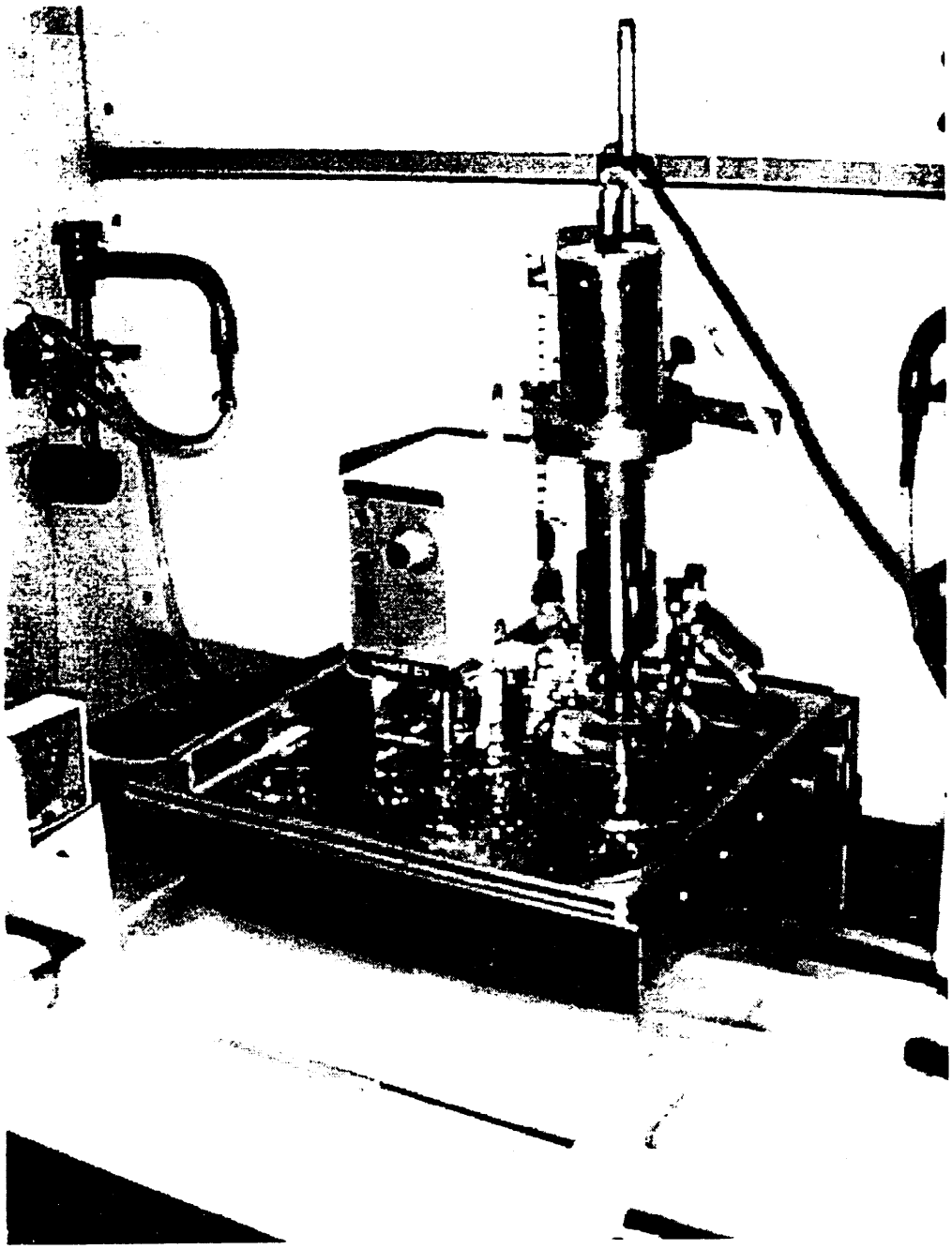

Figure 4. Close-up of the Sonication System Contained in the Constant Temperature Bath

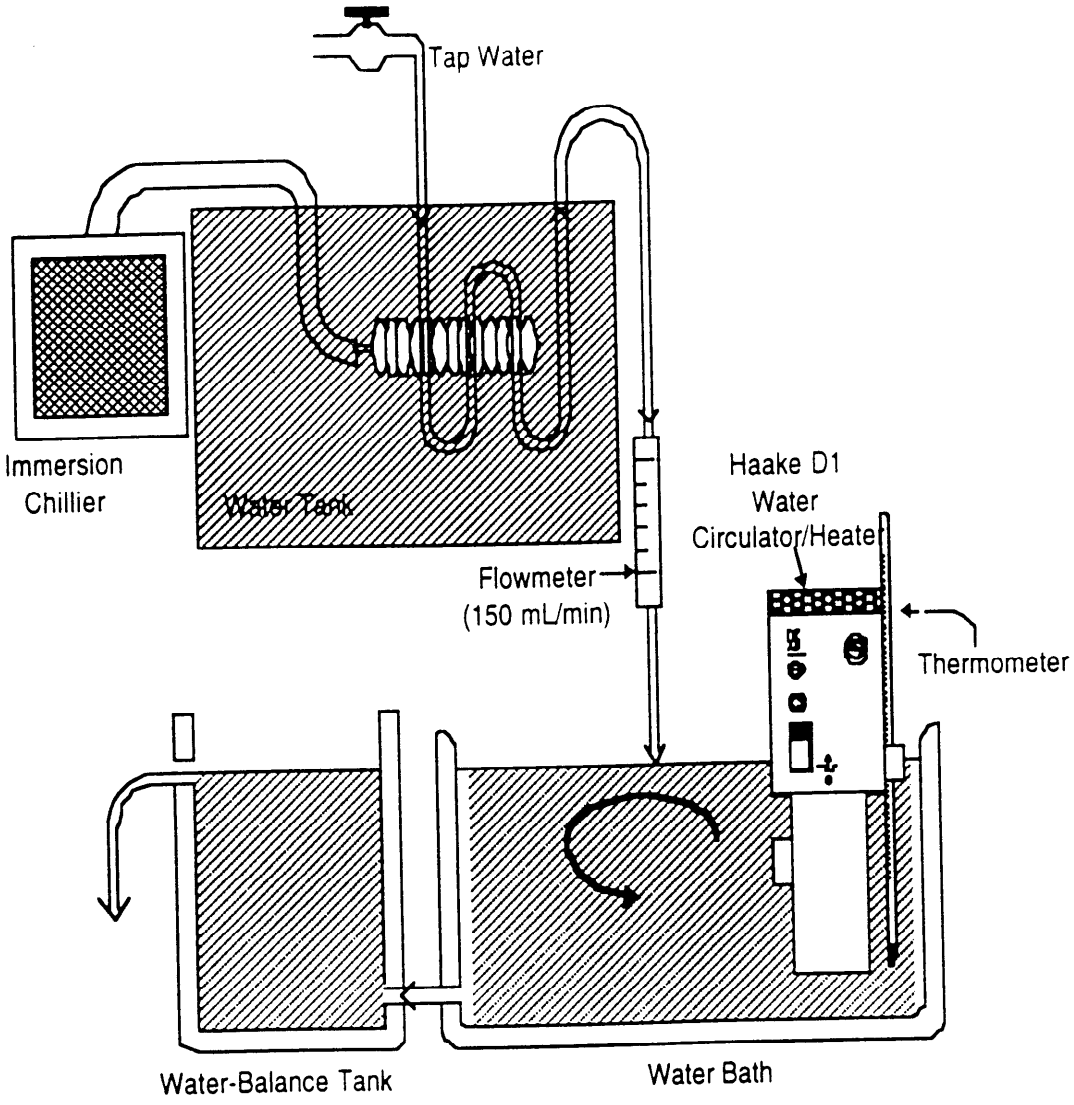


Figure 5. Constant Temperature Bath

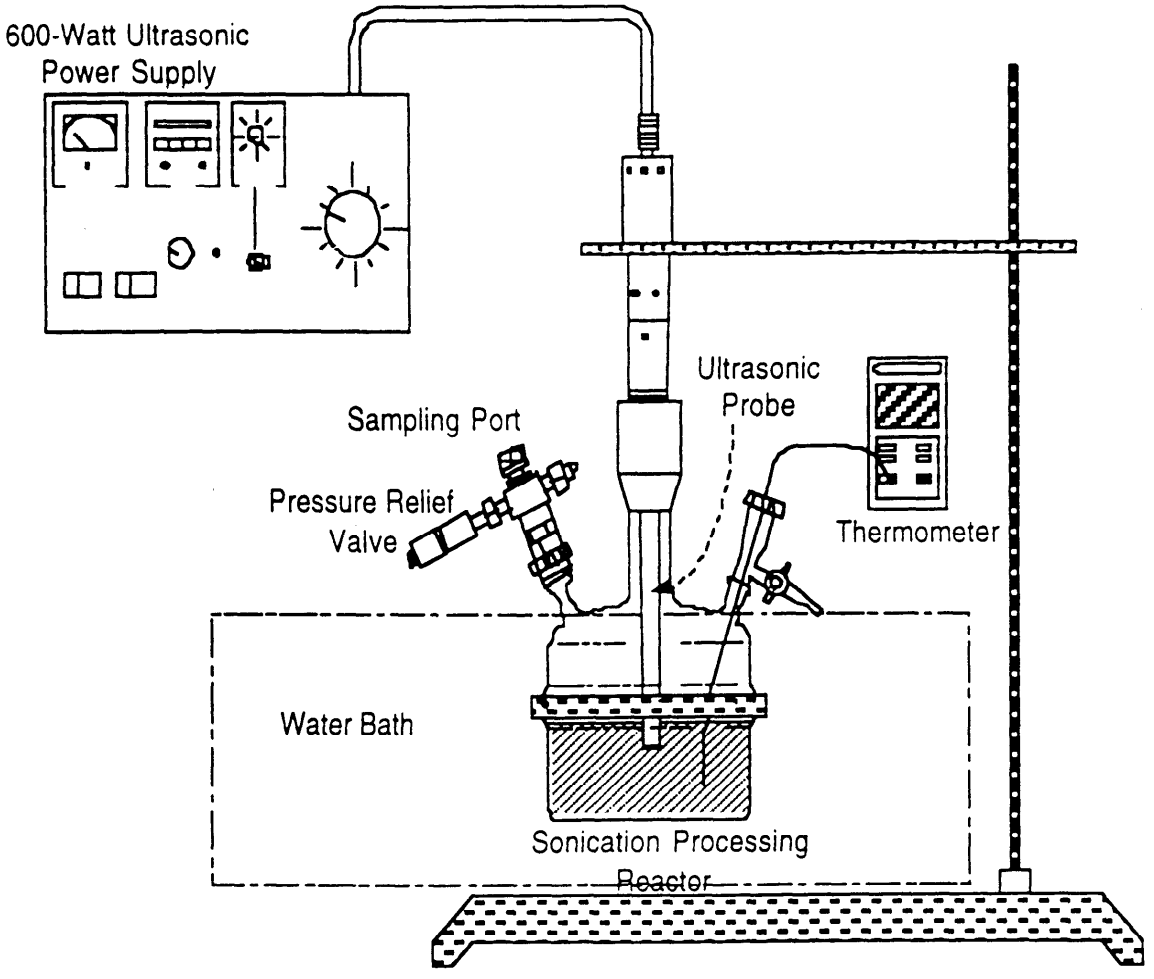


Figure 6. Ultrasonic Power Supply and Reactor

Figure 7.Layout of Laboratory Analytical System

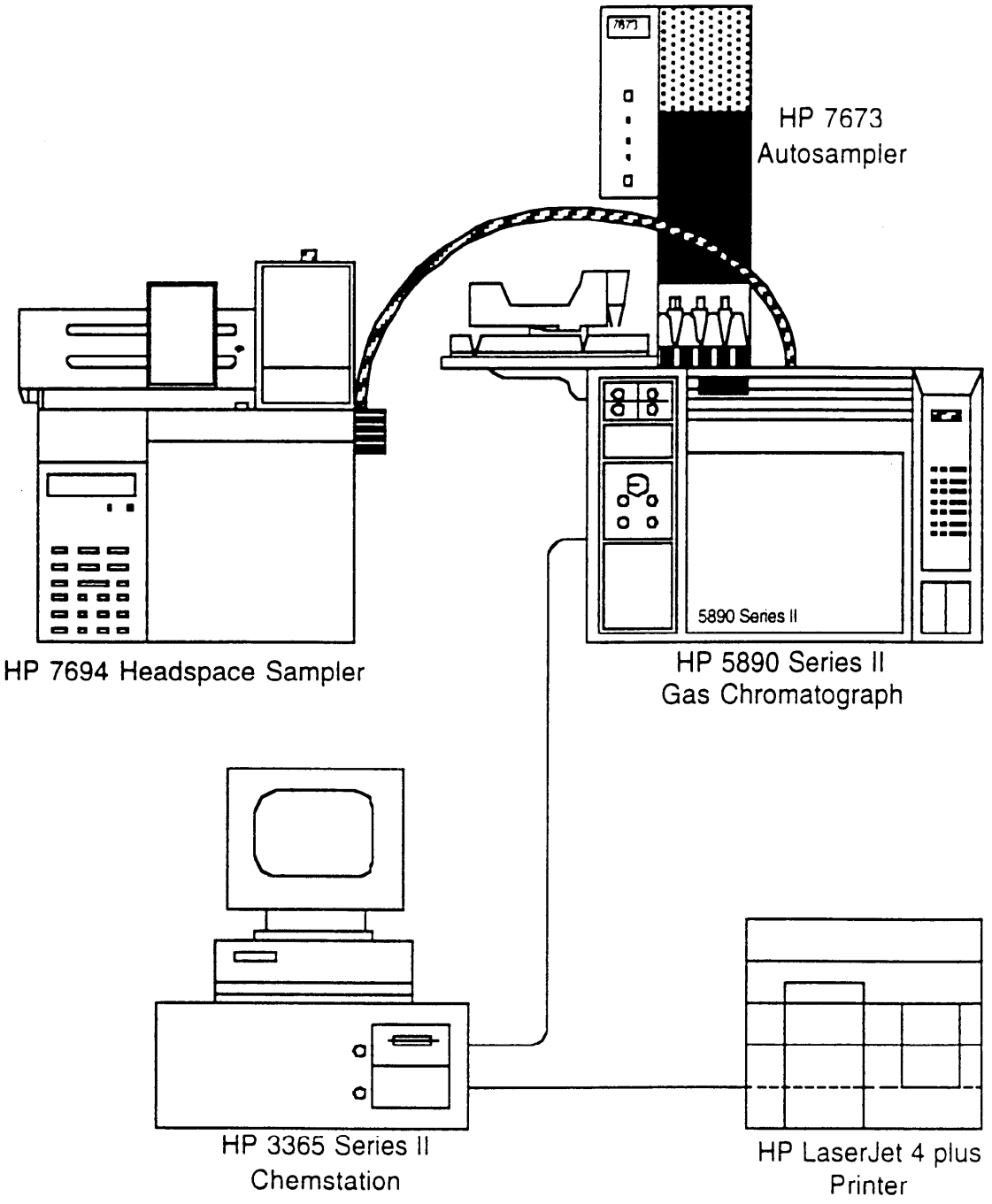


Figure 8. Gas Chromatograph System

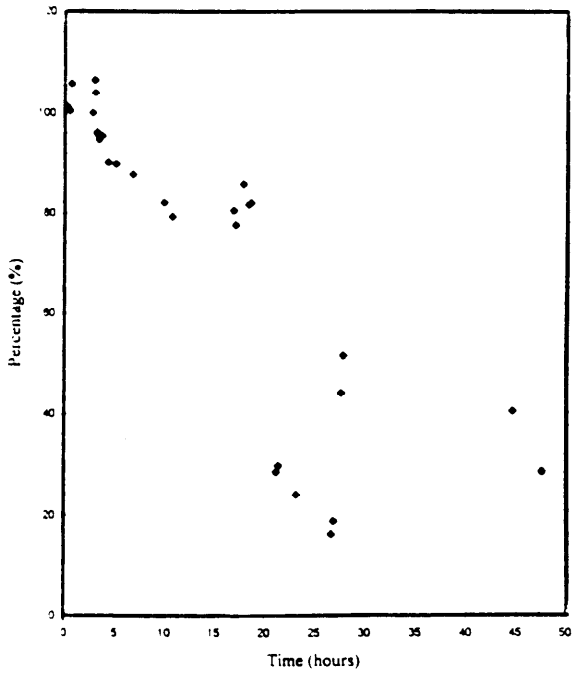


Figure 9. CC1, Analyte Stability over 48 Hours

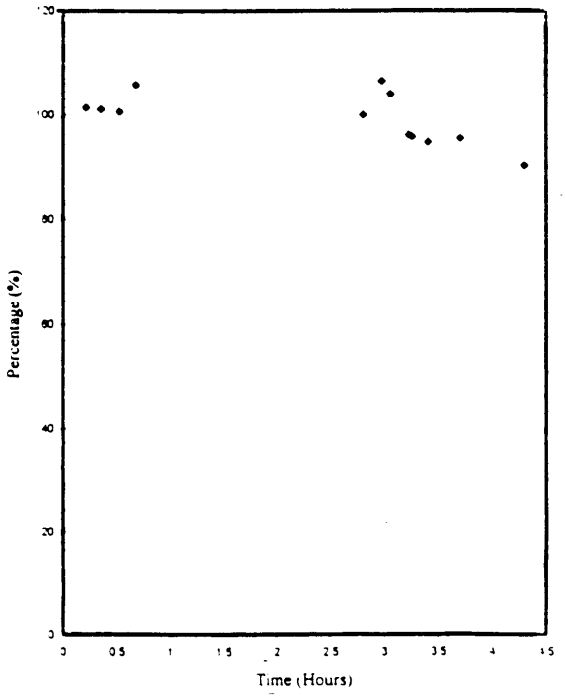


Figure 10. CCl, Analyte Stability over 4.5 Hours

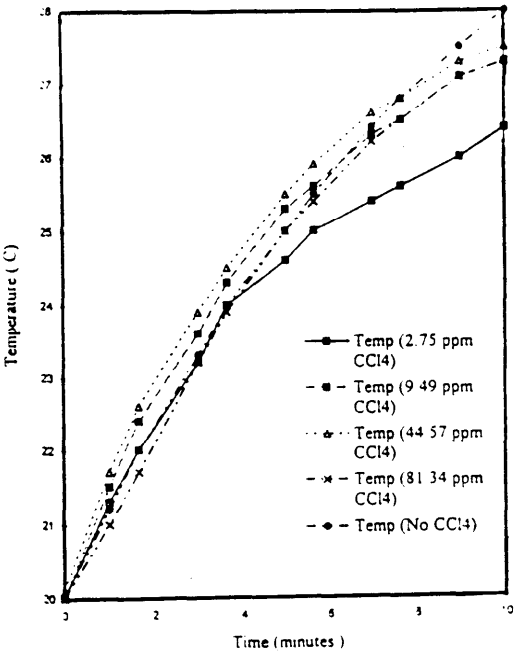


Figure 11 .Temperature Profiles of 10 minutes 35.8 W/cm$^2$ Sonication

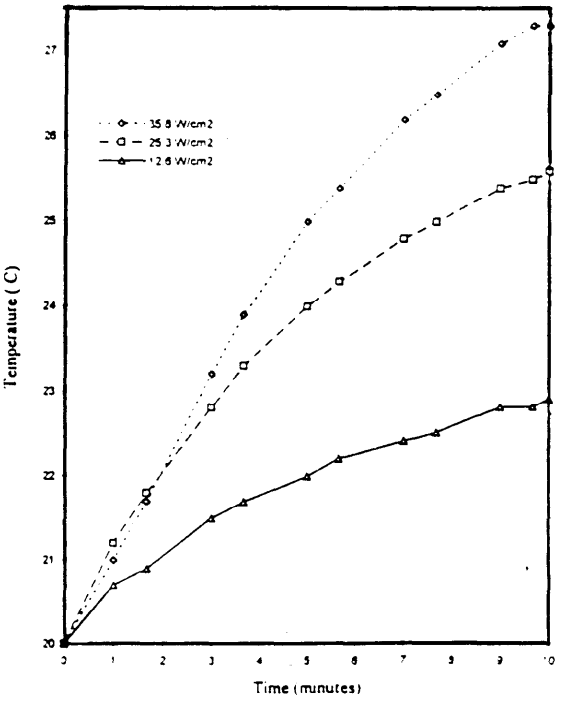


Figure 12. Temperature Profiles at Different Power Intensities of Ultrasonic Irradiation

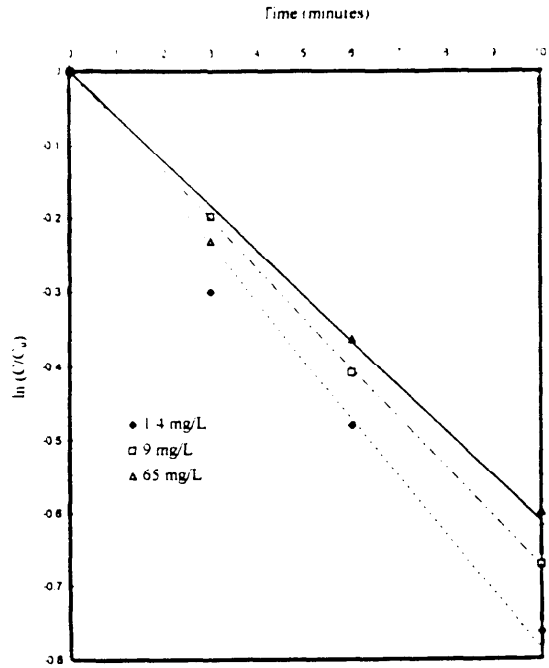


Figure 13. First-Order Plot of Natural Log [$CCl_4$] vs. Sonication Time at 35.8 W/cm$^2$

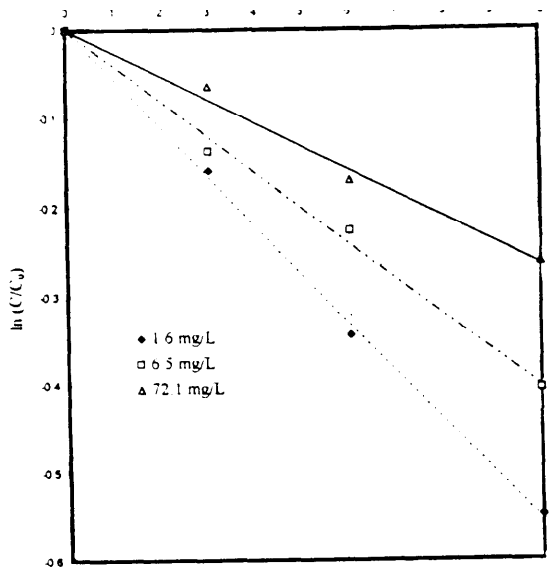


Figure 14. First-Order Plot of Natural Log [TCE] vs. Sonication Time at 35.8 W/cm$^2$

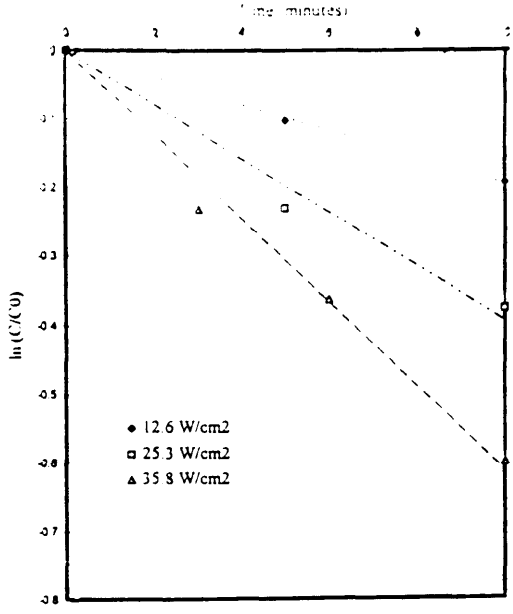


Figure 15. First-Order Plot of Natural Log [$CCl_4$] at Various Power Intensities for Initial $CCl_4$ Concentration of 65 mg/L

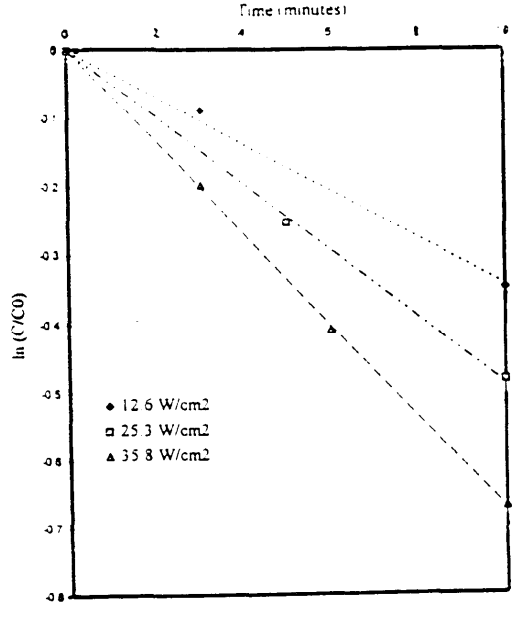


Figure 16. First-Order Plot of Natural Log [$CCl_4$] at Various Power Intensities for Initial $CCl_4$ Concentration of 8 mg/L

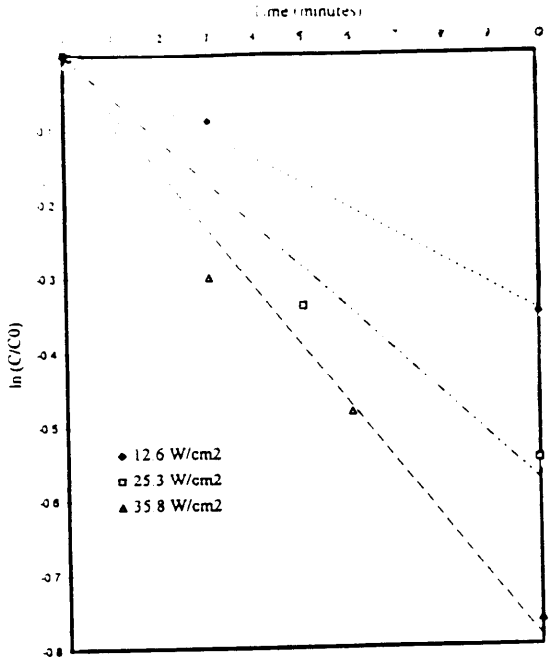


Figure 17. First-Order Plot of Natural Log [$CCl_4$] at Various Power Intensities for Initial $CCl_4$ Concentration of 1.6 mg/L

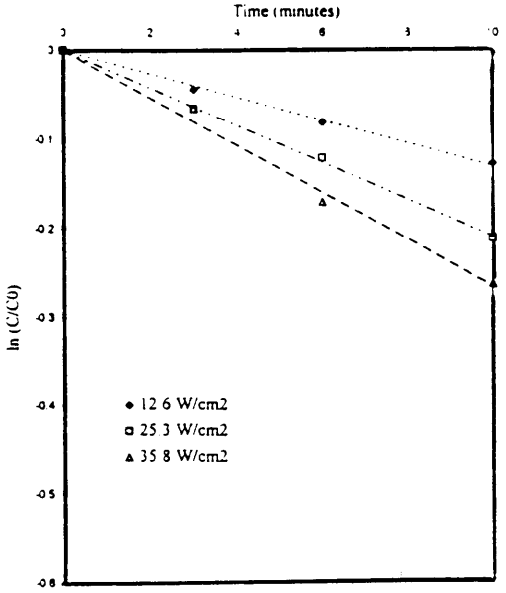


Figure 18. First-Order Plot of Natural Log [TCE] at Various Power Intensities for Initial TCE Concentration of 70 mg/L

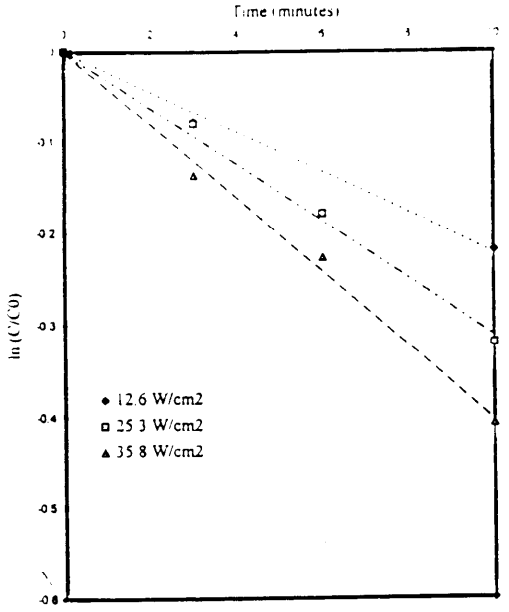


Figure 19. First-Order Plot of Natural Log [TCE] at Various Power Intensities for Initial TCE Concentration of 6.5 mg/L

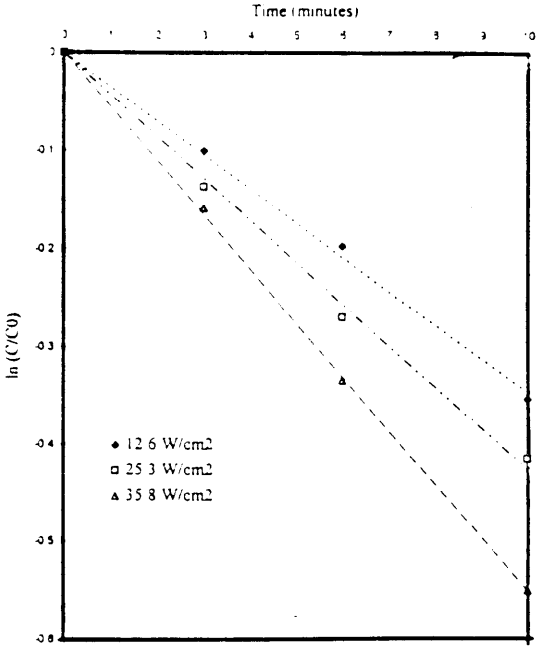


Figure 20. First-Order Plot of Natural Log [TCE] at Various Power Intensities for Initial TCE Concentration of 1.6 mg/L

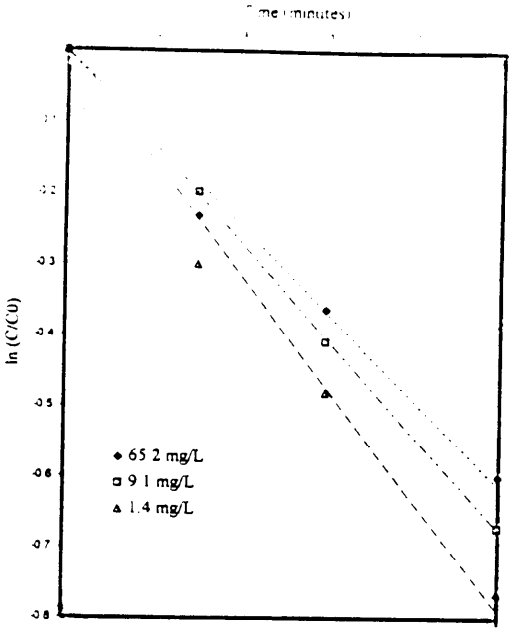


Figure 21. First-Order Plot of Natural Log $[CCl_4]$ at Various Initial $CCl_4$ Concentration (Ultrasound Intensities: 35.8 W/cm$^2$)

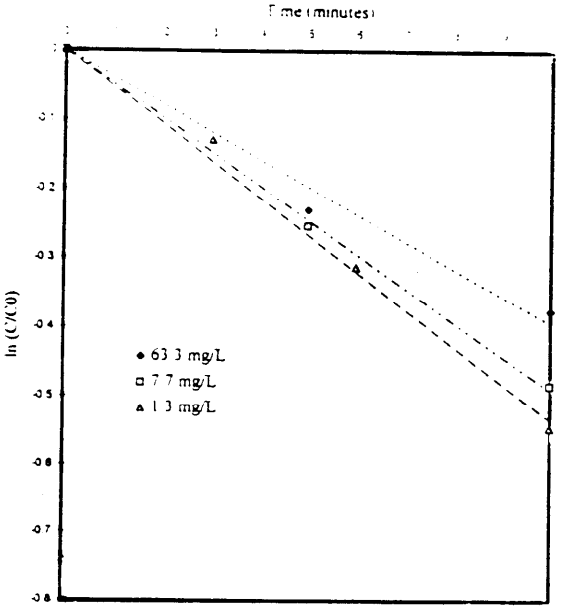


Figure 22. First-Order Plot of Natural Log $[CCl_4]$ at Various Initial $CCl_4$ Concentration (Ultrasound Intensities: 25.3 W/cm$^2$)

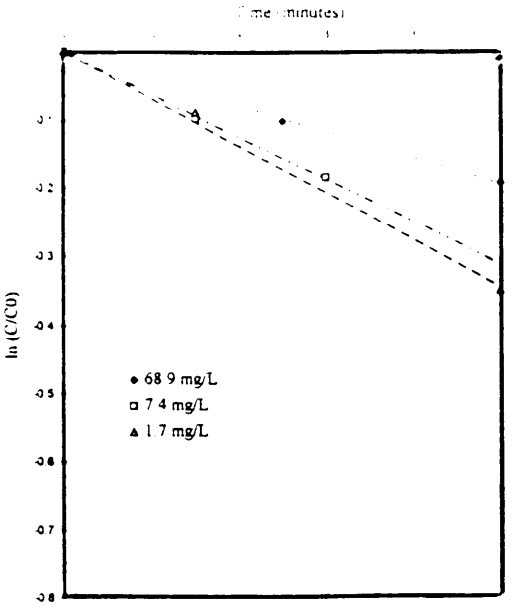


Figure 23. First-Order Plot of Natural Log [$CCl_4$] at Various Initial $CCl_4$ Concentration (Ultrasound Intensities: 12.6 W/cm$^2$)

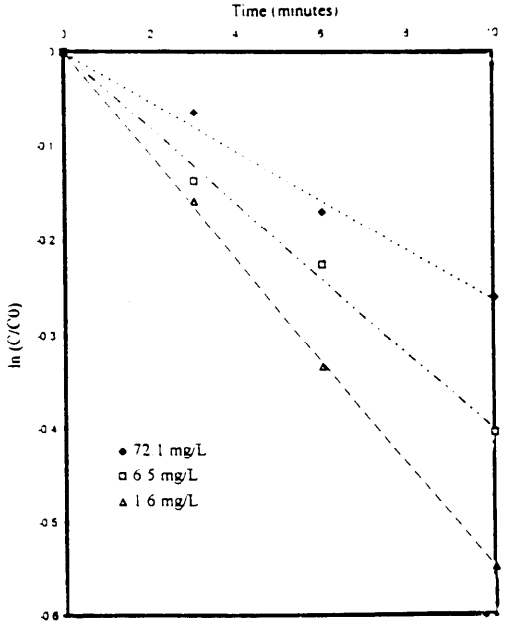


Figure 24. First-Order Plot of Natural Log [TCE] at Various Initial TCE Concentration (Ultrasound Intensities: 35.8 W/cm$^2$)

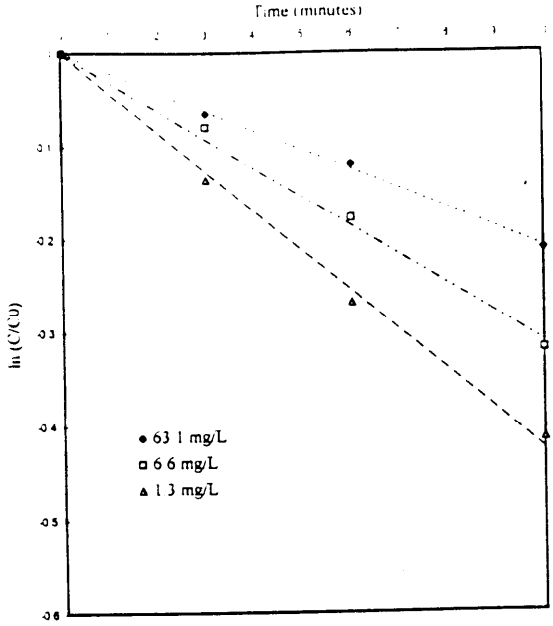


Figure 25. First-Order Plot of Natural Log [TCE] at Various Initial TCE Concentration (Ultrasound Intensities: 25.3 W/cm$^2$)

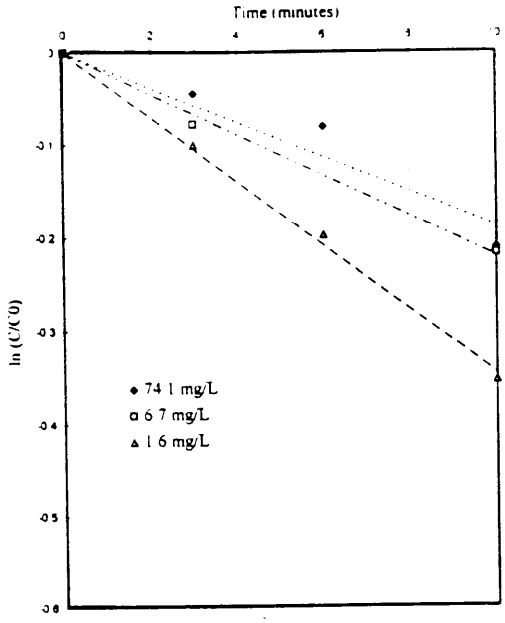


Figure 26. First-Order Plot of Natural Log [TCE] at Various Initial TCE Concentration (Ultrasound Intensities: 12.6 W/cm$^2$)

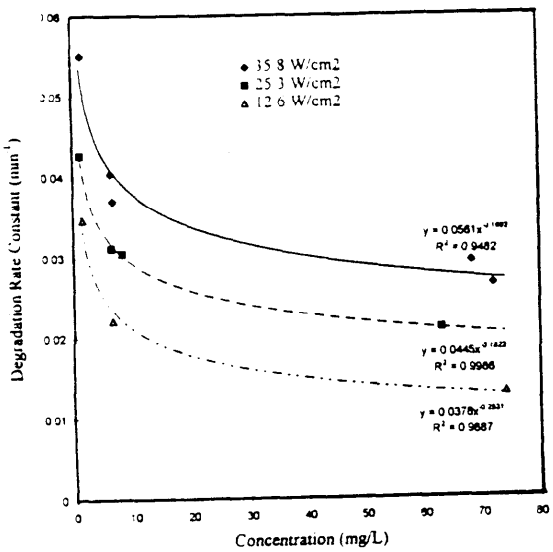


Figure 27. Relationship between Initial $CCl_4$ Concentrations and $CCl_4$ Degradation Rate Constants at Different Ultrasound Intensities

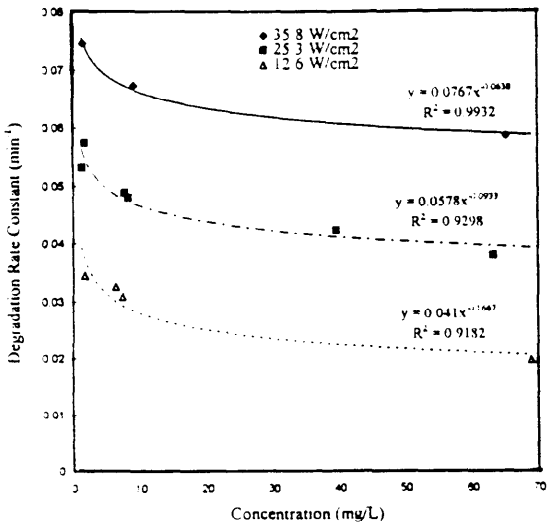


Figure 28. Relationship between Initial TCE Concentrations and TCE Degradation Rate Constants at Different Ultrasound Intensities

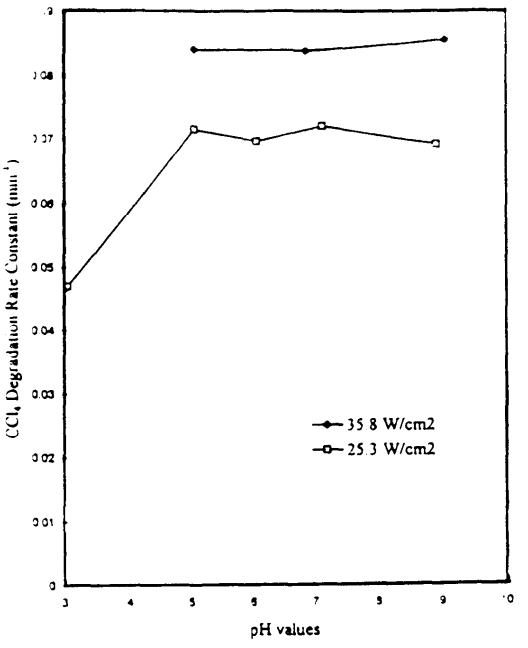


Figure 29. Effect of Initial pH Values on the Reduction of $CCl_4$ with Sonication

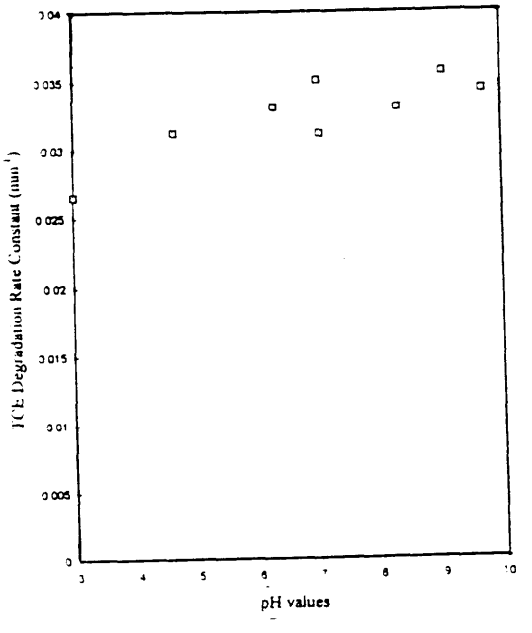


Figure 30. Effect of Initial pH Values on the Reduction of TCE with Sonication

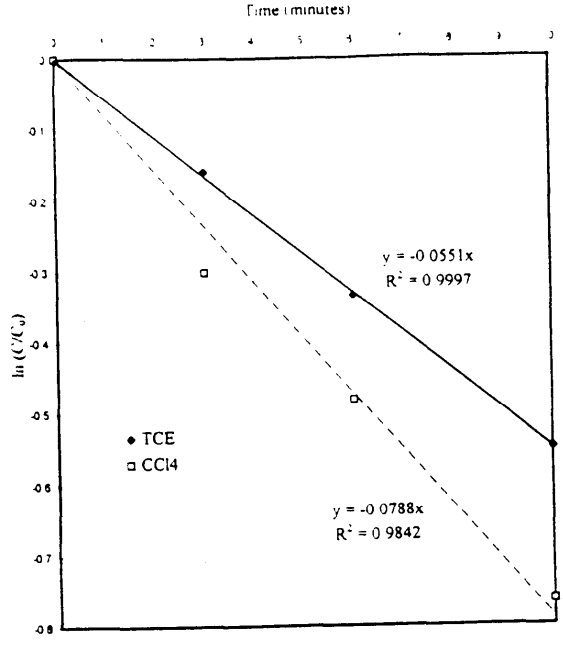


Figure 31. Comparison of Degradation Rates of $CCl_4$ and TCE (Initial $CCl_4$ and TCE Concentration: 1.6 mg/L

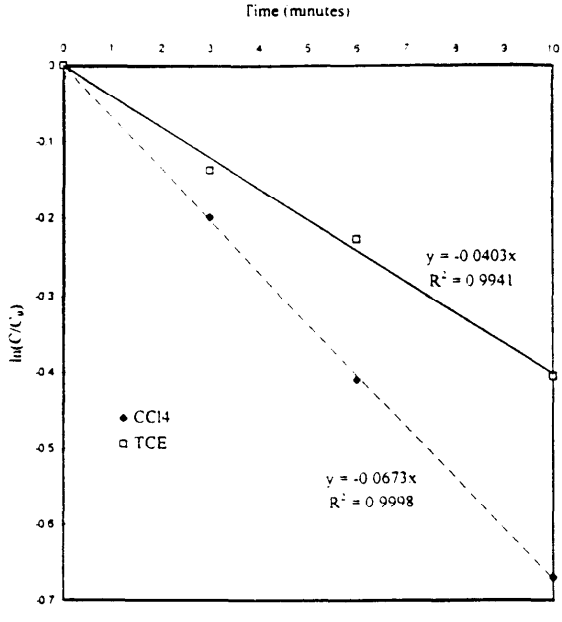


Figure 32. Comparison of Degradation Rates of $CCl_4$ and TCE (Initial $CCl_4$ and TCE Concentration: 8 mg/L

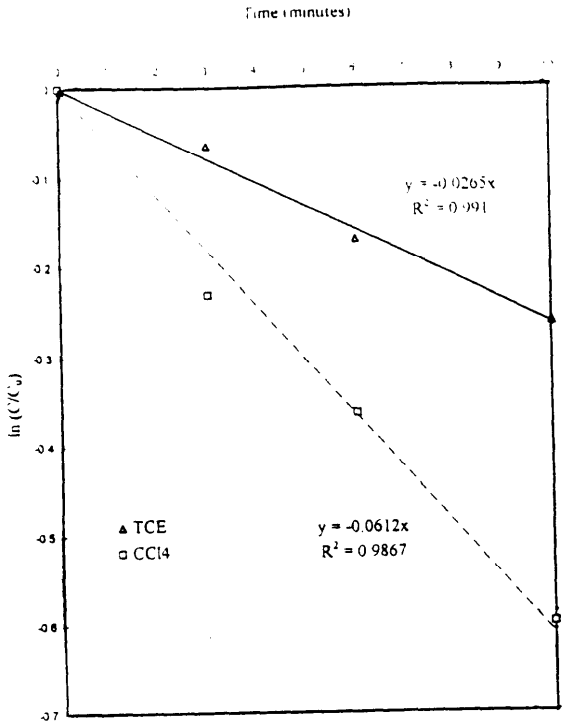


Figure 33. Comparison of Degradation Rates of $CCl_4$ and TCE (Initial $CCl_4$ and TCE Concentration: 72.09 mg/L)

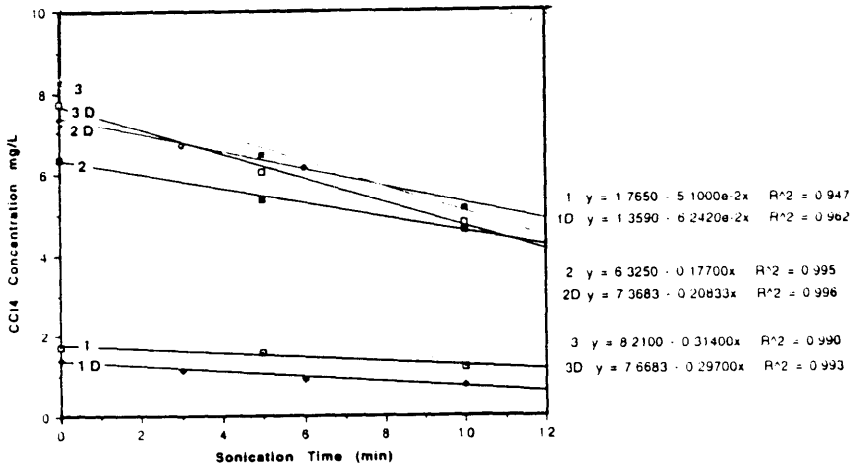


Figure 34. Comparison of Duplicate Tests for $CCl_4$

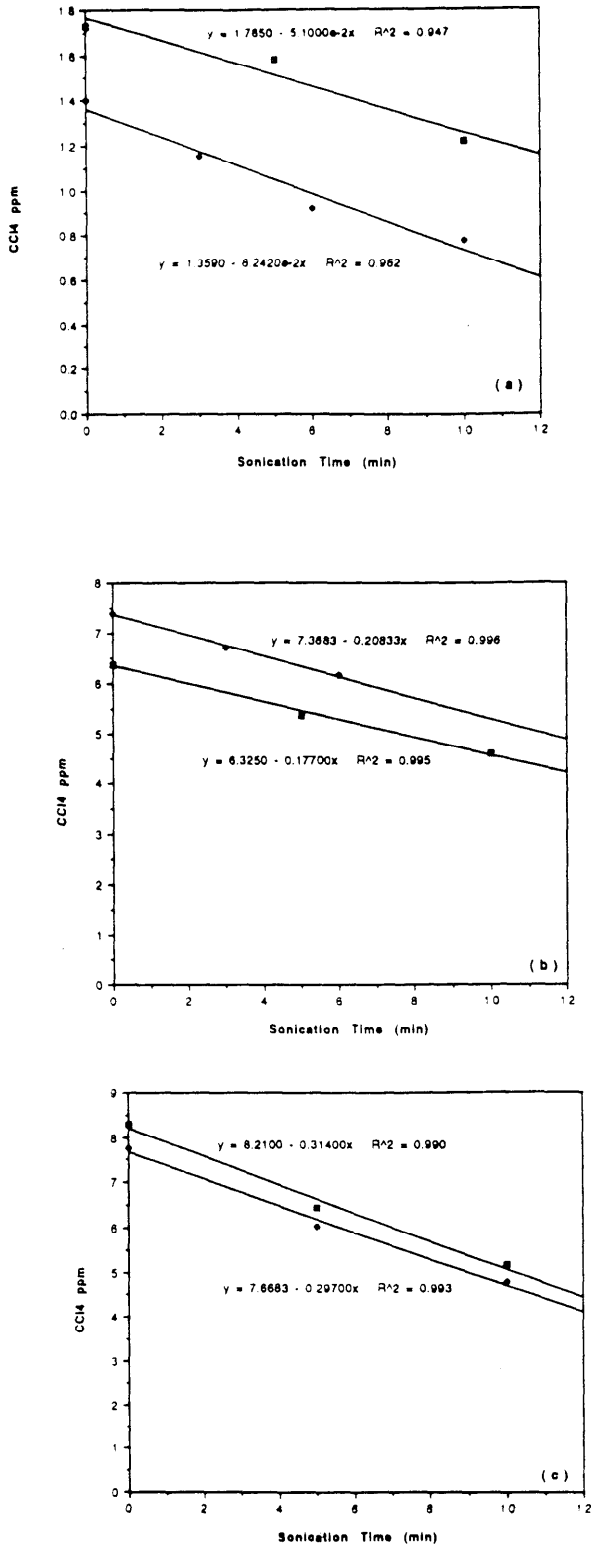


Figure 35. Comparison of $CCl_4$ Experimental Duplicates for $CCl_4$: (a) Initial Concentration ~ 1.6 ppm; Power Intensity: 12.6 $W/cm^2$; (b) Initial Concentration ~ 8 ppm; Power Intensity: 12.6 $W/cm^2$; and (c) Initial Concentration ~ 8 ppm; Power Intensity: 25.3 $W/cm^2$.

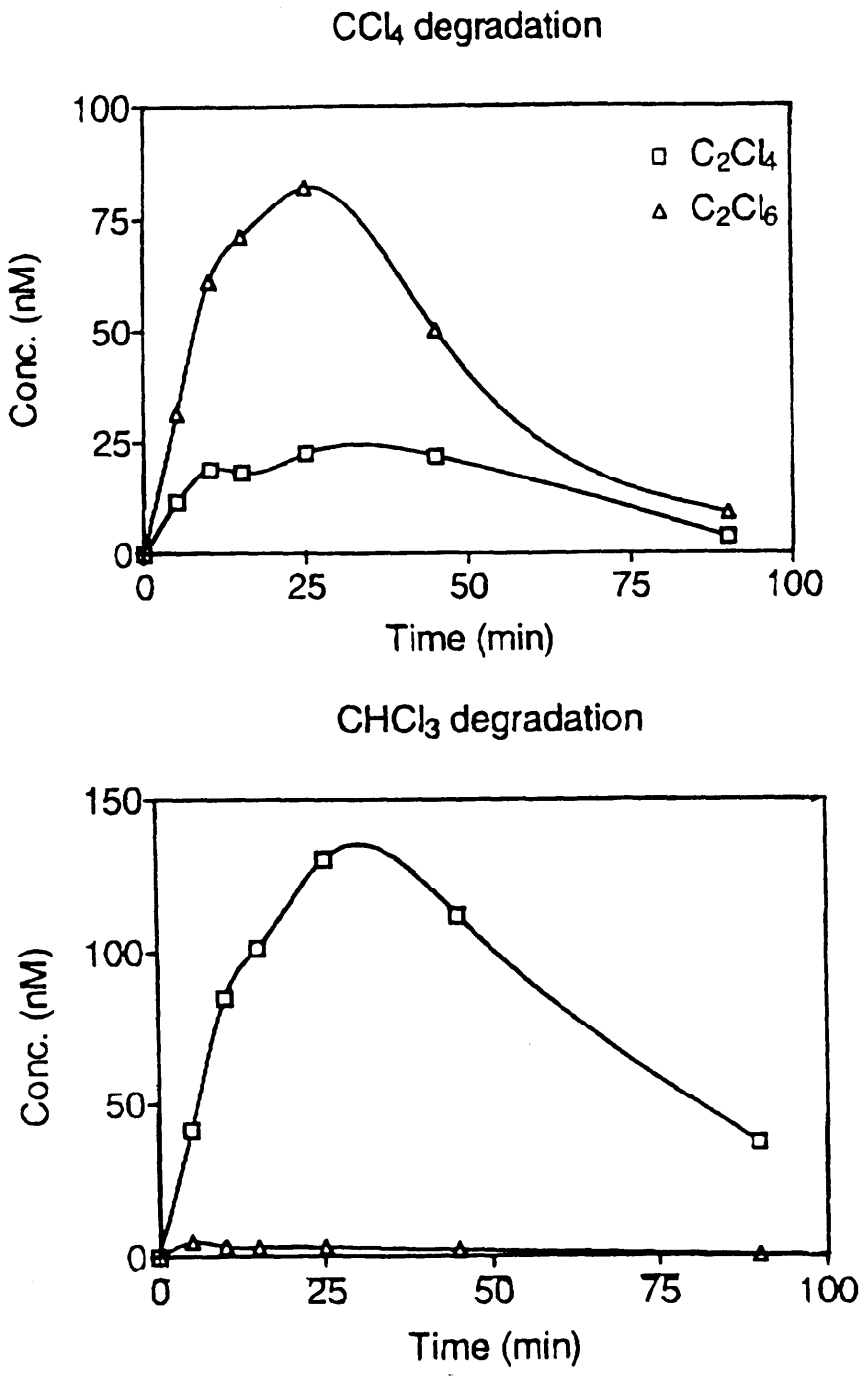


Figure 36. CC1, and $CHCl_3$ Degradations as a Function of Sonolysis Time

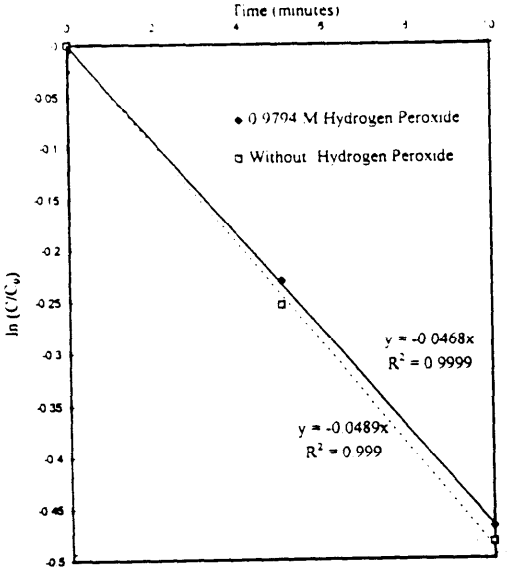


Figure 37. Effect of Adding Hydrogen Peroxide to Enhance Sonication of $CCl_4$

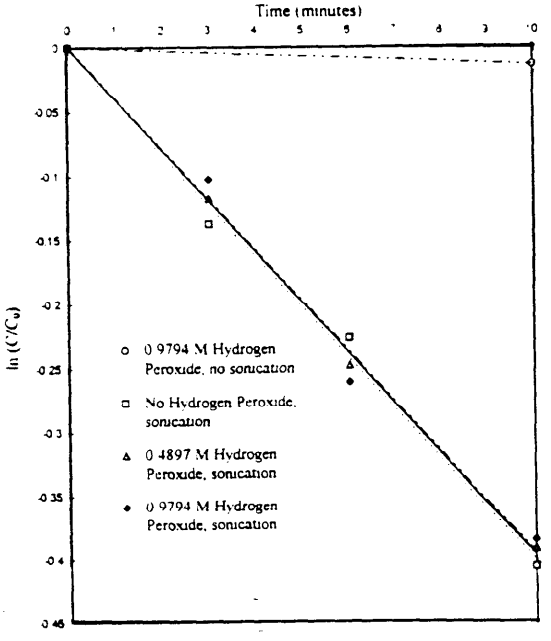


Figure 38. Effect of Adding Hydrogen Peroxide to Enhance Sonication of TCE

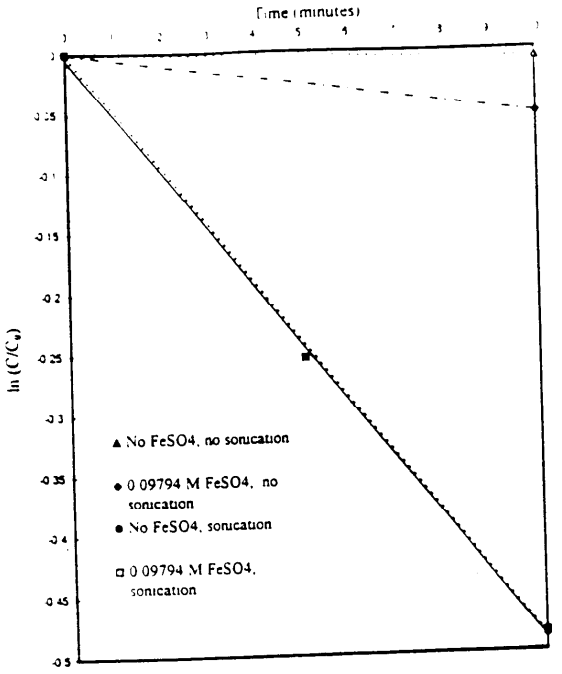


Figure 39. Effect of Adding Ferrous Sulfate to Enhance Sonication (Initial $CCl_4$ Concentration: 8 mg/L; Ultrasound Intensity: 25.3 W/cm$^2$)

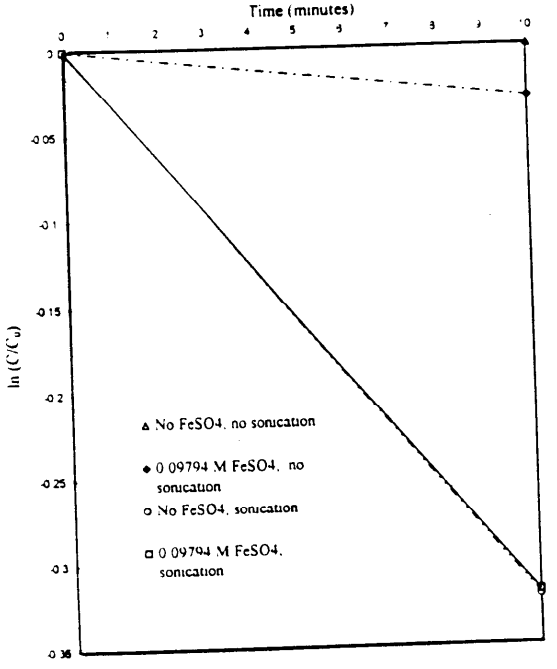


Figure 40. Effect of Adding Ferrous Sulfate to Enhance Sonication (Initial TCE Concentration: 7.5 mg/L; Ultrasound Intensity: 25.3 W/cm$^2$)

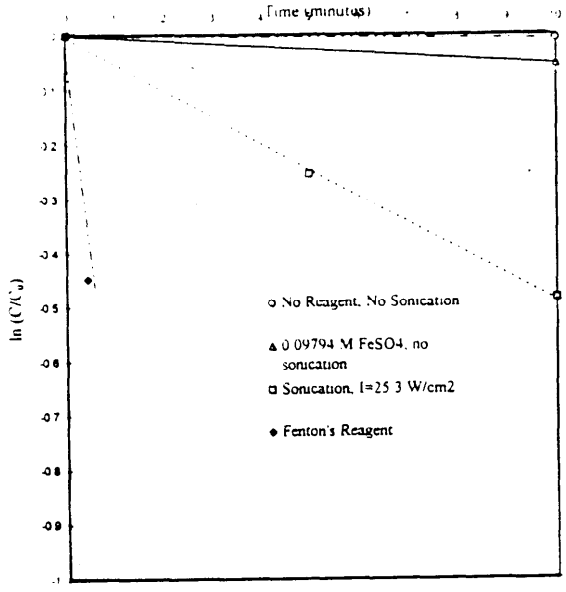


Figure 41. Effect of Sonication, $FeSO_4$, and Fenton's Reagent in the Reduction Rate of $CCl_4$

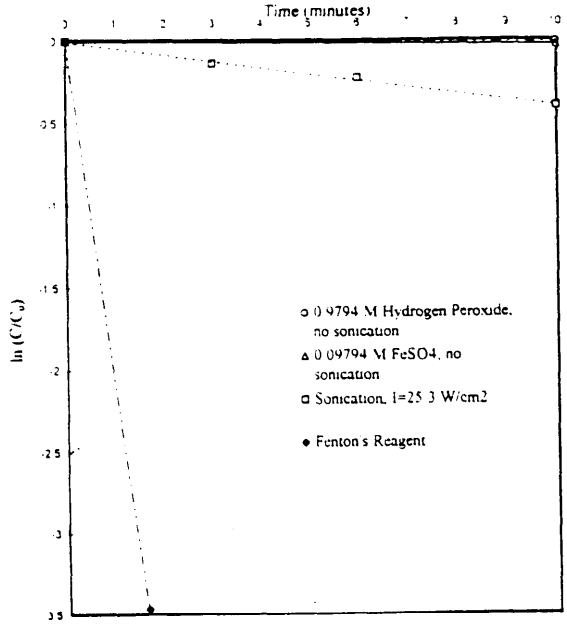


Figure 42. Effect of Sonication, $FeSO_4$, and Fenton's Reagent in the Reduction Rate of TCE

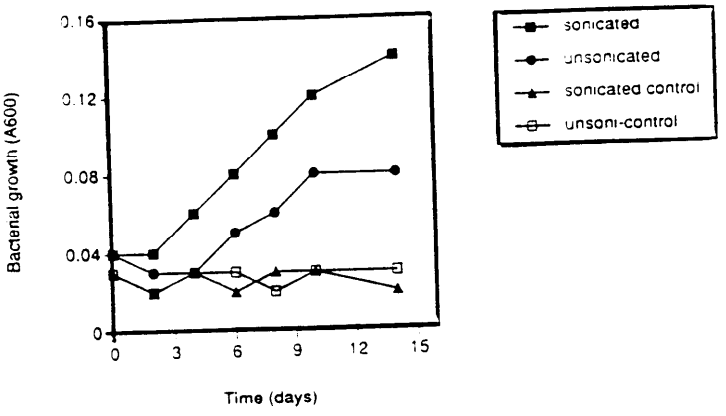


Figure 43. Bacterial Growth in Sonicated and Unsonicated Samples

# APPENDIX A. PHYSICAL PROPERTIES OF ORGANIC CONTAMINANTS SELECTED FOR STUDY

Table A.1. Physical Properties of Target Halogenated Compounds and Potential Degradation Products

| Parent Compound or Degradation Product | Molecular Formula | Molecular Weight, (g/mole) | Boiling Point, (°C) | Freezing Point, (°C) | Flash Point, (°C) | Melting Point, (°C) | Density, (g/mL) | Vapor Pressure | Vapor Density | Lower Explosive Limit (LEL), (%) | Upper Explosive Limit (UEL), (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Carbon Tetrachloride | $CCl_4$ | 153.81 | 76.8 | -22.9 | None | -22.6 | 1.597@ 20°C | 100mm@23°C; 91.3mm@20°C | 5.3 | — | — |
| Trichloroethylene (TCE) | $CCl_2CHCl$ | 131.5 | 86.7 | -86.8 | 89.6 | -73 | 1.4649@ 20°/4°C | 20mm@0°C; 100mm@32°C | 4.53 | 12.5 | 90@730°C |
| Trichloroethane (TCA) | $CCl_3CH_3$ | 133.41 | 74.1 | -32.5 | None | -32 | 1.3376@ 20°/4°C | 100mm@20°C | 4.63 | 7.0 | 10.5 |
| Tetrachloroethylene (PCE) | $CCl_2CCl_2$ | 165.82 | 121.4 | -22.4 | None | -23.35 | 1.6311@ 15°/4°C | 14mm@20°C; 15.8mm@22°C | 5.83 | — | — |
| Ethylene Dibromide (EDB) | $CH_2BrCH_2Br$ | 187.88 | 110 | -35.5 | 43.2 | 9.97 | 1.089@ 20.5°/4°C | 11mm@20°C | 6.5 | — | — |
| Chlorine | $Cl_2$ | 70.91 | -34.5 | — | — | -101 | 1.565@ -34.06°C; 2.49@0°C | 4800mm@20°C; 7600mm@30°C | 2.49 | — | — |
| Phosgene | $CCl_2O$ | 98.91 | 8.3 | -128 | — | -118 | 1.37@20° C | 1215mm@20°C; 1180mm@20°C | 3.4 | — | — |
| Hydrogen Bromide (Hydrobromic Acid) | HBr | 80.90 | -66.5 | -87 | — | -87 | 2.160@ -66.73°C; 3.50@0°C | — | — | — | — |
| Carbon Dioxide | $CO_2$ | 44.01 | — | -199 | — | -78.5 | 1.53 (as a gas) | — | 1.53 | — | — |
| Carbon Monoxide | CO | 28.01 | -191.3 | — | None; 1128- (Autoignition) | -207 | 0.61672 | — | 1.25 | 12.5 | 74.2 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Methyl Chloride (Chloromethane) | $CH_3Cl$ | 50.49 | -23.7 | -99.6 | <0°C | -97.1 | 0.918@ 20°/4°C | 349mm@20°C | 1.78 | 8.1 | 17 |
| Hydrogen Chloride (Hydrochloric Acid) | HCl | 36.46 | -84.8 | -25.4 | None | -114.2 | 1.187@ -85.05°C; 1.194@ -26°C; 1.639@0°C | 4.0atm@17.8°C | 1.268 | — | — |
| Hexachloroethane | $C_2Cl_6$ | 236.72 | 186.8 (triple point) | — | — | 186.6 | 2.091 | 1mm@32.7°C | — | — | — |