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X-231B Technology Demonstration for In Situ Treatment of Contaminated Soil: *Laboratory Evaluation of In Situ Vapor Stripping*

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ACRONYMS AND ABBREVIATIONS

ACD - Analytical Chemistry Division
C_a - contaminant concentration in interaggregate pores
C_c - contaminant concentration in intra-aggregate pores
D_{eff} - intra-aggregate vapor phase diffusion coefficient
ECD - electron capture detector
EPA - U.S. Environmental Protection Agency
F_c - mass flux between intra- and interaggregate pores
FI - flow indicator
FID - flame ionization detector
GC - gas chromatograph
GSB - gas sampling bulb
ID - inner diameter
K_d' - vapor phase partitioning coefficient
MeCl - methylene chloride
OD - outer diameter
ORNL - Oak Ridge National Laboratory
PI - pressure indicator
PORTS - Portsmouth Gaseous Diffusion Plant
q - normalized stripping air flow rate
QA/QC - Quality Assurance / Quality Control
r_c - soil aggregate density
R_c - intra-aggregagate retardation coefficient
RCRA - Resource Conservation and Recovery Act
r.v. - reactor volumes
S.D. - standard deviation
t - time
T - temperature
TCE - trichloroethylene
1,1,1-TCA - 1,1,1-trichloroethane
THC - total hydrocarbon content
TI - temperature indicator
TOC - total organic carbon
DOE - U.S. Department of Energy
VOCs - volatile organic compounds
VOA - volatile organic analysis
α - mass transfer coefficient
ε_c - intra-aggregate porosity
ε_s - interaggregate porosity
ε_t - mixed soil porosity

ρ_t - dry density of the mixed soil
ρ_c - dry density of the unmixed soil
τ - dimensionless time

PREFACE

Fine-textured soils and sediments contaminated by trichloroethylene (TCE) and other chlorinated organics present a serious environmental restoration challenge at U.S. Department of Energy (DOE) sites. Although in situ processes such as bioremediation and soil vapor extraction are feasible at sites with permeable soils (e.g., $K > 10^{-3}$ cm/s), their application is normally infeasible in wet, clay soils, and sediments. Environmental restoration of these sites has normally consisted of either (1) excavation and on-site storage, off-site land filling, or thermal treatment; or (2) in-place containment by capping and slurry wall emplacement.

In November 1990, DOE and Martin Marietta Energy Systems, Inc. initiated a research and demonstration project at Oak Ridge National Laboratory (ORNL). The goal of the project was to demonstrate a feasible and cost-effective process for closure and environmental restoration of the X-231B Solid Waste Management Unit at the DOE Portsmouth Gaseous Diffusion Plant located in southern Ohio. The X-231B Unit was used from 1976 to 1983 as a land disposal site for waste oils and solvents. Silt and clay deposits ($K < 10^{-6}$ cm/s) beneath the unit were contaminated with volatile organic compounds (VOCs) such as TCE (approx. 1–100 ppm range) and low levels of radioactive substances. The shallow groundwater (water table at approx. 12–14 ft depth) was also contaminated, and some contaminants were at levels well above drinking water standards.

After an initial technology evaluation and screening phase, the X-231B project focused on research and demonstration of in situ vapor stripping, chemical oxidation, and solidification; and reagent delivery to the subsurface was achieved by soil mixing techniques. The primary objectives of the project were to develop processes as necessary and appropriate and to characterize the operation and performance of each process with regard to in situ treatment of VOCs in clay soils. Secondary objectives were to determine the treatment process zone of influence; the treatment process effects on air emissions, soil chemistry, and microbiology properties; and the fate of heavy metal and radioactive materials. Soil homogenization and translocation were also studied.

Since July 1991 varied research activities have been conducted. Site characterization and contaminant modeling work has included use of a hydraulic probe for collection of nearly 200 soil samples with on-site laboratory analysis for target VOCs. These data were used for statistical simulation and 3-dimensional modeling of contaminant distribution. A series of laboratory experiments were completed using bench-scale apparatus as well as a pilot-scale soil mixing system in which soil cores from the site were treated. A full-scale field demonstration was completed at the X-231B site in June 1992. Replicated tests of in situ vapor stripping, peroxidation, and solidification were made in soil columns measuring 10 ft in diameter and 15 to 22 ft deep. A computerized data acquisition system linked to approx. 60 sensors enabled near-continuous monitoring of process operation and performance (e.g., recording intervals of 0.2 to 2 min. for auger position, off-gas air flow rate and VOC content, soil vapor pressure and temperature). In addition, nearly 500 soil and gas samples were collected before, during, and after soil treatment, for analyses of physical, chemical, and biological parameters. Soil matrix, soil vapor, and off-gas VOC measurements were made by multiple methods.

The X-231B project has been a multidisciplinary and multi-institutional, fast-track, applied research and demonstration effort. Directed by ORNL, the project has benefited from the significant contributions of research staff from six divisions at ORNL, technical and management staff at Portsmouth and Energy Systems, and principal collaborators from two universities (The University of Tennessee and Michigan Technological University) and several private industries (e.g., Chemical Waste Management, Millgard Environmental, Envirosurv, and NovaTerra).

Results of the project have been very insightful regarding in situ environmental restoration of contaminated clay soils. For example, the use of a hydraulic probe for soil sampling with on-site VOC analyses, followed by 3-D visualization, provided enhanced information compared with conventional sampling, off-site analyses, and routine data treatment. In situ treatment of VOCs in clay soils was effectively (e.g., >85% reduction) and rapidly accomplished (e.g., >15 yd^3/h) and the fate of VOCs and radioactive substances was controlled. Moreover, in situ treatment costs were acceptably low. Operation and performance did vary for the different processes evaluated, and there were advantages and disadvantages associated with each. Ancillary study results indicated interesting changes in soil properties following treatment. For example, soil bacteria levels were increased by several orders of magnitude following ambient air stripping. The favorable project results are being used to design and implement a cost-effective in situ treatment process for full-scale closure of the X-231B Unit.

This report describes the methods and results of one part of the X-231B project. Details regarding other aspects of the work are available in other project publications. Information regarding these publications may be obtained by contacting Dr. Robert L. Siegrist, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN, 37831-6038; 615-574-7286.

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ABSTRACT

The goal of the study described in this report was to determine the efficiency of vapor stripping coupled with soil mixing for removing volatile organic compounds (VOCs) from clay soils such as those that underlie the PORTS X-231B Solid Waste Management Unit. This was accomplished by conducting experiments wherein contaminated soil cores were treated in the laboratory using a system that simulated a field-scale vapor stripping/soil mixing treatment process. Treatment efficiencies obtained using several sets of process conditions, such as air temperature and flow rate, were determined through subsampling of the soil cores to establish pre- and posttreatment levels of VOCs in the soil.

Two series of experiments were conducted under this study. In the first series, laboratory treatment was performed on intact soil cores that were taken from contaminated zones within the PORTS X-231B Unit using sampler liners that could be adapted as reaction lysimeters. Since soil core disturbance was minimized using this approach, the treatability experiments were conducted on soil that was fairly close to in situ conditions in terms of both soil structure and contaminant levels. The second series of experiments were performed on cores that were packed using X-231B soil and spiked with known amounts of trichloroethylene (TCE). This approach was taken for the second series because the VOC levels in the intact cores were found to be much lower than field values. In addition, the packed cores were smaller than the intact soil cores, with treatment volumes that were about a fifth of the treatment volumes in the intact soil cores. The smaller packed cores were not only easier to handle but were also more reliably characterized due to smaller treatment volumes from which samples were taken.

Under the first series of experiments, one intact core was treated with ambient air (T=24°C), and another intact core was treated with heated air (T=121°C). Pre- and posttreatment samples revealed that 1 h of ambient-air treatment (between 180 – 240 reactor volumes of air) was not sufficient to remove VOCs, whereas 3 h of heated-air treatment (between 540 and 720 reactor volumes of air) was sufficient to decrease soil VOC content to nondetectable levels. The higher treatment efficiency obtained from the latter may be due to either the use of heated air as a stripping gas, longer treatment time, or both.

Vapor stripping with ambient and heated air was evaluated in the second series of experiments using the packed cores that had been spiked with TCE to levels measured in the field. Treatment efficiencies ranged from 64 to 98%, with the majority of values lying between 85 to 95%. There was a slight indication that vapor stripping with heated air resulted in improved removal efficiencies.

Removal efficiency as a function of time was quantified by sampling a subset of the packed cores during treatment. A kinetic model which incorporates contaminant diffusion through soil aggregates was formulated and was successful in simulating trends in removal efficiencies. This kinetic model was then used to predict field-scale process performance from laboratory results.

1. INTRODUCTION

1.1 BACKGROUND

The X-231B Oil Biodegradation Unit is located in the Portsmouth Gaseous Diffusion Plant (PORTS), a U.S. Department of Energy production facility in Piketon, Ohio. The X-231B Unit encompasses ~0.8 acres and was reportedly used for the treatment and disposal of waste oils and degreasing solvents from 1976 to 1983. From 1989 to 1990, efforts were made to close the X-231B Unit in compliance with Resource Conservation and Recovery Act requirements. Site characterization activities revealed the presence of several volatile organic compounds (VOCs) [e.g., trichloroethylene (TCE) and 1,1,1-trichloroethane (TCA)] in fine-textured soils from the ground surface to a depth of ~25 ft.[1] Furthermore, TCE at levels higher than the Federal drinking water standard was found in the shallow groundwater directly beneath and 750 ft downgradient from the unit.

Concerned over the continuous release of contaminant VOCs into the ground water, the Ohio Environmental Protection Agency (Ohio EPA) required that soil remediation be included in the closure of the X-231B Unit. A team of scientists and engineers from Oak Ridge National Laboratory (ORNL) was assembled by Martin Marietta Energy Systems (MMES), the PORTS management contractor, to identify technologies for the effective removal of VOCs from fine-textured soils such as those that underlie the X-231B Unit (see Table 1.1 for characteristics). The ORNL project team selected the following in situ technologies for potential application at the X-231B unit: (1) vapor stripping, (2) solidification/stabilization, and (3) peroxidation. All three technologies were to be coupled with soil mixing in order to overcome problems associated with delivering treatment fluids to low-permeability soils (i.e., air for vapor stripping, grout for solidification/stabilization, and hydrogen peroxide for peroxidation). These technologies were evaluated through laboratory-scale treatability studies using X-231B soil, and field-scale process implementations that were conducted within the X-231B Unit. This document contains details of the laboratory evaluation of vapor stripping coupled with soil mixing conducted by ORNL. Other aspects of the overall X-231B technology demonstration project can be found in other project publications.[1-5]

Vapor stripping coupled with soil mixing is similar to conventional soil vacuum extraction (SVE) techniques in that treatment occurs through the volatilization of organic contaminants into a moving air phase. The primary difference between vapor stripping coupled with soil mixing and conventional SVE is the strategy for inducing air flow and for treating larger volumes of soil. In conventional SVE, vents (i.e., wells) are drilled into the contaminated soil volume, and air flow is induced throughout the soil volume by applying a vacuum at these extraction vents. This technology has been proven effective only in sites where the soil conductivity is sufficiently high (e.g., $K > 10^{-3}$ cm/sec) that adequate air flow is induced at low vacuums applied to the extraction vents. In vapor stripping coupled with soil mixing, a soil volume is treated in columns as shown in Fig. 1.1. While the soil is continuously being mixed, high-pressure air is delivered into the soil through injection ports distributed along the mixing blades. A slight vacuum is applied to a shroud that is placed over the treatment column (see Fig. 1.1) in order to induce air to flow through the soil column and into the shroud. The stripping air is then channeled through a gas treatment process train (e.g., activated carbon or catalytic oxidation) before being released into the atmosphere.

The X-231B technology demonstration was conducted under strict time constraints because PORTS had made a commitment to Ohio EPA to develop a closure plan for the X-231B Unit by June 1992. Since the objective of the technology demonstration was to provide technical guidance for this closure plan, the laboratory and field experiments were completed by the end of May 1992. In addition, a majority of the laboratory experiments was completed before the initiation of the field demonstration in April since the field process conditions were partially determined by the results of the laboratory treatability studies. The ORNL vapor stripping/soil mixing experiments were designed to provide as much reliable information as possible within the tight scheduling of the overall X-231B technology demonstration project. The treatability apparatus used for the experiments was constructed between January and March 1992. The experiments described in this report were conducted from April through May 1992.

1.2 OBJECTIVES AND SCOPE

The main goal of the study described in this report was to determine if vapor stripping coupled with soil mixing could achieve high removal efficiencies for VOCs in fine-textured soils. This was accomplished by simulating the treatment process in the laboratory using intact soil cores that were taken from contaminated areas within the X-231B Unit, and packed cores which were prepared from X-231B soil and spiked with TCE. The results of this study were used to design process conditions for the field-scale demonstration.[5]

ORNL staff and NovaTerra conducted the vapor stripping experiments. The group at ORNL evaluated vapor stripping combined with soil mixing with and without thermal enhancement through the use of heated air as a stripping gas. The group from NovaTerra performed experiments on vapor stripping combined with soil mixing and thermal enhancement through simultaneous heated-air and steam injection. Only the results of the ORNL vapor stripping experiments are included in this report. The results of the NovaTerra experiments can be found in a separate report written by NovaTerra scientists.[6]

1.3 REPORT ORGANIZATION

Two series of experiments were conducted under this study: (1) vapor stripping of large (8 in. in diameter, 24 in. long) intact soil cores and (2) vapor stripping of packed cores that were spiked with TCE. Sects. 2 and 3 contain descriptions of materials, methods and results for each of these series of experiments. Modeling of results is discussed in Sect. 4, and conclusions are presented in Sect. 5.

Table 1.1. Characteristics of subsurface soil at X-231B as measured in samples collected by ORNL in December 1990 (taken from Siegrist et.al, 1993[1]). Range of values taken from several samples

	Nominal depth	
Characteristic	Shallow (7 ft)	Deep (15 ft)
Grain size distribution		
Clay: <0.002 mm (wt %)	22.5 – 25.0	12 – 15
Silt: 0.002–0.05 mm (wt %)	65.5 – 67.0	39 – 64
Sand: 0.05–2.0 mm (wt %)	8 – 12	22 – 46
USDA Texture	Sandy clay loam	Silt loam
Water content (wt%)	13.4 – 19.0	18.8 – 19.0
Total organic carbon (mg/kg)	579–1190	184–472

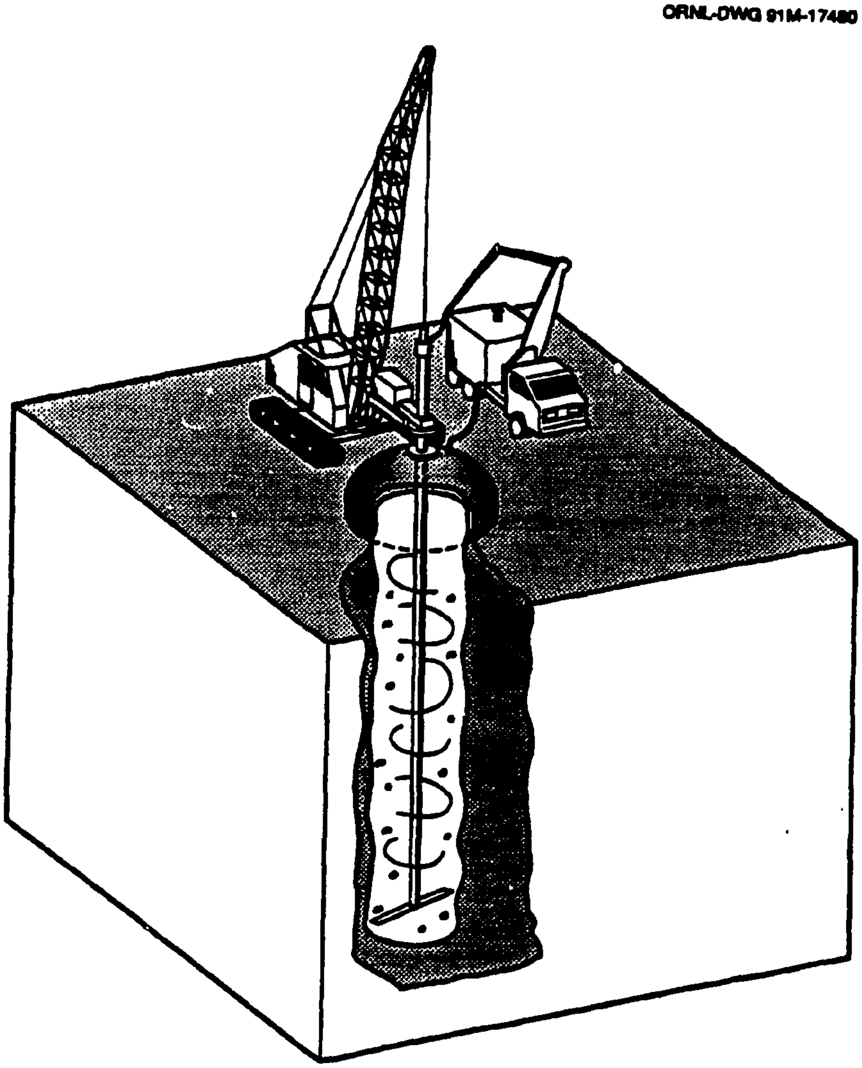

Figure 1.1. **Schematic diagram of a vapor stripping/soil mixing field implementation.**

2. VAPOR STRIPPING OF INTACT SOIL CORES

2.1 INTRODUCTION

The series of experiments described in this section were performed on large (8 in. in diameter, 24 in. long) undisturbed soil cores that were collected from contaminated zones within the PORTS X-231B unit. Pretreatment and posttreatment characterizations of these soil cores were used to determine the effectiveness of vapor stripping with ambient and heated air. To minimize sample disturbance by eliminating the need for extracting cores prior to conducting experiments, the cores were collected in sampler liners that were specially designed to adapt as reaction lysimeters. The objective for using the undisturbed soil cores was to conduct treatability experiments on soil that was as close as possible to in situ conditions in terms of both soil structure and contaminant levels.

2.2 MATERIALS

2.2.1 Description of Reaction Lysimeter and Treatability System

The reaction lysimeter, shown in Fig. 2.1, consisted of a stainless steel sampler liner and stainless steel end caps. The caps were attached to the sampler liner using threaded rods that were screwed on to the top and bottom end caps, with the sampler liner set between them. Viton gaskets were placed between the cylinder and the caps to provide proper sealing. Thermocouples for monitoring soil temperature were installed through the thermocouple ports using Swagelok fittings.

The reaction lysimeter was not completely filled with soil, as shown in Fig. 2.1. The 6-in. headspace between the top of the soil core and the lysimeter top cap left room for soil to expand during mixing and also prevented soil particles from entering and plugging the off-gas line. During core preparation (see Sect. 2.3.1), excess soil was removed from the intact cores in order to create this headspace.

A schematic and a photograph of the treatability system for the ORNL vapor stripping studies are shown in Figs. 2.2 and 2.3, respectively. This system was designed in order to accomplish the following experimental objectives: (1) to perform simultaneous soil mixing and injection/extraction of ambient or heated air into the soil core, (2) to monitor temperature, pressure, and flow rate of air injected into and extracted from the soil core, (3) to monitor the temperature of the soil core at different locations, and (4) to monitor the hydrocarbons that are carried away by the stripping air (i.e., the off-gas). The system's main components are: (1) the reaction lysimeter described previously, (2) a mixer equipped with a hollow mixing shaft through which air is injected into the soil core during mixing, (3) air and vacuum sources, (4) a furnace for heating the air, (5) a flame ionization detector (FID) that provides a real-time measurement of the total hydrocarbons (THC) in the off-gas, and (6) an off-gas sampling system that was used to identify and quantify specific hydrocarbons in the off-gas. The off-gas THC was assumed to be a good indicator of the level of VOCs remaining in the soil being treated, and was used to control the treatment process.

The treatability system was set up inside a fume hood equipped with a sliding glass shield that was lowered prior to the conduct of the experiments. The system was placed inside a hood in order to prevent hazardous fumes generated during the vapor stripping process from escaping into the atmosphere. Room temperature during all experiments was ~22°C.

Temperature, flow, and pressure indicators were installed at various locations along the air lines and on the top cap of the reaction lysimeter. Readings from these indicators were either continuously recorded or periodically read throughout the duration of a treatment run. The FID sampling line was connected to the off-gas line close to the outlet port on the cap of the reaction lysimeter (see Fig. 2.2). A sampling pump pulled a small fraction of off-gas flow through the FID for analysis.

The mixer consisted of a heavy-duty Milwaukee drill motor (Model 4090, 15 amp capacity, 120 VAC, drill rotation speed range = 375 – 750 rpm) mounted on a Milwaukee drill stand (Model 4125, with 28 in. spindle travel). The drill motor was equipped with a swivel joint, a type of linkage between the drill motor and the drill bit which allows the injection of fluids (e.g., water for typical drilling operations) from a stationary delivery system to a rotating drill bit. During the treatability studies, ambient or heated air was delivered to the soil cores through the swivel joint.

The design details of the mixer shaft are shown in Fig. 2.4. It consists of four blades made out of 1/8-in. stainless steel plates and a drill bit welded to a ~28 in. piece of stainless steel tubing (1/2-in. OD x 1/8-in. wall thickness). The blades were machined to produce saw-toothed forward edges (not shown in Fig. 2.4), and were inclined at ~30° with one pair of blades positioned above the other pair and inclined in a direction opposite to that of the lower pair of blades. During shakedown tests, the original mixer design in which all the blades were inclined in the same direction caused the soil in the mixed zone to be lifted up to the soil surface. In the revised blade design, the lower set of blades cut into the soil during downward movement of the mixing shaft while the upper blades kept the soil from being lifted up.

Perforated 1/8-in. ID pipes were welded to the lower blades through which air was delivered to the soil. If the mixing shaft were held at the same level, the thickness and diameter of the mixing zone were ~2.5 and 5 in., respectively.

2.2.2 Collection and Handling of Intact Soil Cores

The intact soil cores were collected from soil borings that were drilled into the central portion of the X-231B Unit using an 11 5/8-in. hollow stem auger with a center bit. The cores were collected from these borings using a split spoon sampler fitted with 8-in. OD, 24 in. long stainless steel sampler liners. These liners became part of the reaction lysimeter (see Fig. 2.1) and eliminated the need to extract the soil from the liners prior to treatment. The central portion of the X-231B Unit was determined to be contaminated during site characterization conducted in January 1992. Borehole locations and soil core collection methods are described in more detail by Siegrist et. al (1993).[3] The soil cores were subsampled for on-site VOC analysis using a heated-headspace technique.[8,10] In order to prevent VOC losses, these soil cores were sealed gas-tight and kept in cold (4°C) storage until core preparation and subsampling, which were performed immediately prior to the treatment runs.

2.3 METHODS

2.3.1 Preparation and Pretreatment Characterization of Soil Cores

Cores were prepared and subsampled in a 4°C laboratory to minimize VOC losses. Preparation normally took 2 h per core and included the following activities: (1) breaking and removing seals that were placed on the core after it was was collected in the field, (2) removing excess soil from the core to create a headspace that was at least 6 in. deep in the reaction lysimeter, (3) obtaining soil samples for pretreatment characterization, and (4) installing the end caps. In order to prevent VOC losses, the cores were prepared in the same 4°C laboratory where the soil cores were stored prior to treatment. The mixer shaft was inserted through the top cap before the latter was attached to the reaction lysimeter. With the end caps installed and the mixer shaft plugging the hole in the top cap, the soil core was effectively sealed again. The core was then transported to the treatability laboratory where it was allowed to equilibrate to room temperature (~22°C) for at least 12 h. After equilibration, thermocouples were inserted through the thermocouple ports (see Fig. 2.1) and the reaction lysimeter was installed into the system.

Pretreatment soil samples were collected using 1-in. OD stainless steel sample probes that were inserted to a depth of ~13.5 in. into the soil cores. Using a single probe for each core, five to six soil plugs were collected at different depths (with at least one sample from a mixing zone, see Fig. 2.5) and placed in 40-mL Dynatech vials. These samples were then analyzed for the target VOCs listed in Table 2.1 by gas chromatography/mass spectroscopy (GC/MS). Soil samples for moisture content and TOC analyses were also collected.

2.3.2 Treatment Procedure

The intact cores were treated by mixing zones, as shown schematically in Fig. 2.5. The first step in the treatment process was to mix the entire soil core from the top of the core to the bottom of mixing zone 1. Once the bottom of the treatment region was reached, the mixer blades were kept at the same level (i.e., in mixing zone 1) while air was continuously injected into the soil and extracted from the reaction lysimeter headspace. During mixing, and air injection/extraction, the hydrocarbon content in the off-gas was continuously monitored by the FID. When the off-gas THC dropped to a low level, the region around the mixing blade was considered as treated, and the mixer shaft was raised up to treat the next mixing region. This approach taken to treat the large intact cores was similar to that used by NovaTerra during field-scale applications of in situ hot air/steam stripping.[5]

During treatment of the first mixing zone, gas samples were collected at different time intervals using the gas-sampling system illustrated in Fig. 2.2. These gas samples were analyzed for specific hydrocarbons using a Perkin Elmer Sigma 2000 gas chromatograph [30 m x 0.53 mm Volco column; carrier gas was N_2; flow rate was 4 mL/min; 80°C oven temperature at isothermal conditions; injector temperature was 250°C) equipped with a Nickel 63 electron capture detector (detection temperature was 300°C)]. These measurements were correlated with total hydrocarbon concentrations measured by the FID attached to the off-gas stream.

Two intact soil cores were treated in the first series of vapor-stripping experiments. Core 1078,collected within a depth interval of 5-7 ft and having total VOC content of 5860 µg/kg as measured during core collection in January 1992 using an on-site GC technique[3], was treated for an hour using ambient air as the stripping gas. Core 1077, collected within a depth interval of 3–5 ft and having a total VOC content of 4672 µg/kg as measured during core collection in January 1992, was treated using heated air as the stripping gas. Results of these runs are presented in Sect. 2.4. In the succeeding discussion, the cores will be referred to as Core 1078-AA and Core 1077-HA, in which AA and HA refer to ambient and heated-air treatments, respectively.

2.3.3 Posttreatment Characterization of Soil Cores

Immediately after a treatment run, the reaction lysimeter was detached from the treatability apparatus and transported back to the 4°C laboratory. The reaction lysimeter was opened, and posttreatment soil samples were collected using 1-in. OD sample probes that were inserted to a depth of ~13.5 in. into the soil cores. Using a single probe for each core, five to six soil plugs at different depths (with at least one sample from a mixing zone, see Fig. 2.5) were collected and placed in 40-mL Dynatech vials. These samples were then analyzed for the target VOCs (see Table 2.1) by GC/MS.

2.4 RESULTS

2.4.1 Effects of Mixing on Soil Structure

Fig. 2.6 shows a photograph of a soil core after it had been mixed and treated. The soil in the annular region was virtually undisturbed by mixing the central 5-in. portion of the 8-in. diameter core. This photograph also shows the difference in structure between mixed and unmixed soils. The mixed soil is more granular in appearance, as shown in Fig. 2.7. This increase in granularity brought about by mixing probably improved treatment efficiency since a larger surface area exists for the mass transfer of the contaminants from the soil matrix to the off-gas stream. Furthermore, smaller aggregates probably increase removal efficiency by decreasing diffusion path lengths within aggregates. The mixed soil also has a higher bulk air conductivity compared with that of the unmixed soil. A rough estimate of the mixed region air conductivity is given in Sect. 2.4.2.

2.4.2 Process Conditions During Treatment

Air temperature, pressure, headspace vacuum levels, and air flow rates are given in Table 2.2 for each of the two treatment runs conducted using intact cores. These measurements were made at locations indicated in Fig. 2.2 by symbols that are also listed in Table 2.2. Since process conditions did not fluctuate appreciably during the treatment runs, only the average measured values are shown in the table.

The difference between the air pressure at the swivel joint (P2) and the headspace pressure (P3) was used to estimate air conductivity values for the mixed soil column. This resulted in a conservative (lower) estimate since the pressure drop across the orifices through which air flows from the mixing shaft into the soil was neglected in the calculations. Using Darcy's law and assuming a pressure drop length of ~18 in., the estimated conductivity values were 1.9×10^{-2} ft/min for the ambient-air run and 1.3×10^{-3} ft/min for the heated air run. The air conductivity increased by approximately four to five orders of magnitude when compared with the air conductivity of the unmixed soil measured in the field ($K_{field} = 10^{-7}$ ft/min).[1] Apart from improving mass transfer of contaminants from the soil to the stripping air, mixing clearly increases soil permeability and thus increases treatment efficiency by increasing air flow rates at lower air injection pressures.

As shown in Fig. 2.2, soil temperature was measured by thermocouples that were inserted at different elevations along the core. Since the thermocouples could not be inserted through the mixing region, temperature measurements were made at the interface between the mixing and annular regions. During ambient-air vapor stripping of Core 1078-AA, the soil temperature above the lowest mixing zone increased from 24°C to 30°C. This increase in temperature occurred ~20 min after the mixing of the first mixing zone was started. All the other zones remained at 24°C during the entire treatment of Core 1078-AA. On the other hand, no such temperature increase was observed during the treatment of Core 1077-HA, where heated air (T = 121°C) was used.[a] The fact that the heated air did not increase the soil temperature could be explained by large heat losses, which may have occurred as the air traveled from the swivel joint to the injection holes on the mixing blades. This was thought to be possible because of the observed drop (28°C) in air temperature as it travelled from the furnace to the swivel joint even though the air lines were heat-traced to prevent heat losses. Since the mixing shaft was not heat-traced, the temperature of the air coming out of the mixing blades could have been much lower than 121°C.

The increase in temperature of the soil during ambient-air vapor stripping could have been induced by the heat generated by friction between the soil and the mixing blades. However, it is still unclear why a similar temperature increase was not observed during heated-air vapor stripping.

The air flow rate can be expressed in terms of the number of reactor volumes injected per minute, where one reactor volume is equal to the volume of the treatment region for a core (0.142 cu.ft.). For both cores, the normalized air flow rate is between 3 and 4 reactor volumes per minute. The total number of reactor volumes injected into Core 1078 was between 180 and 240 reactor volumes. Between 540 and 720 reactor volumes of heated air was injected in Core 1077 during its first-stage treatment.

2.4.3 Hydrocarbon Concentrations in the Off-Gas Stream

Total hydrocarbon concentrations in the off-gas stream as a function of treatment time are shown in Figs. 2.8 through 2.10. Fig. 2.8 was recorded during the ambient-air vapor stripping of Core 1078-AA, whereas Figs 2.9 and 2.10 were recorded during the first and second stages respectively of heated-air vapor stripping of Core 1077-HA. The FID was calibrated using methane so that the reported THC values should be interpreted as methane equivalents. If the off-gas stream were a pure gas, then a response factor can be applied to the FID reading to convert to a proper concentration for that compound (e.g., the response factor for TCE is ~1.3). However, this was not done for the FID measurements described below because of the potential presence of several different compounds in the off-gas stream.

Fig. 2.8 shows the off-gas THC as a function of time for ambient-air treatment of Core 1078. The FID sampling pump was turned on at t = 0 min in order to sample the headspace prior to air injection, vacuum extraction, and mixing. At t = 35 min, air injection and vacuum extraction were initiated. At t=40 min, mixing was begun, and the

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[a] Based on thermodynamic calculations, the temperature of the soil would have risen by 15 - 30°C after 3h of heated-air injection. However, this estimate is based on calculations that neglect heat losses.

first mixing zone was reached at t = 43 min. A calibration check of the FID was performed before and after Core 1078 was treated.

During air injection and vacuum extraction but before mixing (35 min < t < 40 min), the off-gas THC increased to ~110 ppm. It peaked again when the mixer shaft reached the first mixing region. It then started to decline, and it continued to drop off while mixing zone 1 was being treated. The THC level dropped to ~10 ppm after mixing zone 1 had been treated for ~35 minutes. The mixer shaft was then moved to the next higher mixing zone. The headspace hydrocarbon level was expected to increase when the mixer was moved to the next "untreated" mixing region. However, no such increase in off-gas THC was observed, as can be seen from Fig. 2.8. In fact, the off-gas THC continued dropping off, albeit very slightly, as the mixer shaft was moved through the rest of the mixing regions. Core 1078 was vapor stripped for 65 min.

Figs. 2.9 and 2.10 show the off-gas THC as a function of time for the two stages of heated-air treatment of Core 1077. The total run time for the first stage of treatment was 240 minutes. A second-stage treatment was performed because the off-gas THC was still very high (~350 ppm) at the end of the first-stage treatment.

During the first-stage treatment, air injection and mixing were begun after 20 min of sampling the headspace. When mixing was initiated at t = 25 min, the off-gas THC increased very rapidly and went beyond 500 ppm which is the full-scale linear range of the FID. The off-gas THC remained above 500 ppm for 110 min while the first mixing zone was being treated. The mixer shaft was raised to the second mixing zone at t = 170 min, after mixing region 1 had been treated for 140 min. At this time the off gas THC was still at 375 ppm. The mixing shaft was moved to regions 3 and 4 even though off-gas THC readings were still high (> 300 ppm) prior to moving to the next mixing region. When the mixer was moved to mixing region 4, the off-gas THC began to increase rapidly. At this time, the test was suspended in order to check the calibration of the FID as well as to verify through soil sampling whether the soil VOC content was still as high as the off-gas THC was indicating. A calibration check of the FID after the first-stage treatment gave a 3% measurement error (calculated as the difference between the measured and actual THC divided by the actual THC of the span gas). Posttreatment samples were collected after which the soil core was re-sealed. Second-stage vapor stripping was initiated ~24 hours after the first-stage vapor stripping was suspended.

The second-stage treatment of Core 1077-HA did not produce extremely high off-gas THC values such as those observed during the first-stage treatment. As in previous runs, headspace sampling was begun at t = 0 min. Air injection, vacuum extraction and mixing were initiated at t = 20 min, at which point the headspace THC was at 85 ppm. It is interesting to note that the initial headspace THC for the second-phase treatment is only about a quarter of the off-gas THC when the first stage treatment was suspended (see Figs. 2.9 and 2.10). After 35 min of treating the first mixing zone, the off-gas THC had levelled off at ~22 ppm. At this point the mixer shaft was raised up to the second mixing zone. The off-gas THC continued to drop very slightly through the treatment of mixing zones 2, 3 and 4. Treatment was ended at t = 180 min when the off-gas THC had leveled off at 20 ppm.

Analysis results of the off-gas samples collected during the first- and second-stage treatment of the first mixing region in Core 1077 are shown in Figs. 2.11 and 2.12, respectively. In these figures, t = 0 min. corresponds to the start of treatment of the first mixing region. Three hydrocarbons were identified by the GC/ECD: 1,1,1-trichloroethane (TCA), trichloroethylene (TCE) and tetrachloroethylene (PCE). PCE is not listed as a target compound (see Table 2.1) since it was not found in large amounts during any of the PORTS X-231B site characterization activities. During the first stage treatment (Fig. 2.11), both TCE and TCA off-gas concentrations decreased as a function of time. PCE concentrations were low and decreased only very slightly. The initial TCA and TCE concentrations from the second-stage treatment (Fig. 2.12) were slightly less than the last measurement made during the first-stage treatment (Fig. 2.11). However, the initial PCE concentration decreased by an order of magnitude from 0.01 μg/L to 0.001 μg/L.

The GC/ECD analysis of the gas samples confirmed the presence of the target compounds in the off-gas stream. However, the hydrocarbon content measured by the FID was substantially higher than what was measured in the gas sampling bulbs using the GC/ECD. This is illustrated in Figs. 2.13 and 2.14 where the THC is approximated by the sum of TCE and TCA concentrations measured by the GC/ECD converted to ppm units. This assumes that the response factor for the off-gas is 1.3, and that these two compounds account for a majority of the detected FID hydrocarbons. The values in Figs. 2.13 and 2.14 are almost three to four orders of magnitude less than the FID measurements in Figs. 2.9 and 2.10. This discrepancy may be due to several factors, including the presence of other VOCs in the off-gas detected by the FID and probable loss of the volatiles in the gas sampling bulbs, even though the gasses were analyzed on the same day that the samples were taken.

2.4.4 Pre- and Post- Treatment Levels of VOCs in Soil Samples

Three VOCs, namely TCE, methylene chloride and acetone, were detected in the pre- and posttreatment samples obtained for Core 1078-AA. Acetone was detected in the sample blanks, and its presence in the soil analysis might have been due to sample contamination. Figs. 2.15 and 2.16 show the concentrations of TCE and methylene chloride in soil samples taken at different depths in Core 1078-AA before and after vapor stripping. The approximate boundaries of the mixing regions are also in these figures. Methylene chloride was completely removed by 1 h of vapor stripping. On the other hand, it is clear from Fig. 2.15 that the treatment time was not sufficient to remove all of the TCE from the soil. The more efficient removal of methylene chloride is not surprising since it is more volatile than TCE as indicated by its lower boiling point of 40°C when compared to TCE's boiling point of 87°C.

The pretreatment VOC levels (i.e., sum of target VOCs) in Core 1078-AA were substantially lower than 5860 µg/kg, which was the level measured in the field using the heated-headspace technique immediately after it was collected. This decrease may have been due to VOC losses while the core was kept in storage between the time it was collected from the field in January 1992 and the time experiments were conducted in April 1992. Another possible source of discrepancy are losses that occurred before the samples were analyzed, even though holding times for samples were always below the prescribed levels. This discrepancy between on-site and off-site analyses was also observed during site characterization.[3]

TCE, 1,1,1-TCA and methylene chloride were detected in the pretreatment samples obtained for Core 1077-HA. Acetone was detected in the soil core and in the sample blanks so that its presence in the soil analysis might have been due to sample contamination. The pre- and first-stage posttreatment levels for TCE, 1,1,1-TCA and methylene chloride are shown in Figs. 2.17 through 2.19. These compounds were not detected in the either the first- or second-stage posttreatment samples, thus indicating that the first-stage treatment (vapor stripping for ~3 h) was sufficient to remove these three compounds from the soil matrix. A compound that was tentatively identified as trichlorofluoromethane was detected at rather high levels (48 to 650 µg/kg) in the pre-treatment soil samples but was not detected in the post-treatment samples. This compound was also effectively removed by ~3h of vapor stripping with heated air.

The pre-treatment VOC levels were also substantially lower than the levels measured in the field (4672 µg/kg) immediately after Core 1077-HA was collected. The reasons given above for Core 1078-AA probably hold true for this core as well.

2.4.5 Discussion

Results of the first series of experiments revealed that the effectiveness of vapor stripping is dependent on treatment time. VOC analysis of posttreatment samples from Core 1078-AA show that vapor stripping using ambient air for 1 h was successful in removing methylene chloride but was ineffective in removing TCE from the soil. Increasing the treatment time to 3 h may have been the primary reason for the complete removal of the target compounds from Core 1077-HA. It is also possible that the use of heated air facilitated the vapor stripping of Core 1077-HA.

The FID attached to the off-gas line was used as a means of controlling the treatment process by using the off-gas THC as an indicator of when a mixing region has been sufficiently "cleaned." This procedure assumes that there is a direct correlation between THC in the off-gas and the VOC content of the soil. Such a correlation between the THC measured by the FID and the VOC content of the soil did not exist for the intact core experiments. This is particularly true for the THC profile measured during the first-stage treatment of Core 1077-HA. At the end of the first-stage treatment, the off-gas THC was at 400 ppm and rising. Assuming that most of the hydrocarbons in the off-gas were either TCE or 1,1,1-TCA (both of which have a molecular weight of ~133 g) and a response factor of ~1.3, 400 ppm is approximately equivalent to 1380 µg/L. If it is assumed that equilibrium exists between the vapor and sorbed phases, and that the vapor sorption coefficient is on the order of 1 mL/g, then the soil should have 1800 ug/kg of VOCs.[9] This estimate contradicts the non-detectable VOC levels measured in the first-stage posttreatment sample analyses. The off-gas TCE levels measured by the GC/ECD during the second-stage treatment (< ~0.02 µg/L, Fig. 2.12) were more consistent with the non-detectable levels of TCE in the first-stage posttreatment samples.

An alternative explanation for the high FID readings in Core 1077-HA might be a pocket of nonaqueous phase liquid that was not picked up by the first-stage posttreatment sampling of the core.

The posttreatment soil samples from Core 1078-AA show that 180–240 reactor volumes of ambient air injected into the core was not sufficient to remove VOCs from the core to non-detectable levels. On the other hand, 540–720 reactor volumes of heated air successfully stripped the VOCs in Core 1077-HA down to nondetectable levels. If the number of reactor volumes can be used as a factor for scaling up the laboratory results to expected treatment performance in the field, then a soil column that is 10 ft in diameter and 15 ft deep can be stripped of VOCs in 4 h if an air flow rate of between 1000 and 4000 cfm is injected into the soil. The lower and higher bound for the estimated flow rates were based on the computed reactor volumes injected in Cores 1078-AA and 1077-HA, respectively.

The first series of experiments using intact soil cores revealed that vapor stripping combined with soil mixing is effective for removing VOCs from X-231B fine-textured soil if the time for treatment is sufficiently long. However, it was not possible to accurately quantify the minimum required time for meeting the treatment objectives because the off-gas THC in the first series of experiments did not give a reliable indication of the soil conditions during treatment. In a subset of the second series of experiments described in the following section, soil samples were taken during the treatment process to better quantify residual VOCs in the soil as a function of treatment time. This procedure is more reliable than off-gas monitoring because it does not depend on the existence of a correlation between off-gas THC and soil VOC content. However, soil sampling during treatment is difficult if not impossible to implement in the field. Because of a better method for establishing soil VOC content during treatment, the second series of experiments were more successful in quantifying minimum required treatment times.

Table 2.1. Target volatile organic compounds (VOC) and their detection limits

Target VOC	Soil EPA method 8240/8010 (μg/kg)
Trichloroethylene	5.0 / 1.2
1,1,1-Trichloroethane	5.0 / 0.3
Methylene chloride	5.0 / -
1,1-Dichloroethylene	5.0 / 1.3
1,2-Dichloroethylene	5.0 / 1.0
1,1-Dichloroethane	5.0 / 0.7
1,2-Dichloroethane	5.0 / 0.3
Vinyl chloride	5.0 / 1.8
Chloroform	5.0 / 0.5
Carbon tetrachloride	5.0 / 1.2

Table 2.2. Monitored experimental conditions for ambient and heated-air treatments

Operating Conditions[a]	Ambient-air: Core 1078	Heated-air: Core 1077
Pressure at air source (P1)	2.5 psig	5.0 psig
Pressure at swivel joint (P2)	0.5 psig	3.5 psig
Headspace pressure (P3)	0.24 psig	0.1 psig
Pressure at off-gas line (P4)	-0.31 psig	0.2 psig
Pressure at vacuum source (P5)	-3.93 psig	-2.7 psig
Temperature of air source (T1)	24°C	149°C
Temperature of air at swivel (T2)	24°C	121°C
Flow rate near air source (F1)	0.4 cfm	0.4 cfm
Flow rate near vacuum source (F2)[b]	0.55 cfm	0.5 cfm

[a] Labels in parentheses refer to labels in Fig. 2.2.

[b] The differences between inflow and outflow rate was probably due to leaks in the system. It was very difficult to maintain a good seal between the mixing shaft and the top cap of the reaction lysimeter.

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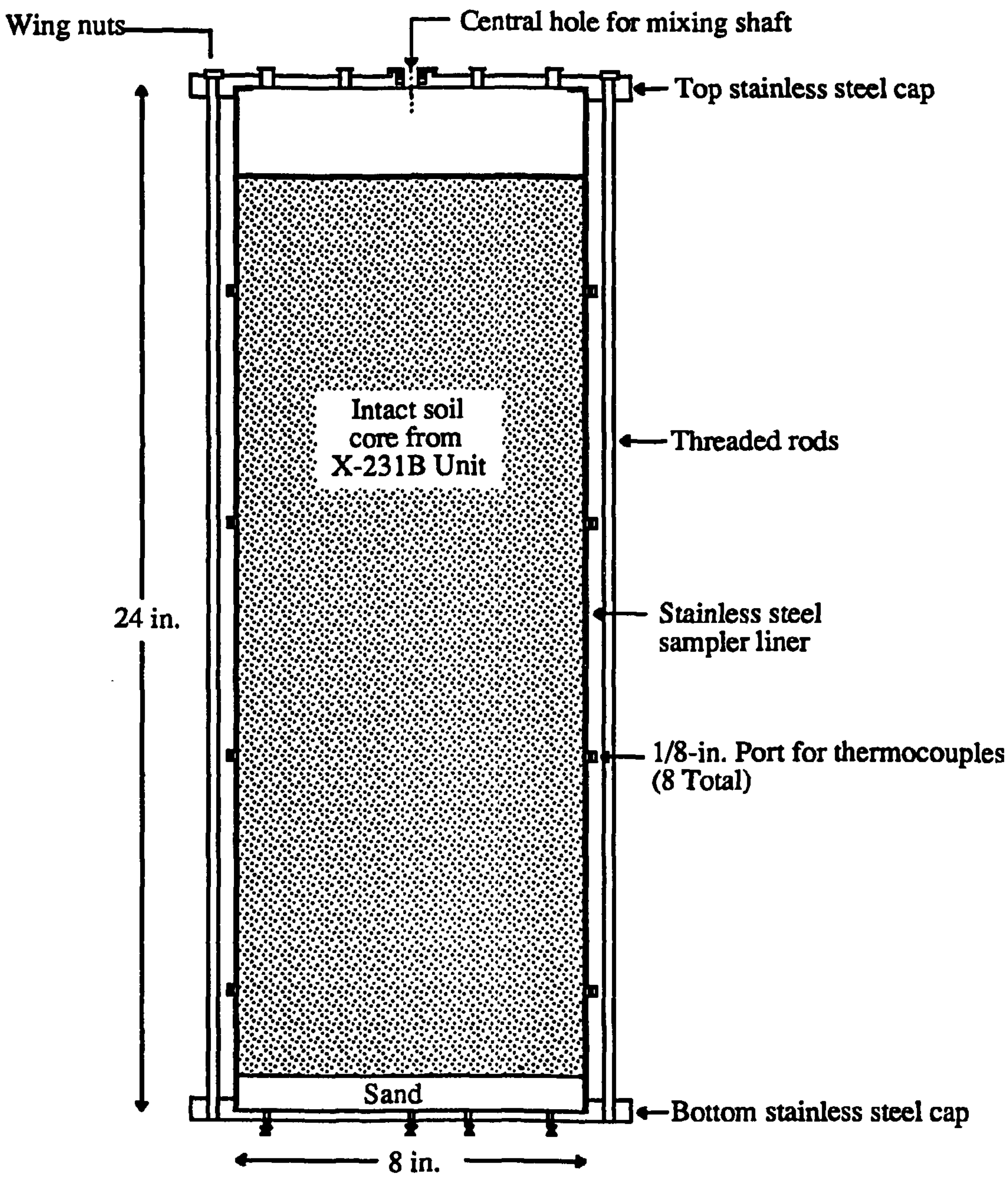

Figure 2.1. Components of the reaction lysimeter.

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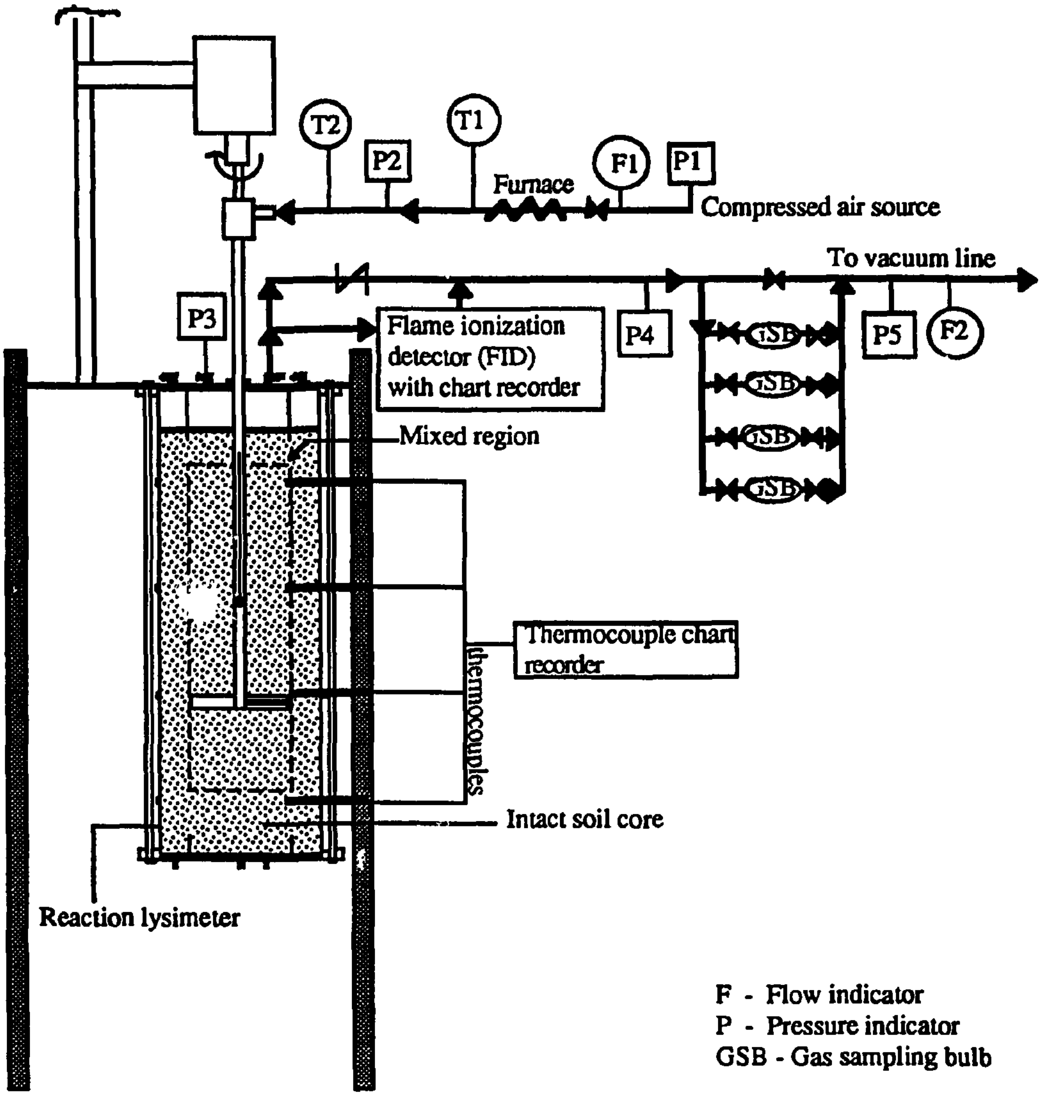

Figure 2.2. Treatability system used in the treatment of intact cores.

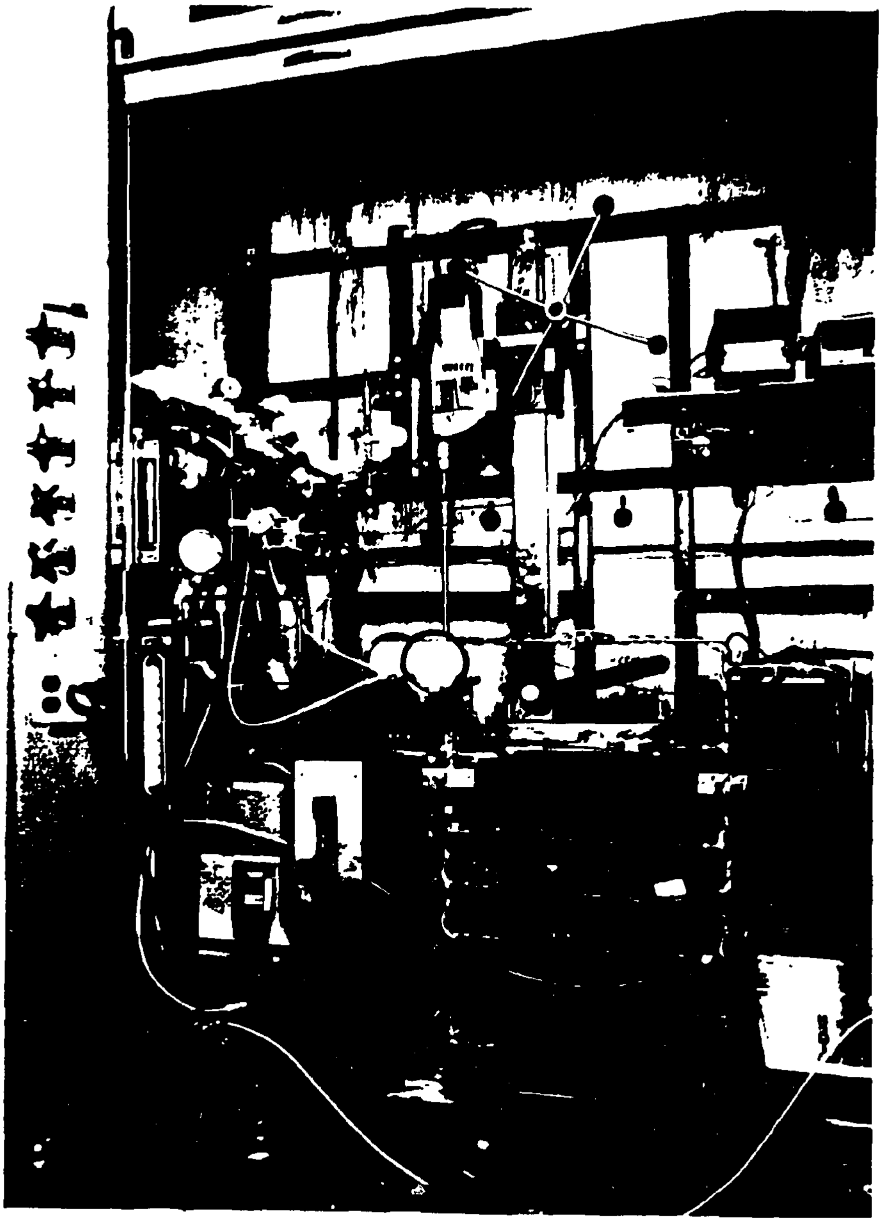

Figure 2.3. Photograph of treatability set-up used in first series of vapor stripping experiments.

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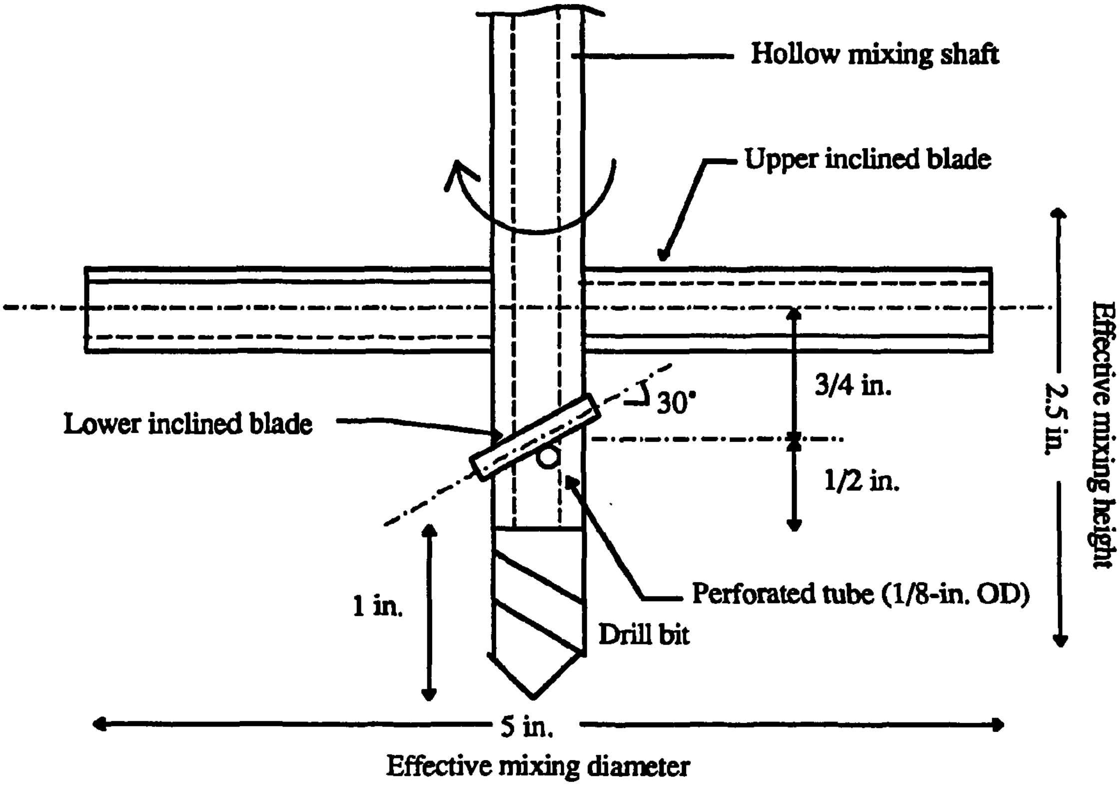

Figure 2.4. **Mixing blade design.**

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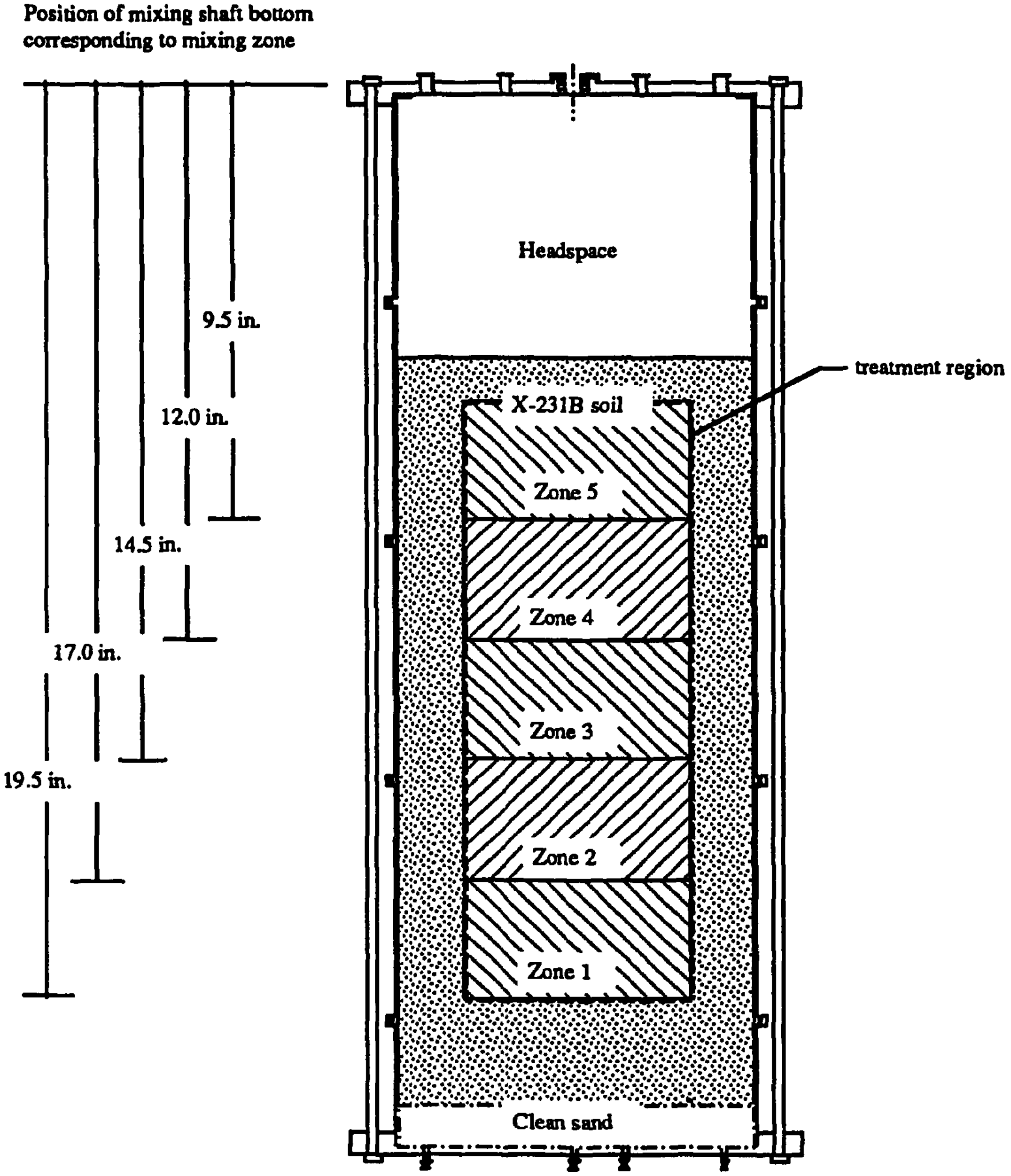

Figure 2.5. Mixing zones in a soil core.

Figure 2.6. Photograph of a soil core after treatment (annular region is unaffected by the mixing).

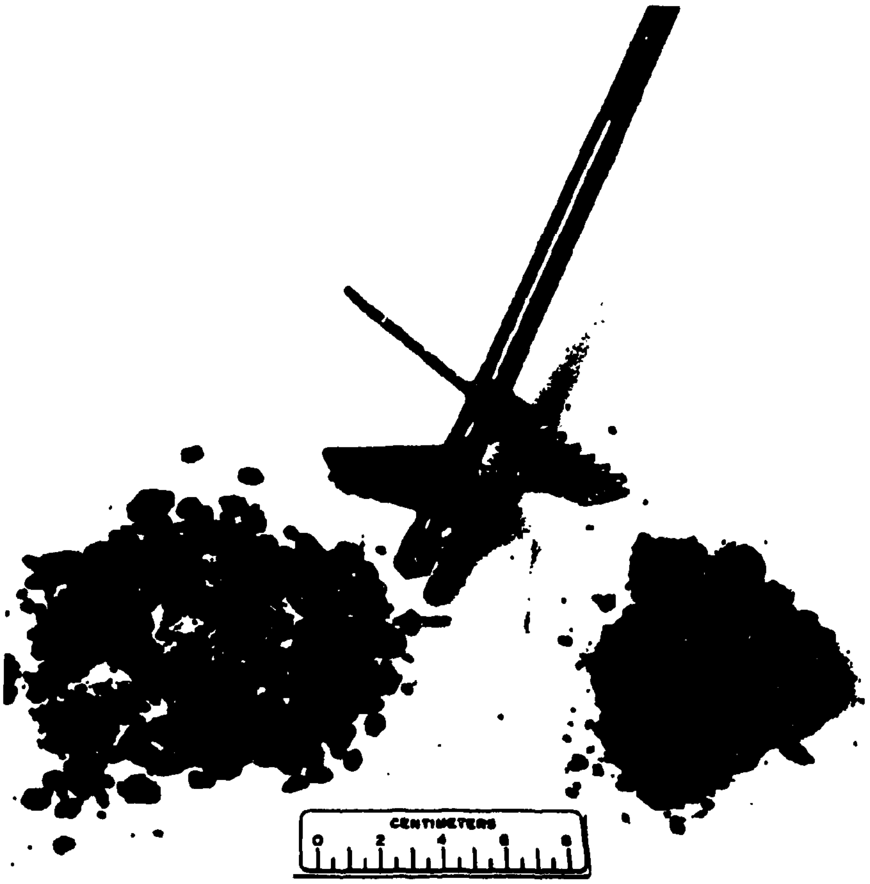

Figure 2.7. Comparison between mixed (left) and unmixed (right) soil. Mixing shaft also shown in picture.

ORNL-DWG 93-11760

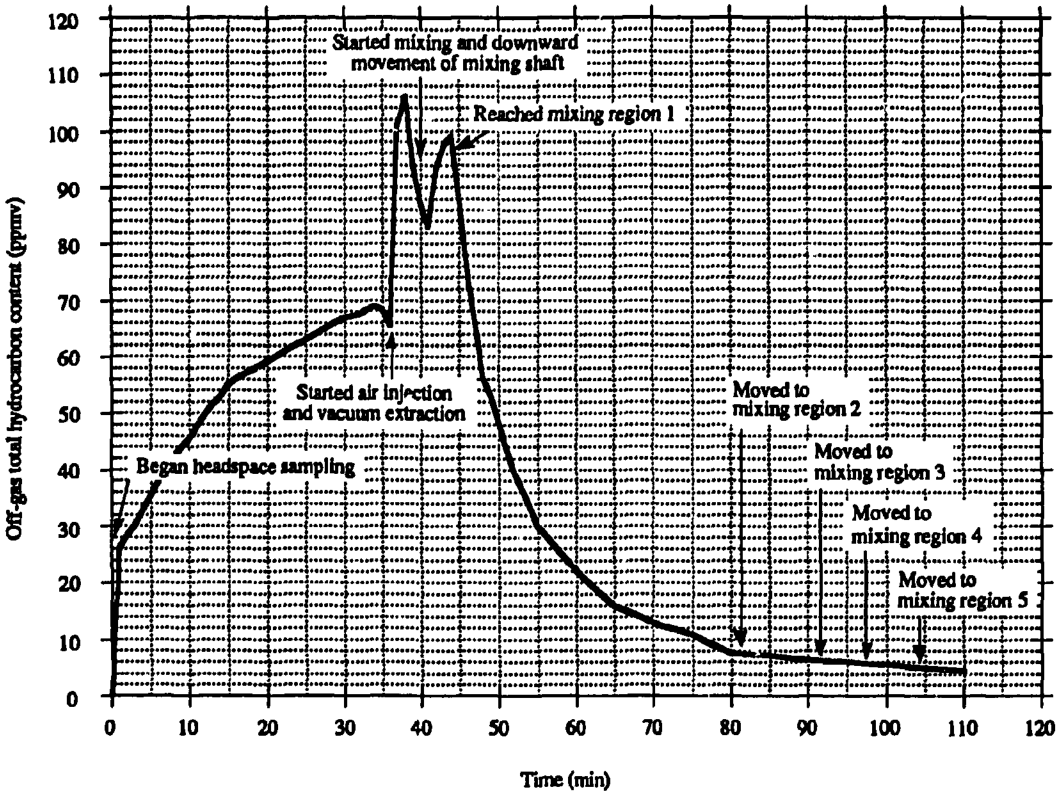

Figure 2.8. Off-gas total hydrocarbon content measured by the FID during ambient-air vapor stripping of Core 1078-AA.

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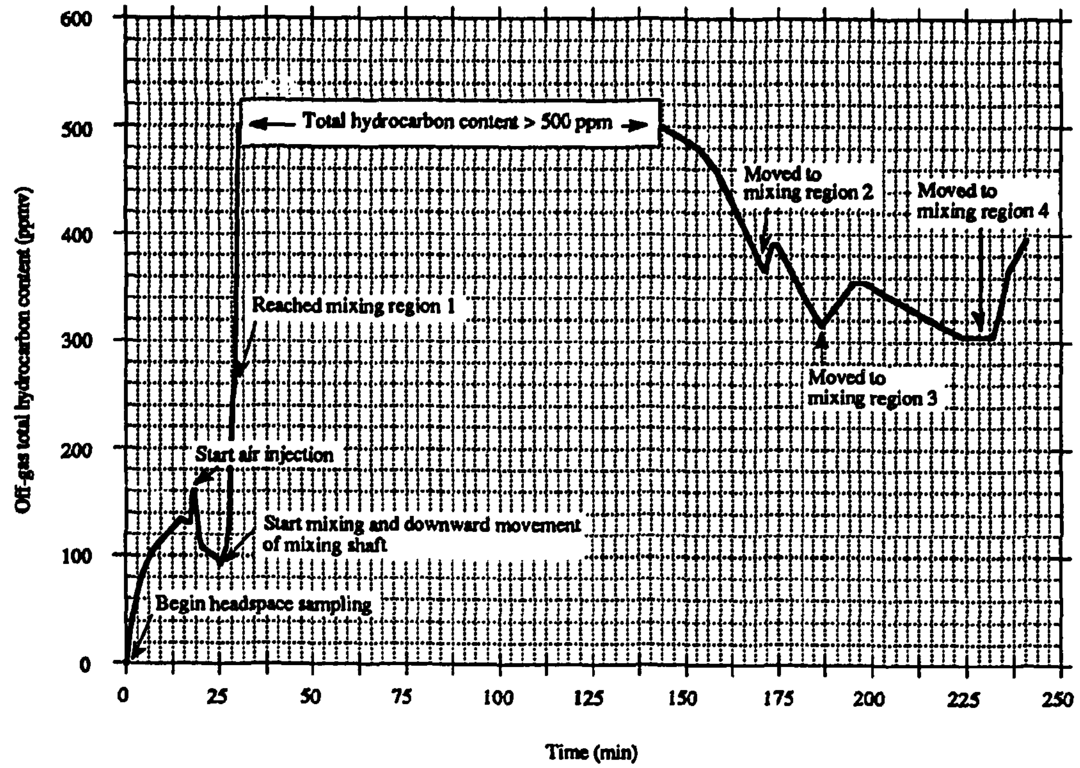

Figure 2.9. Off-gas total hydrocarbon content measured by the FID during first-stage heated-air vapor stripping of Core 1077-HA.

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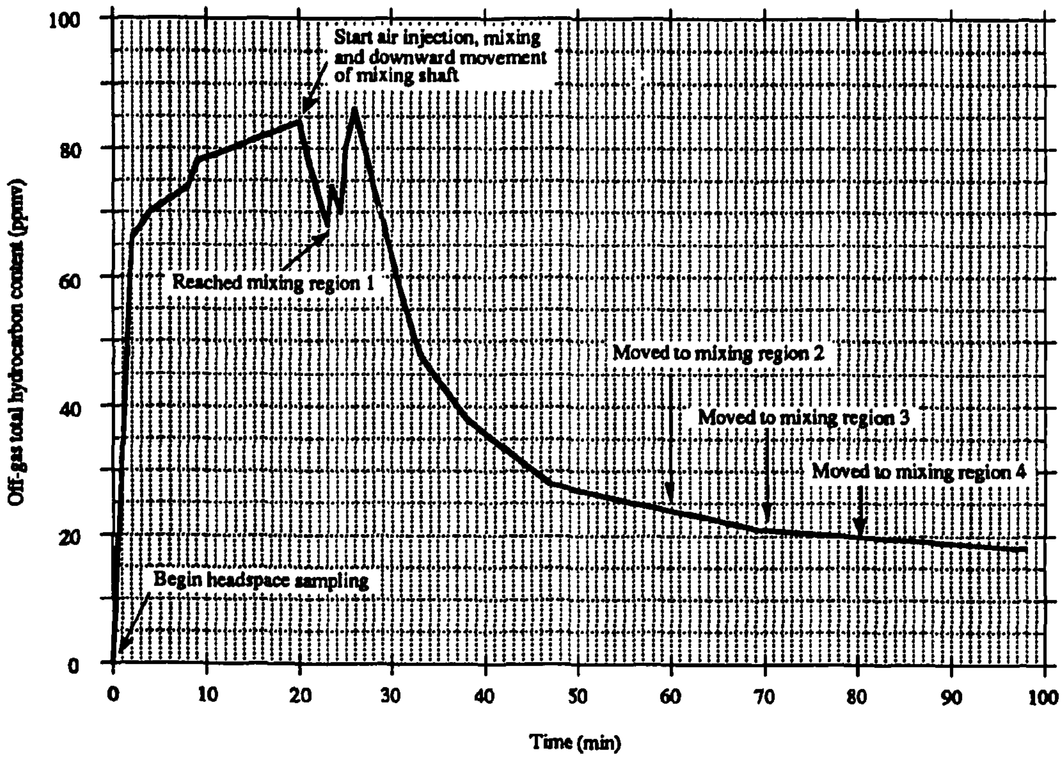

Figure 2.10. Off-gas total hydrocarbon content measured by the FID during second-stage heated-air vapor stripping of Core 1077-HA.

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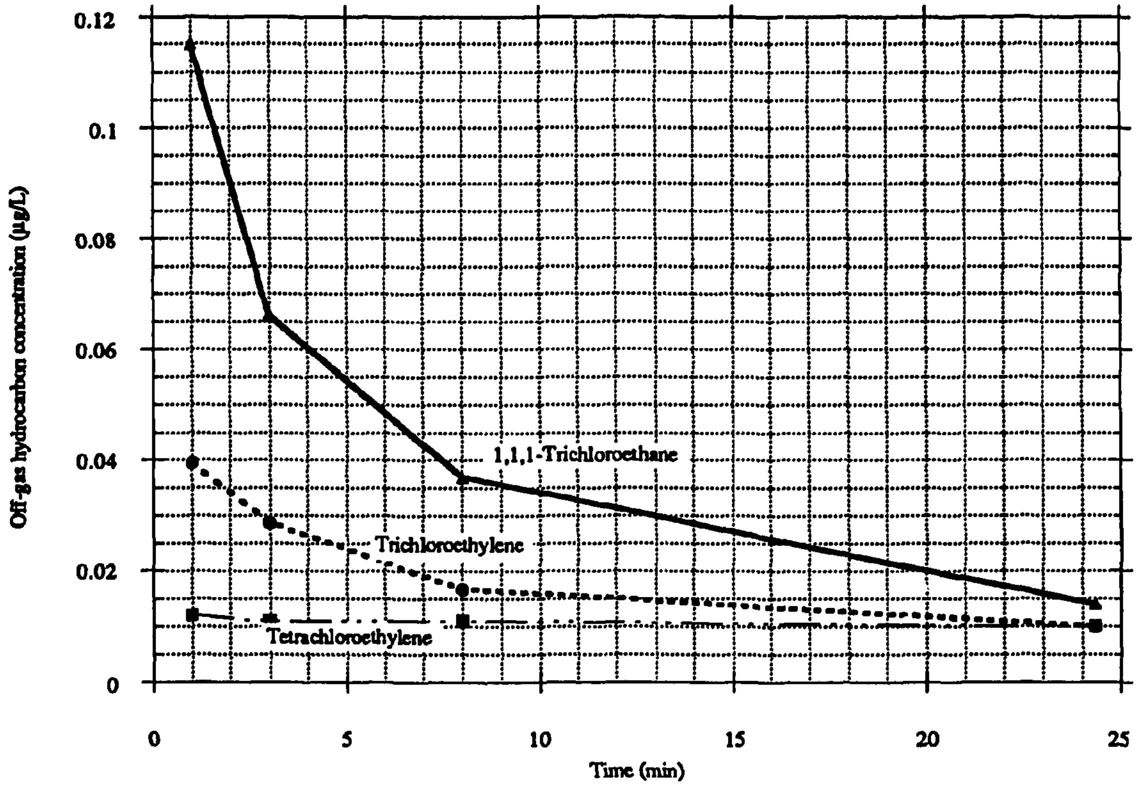

Figure 2.11. Off-gas total hydrocarbon concentration of compounds measured by GC/ECD. Samples taken during treatment of first mixing zone in first-stage heated-air vapor stripping of Core 1077-HA.

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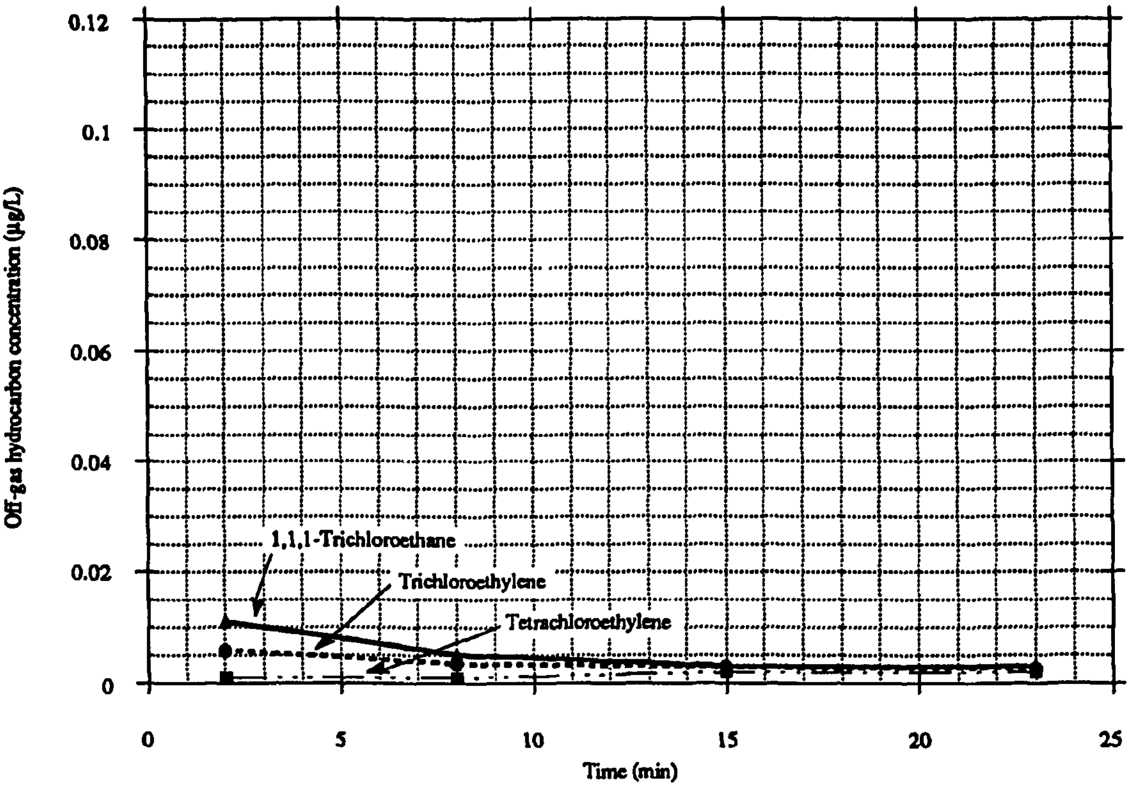

Figure 2.12. Off-gas total hydrocarbon concentration of compounds measured by GC/ECD. Samples taken during treatment of first mixing zone in second-stage heated-air vapor stripping of Core 1077-HA.

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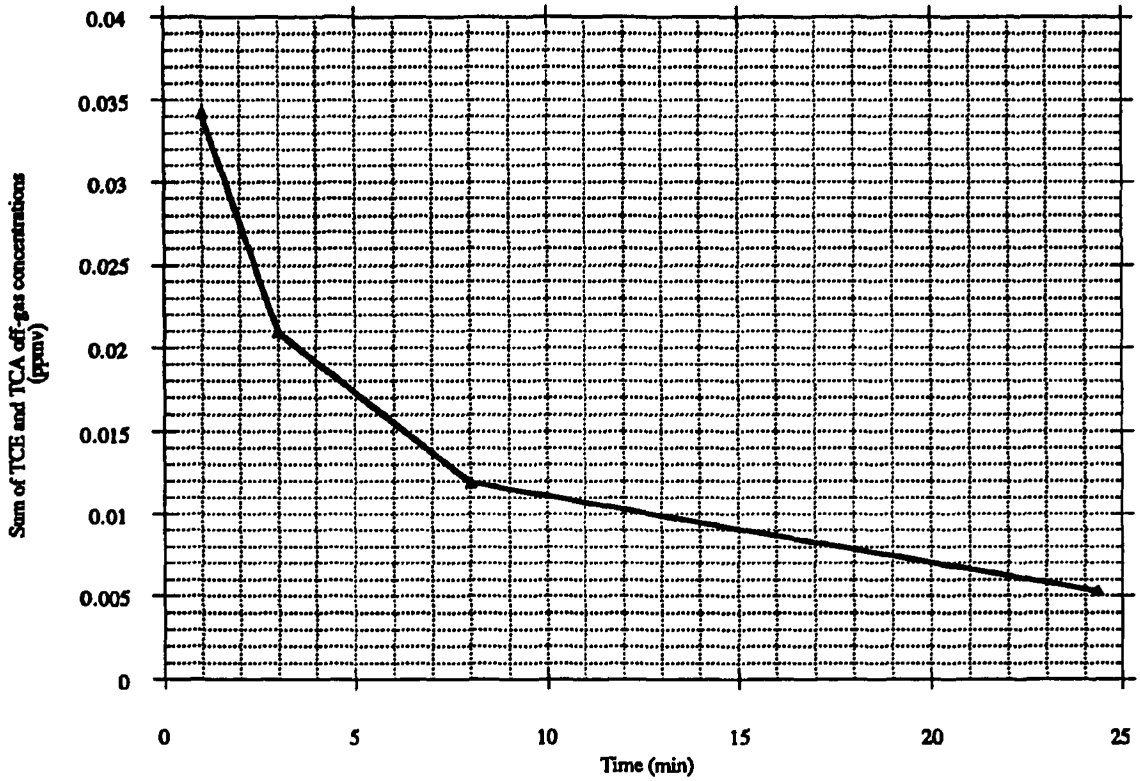

Figure 2.13. Off-gas total hydrocarbon content estimated by summing hydrocarbon concentrations detected by GC/ECD in gas samples. Samples taken during treatment of first mixing zone in first-stage heated-air vapor stripping of Core 1077-HA.

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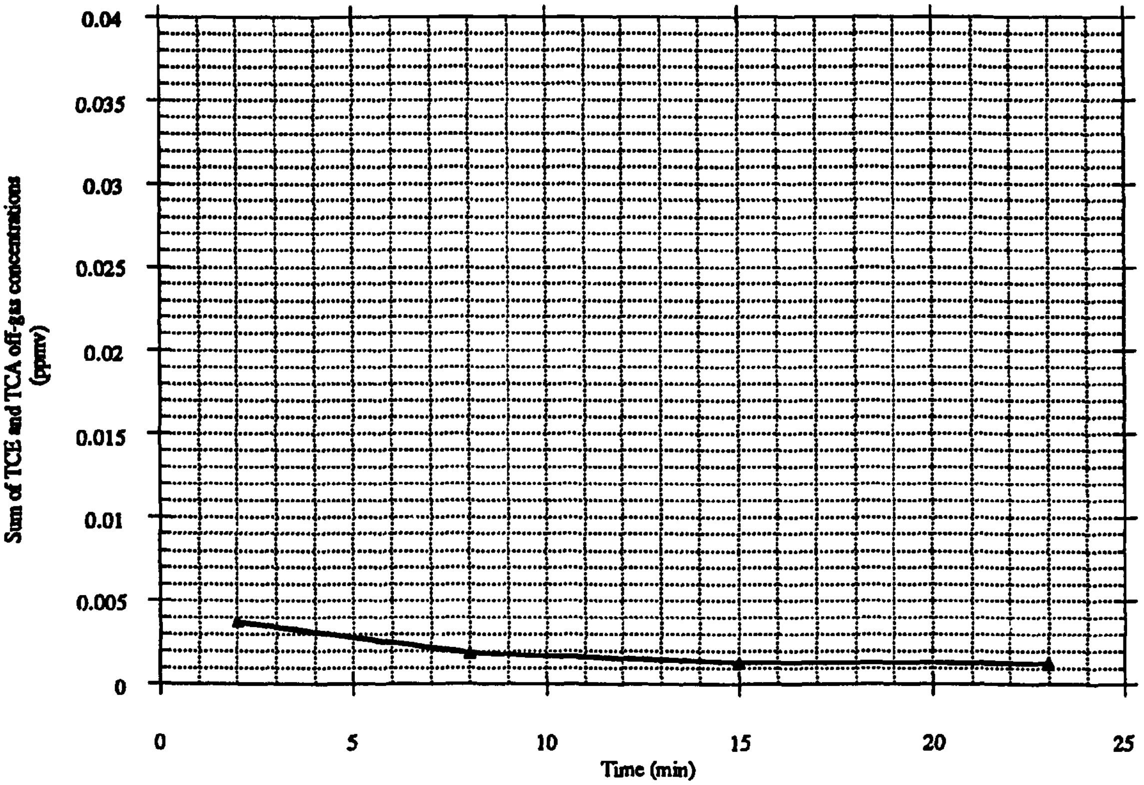

Figure 2.14. Off-gas total hydrocarbon content estimated by summing hydrocarbon concentrations detected by GC/ECD in gas samples. Samples taken during treatment of first mixing zone in second-stage heated-air vapor stripping of Core 1077-HA.

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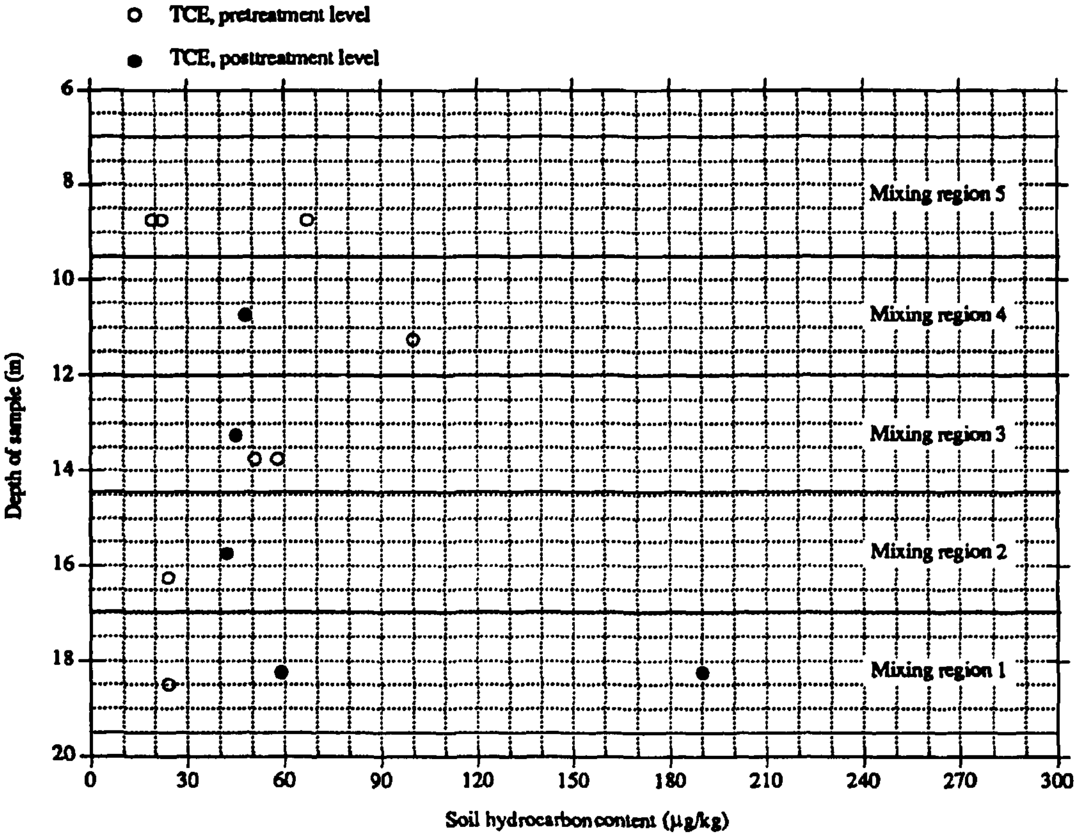

Figure 2.15. Pre- and posttreatment levels of TCE in Core 1078-AA. Treatment used was vapor stripping with ambient air. Hydrocarbon content based on dry weight of soil.

ORNL-DWG 93-11768

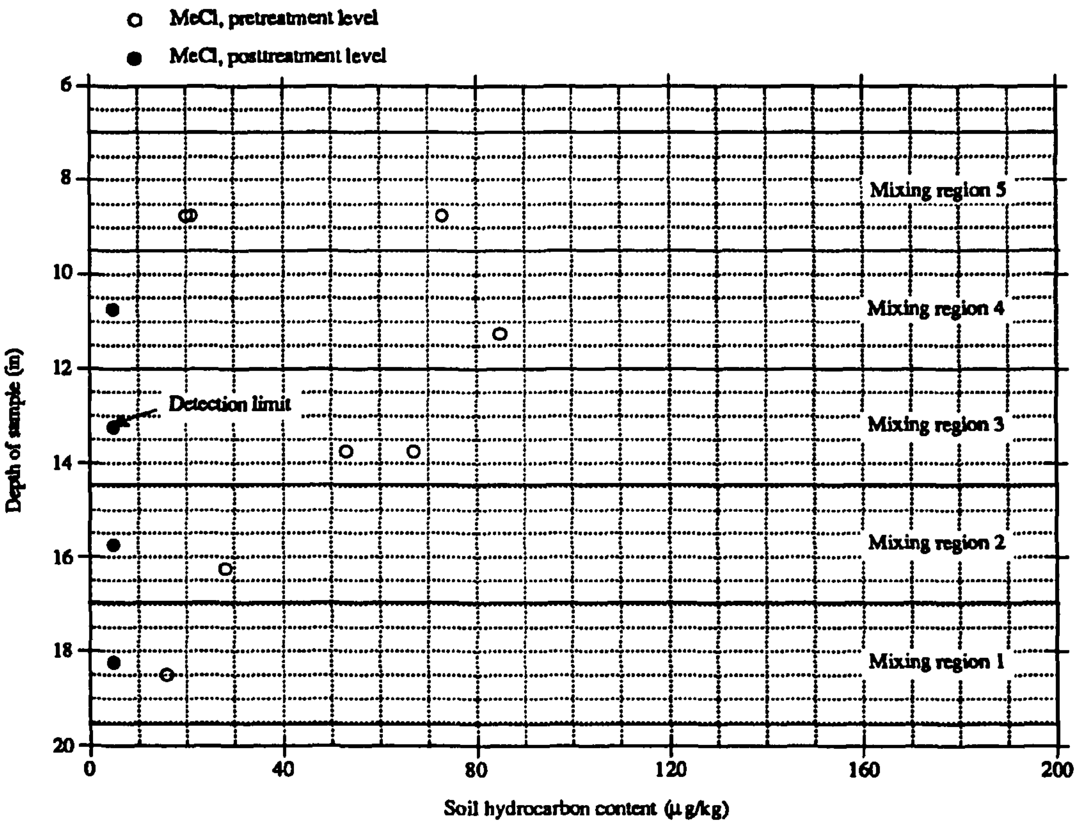

Figure 2.16. **Pre- and posttreatment levels of methylene chloride in Core 1078-AA. Treatment used was vapor stripping with ambient air. Hydrocarbon content based on dry weight of soil.**

ORNL-DWG 93-11769

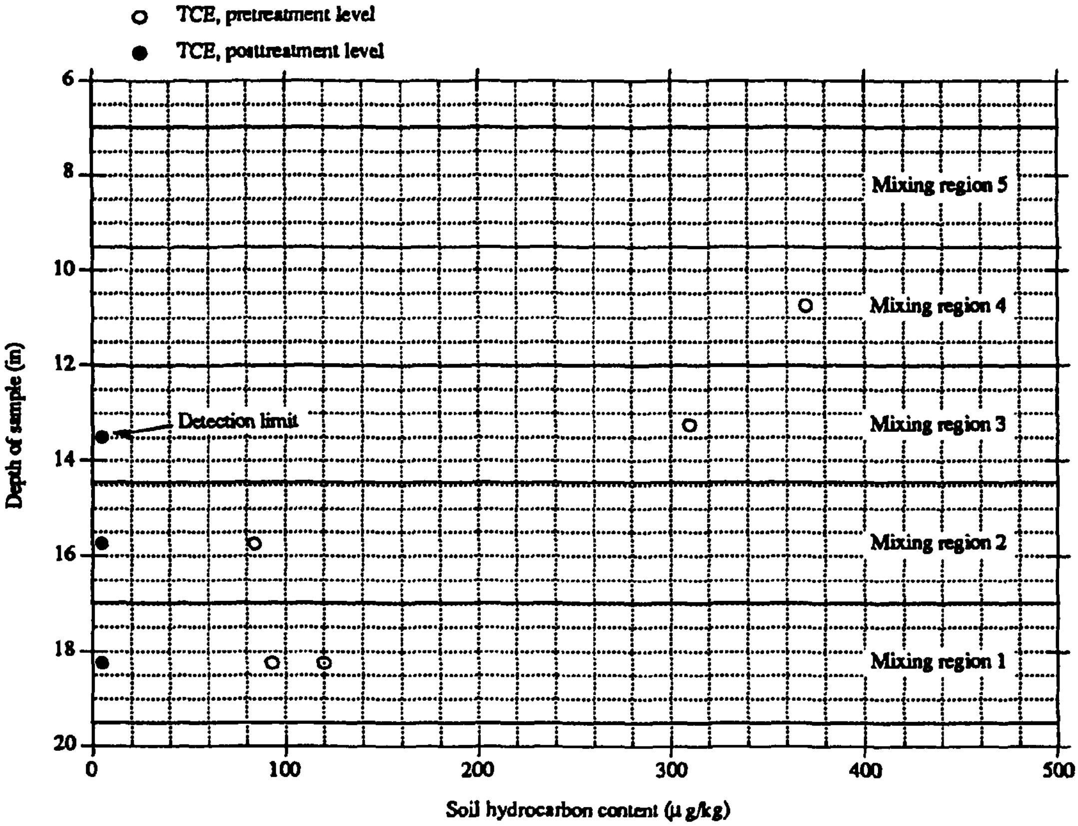

Figure 2.17. Pre- and first-stage posttreatment levels of TCE in Core 1077-HA. Treatment used was vapor stripping with heated air. Hydrocarbon content based on dry weight of soil.

ORNL-DWG 93-11770

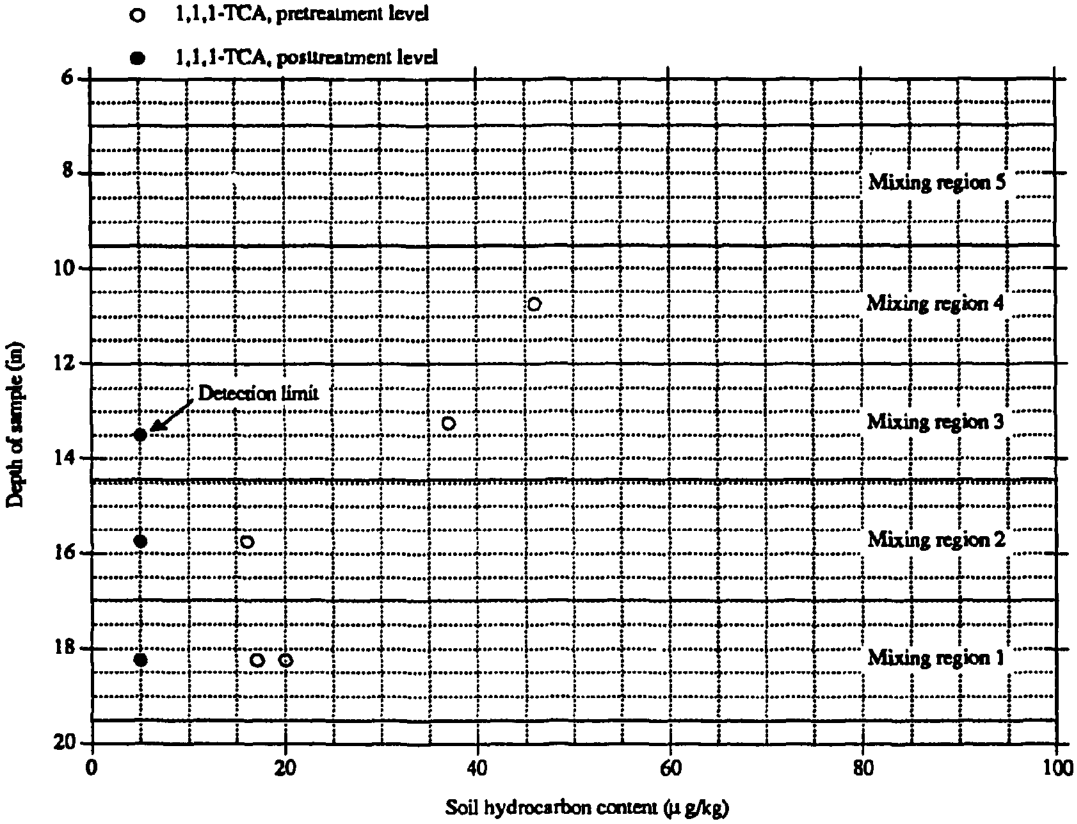

Figure 2.18. Pre- and first-stage posttreatment levels of 1,1,1-TCA in Core 1077-HA. Treatment used was vapor stripping with heated air. Hydrocarbon content based on dry weight of soil.

ORNL-DWG 93-11771

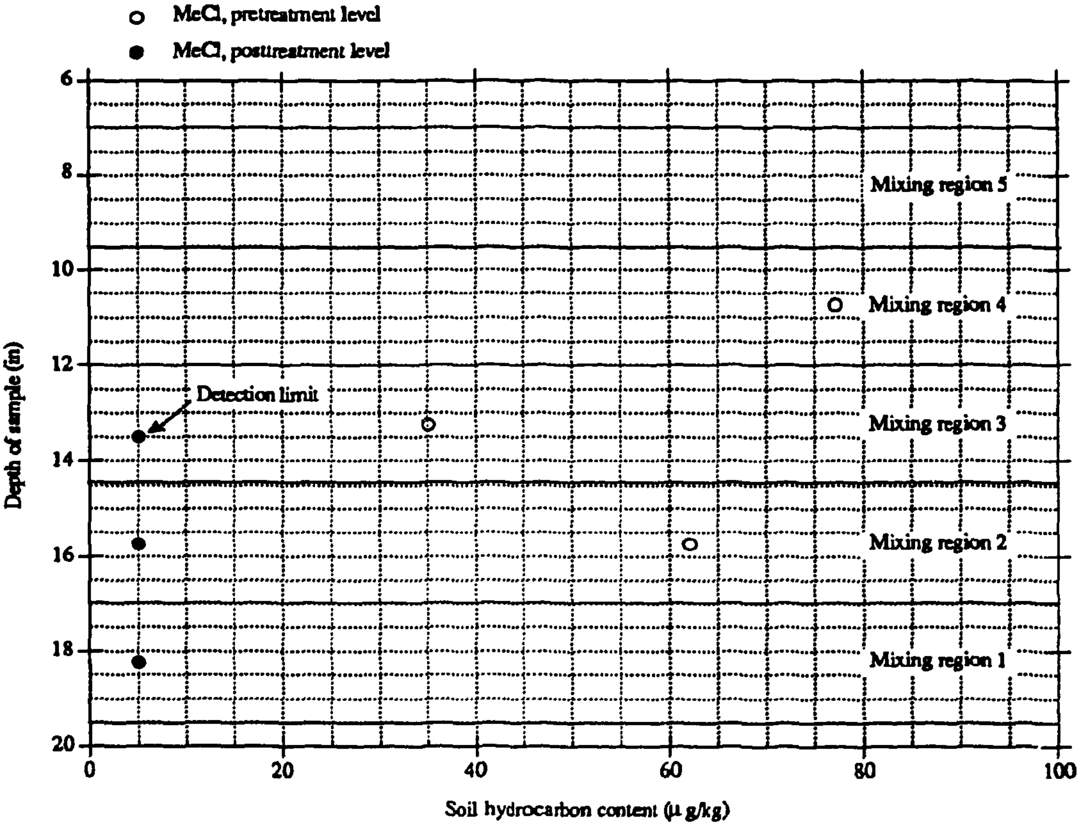

Figure 2.19. Pre- and first-stage posttreatment levels of methylene chloride in Core 1077-HA. Treatment used was vapor stripping with heated air. Hydrocarbon content based on dry weight of soil.

3. VAPOR STRIPPING OF PACKED CORES

3.1 INTRODUCTION

The series of experiments described in this section were performed on cores that consisted of repacked "clean" soil from the X-231B Unit. The soil cores were spiked with measured amounts of TCE, allowed to equilibrate, and subsequently treated through mixing and vapor stripping with ambient or heated air. The smaller treatment volumes in the smaller reaction lysimeters (8 in. in diameter, 9 in. long) resulted in better characterization of the pre- and posttreatment levels of VOCs in the soil. During the intact core experiments, only one sample was obtained from each mixing region in order to keep the number of samples per core within a feasible limit. However, using a single sample to characterize an entire mixing region was invalidated by the heterogeneity of the intact cores and the inherent variability of VOC analysis. Based on this experience, the packed soil cores consisted of only one mixing region from which between three to six soil samples (~5–10 g) were collected. In addition, a modified heated-headspace technique was used to quantify the levels of TCE in the soil samples. This method resulted in shorter holding times for the samples as well as a quicker availability of analysis results.

The smaller dimensions of the reaction lysimeters used for the packed-core experiments also made core handling, sampling, and treatment less time consuming. This advantage to using the smaller packed cores was very critical for obtaining experimental results and treatment efficiencies for different process conditions within the time constraints of the overall X-231B project.

3.2 MATERIALS

The treatability system used for the intact-core experiments was modified in accordance with the revised procedures for treatment and monitoring in the packed-core experiments. The objectives of these experimental procedures were (1) to perform simultaneous soil mixing with and without air injection or vacuum extraction and (2) to monitor the temperature, pressure, and flow rate of the air injected into the soil core. The main modification made in the treatability setup, which is shown in Fig. 3.1, was the elimination of the FID and the off-gas sampling system. In addition, the reaction lysimeter had to be left open during the experiments in which soil samples were taken from the top of the core while it was undergoing treatment. When the reaction lysimeter was left open, vacuum extraction was not included as part of the treatment procedure. The injection pressure was adjusted to maintain a constant flow rate for all the experiments, whether or not vacuum extraction was performed.

The reaction lysimeter was shortened to 9 in., and only a single mixing region was treated (Fig. 3.2). Being substantially smaller than the larger intact cores (Sect. 2), the modified reaction lysimeters were much easier to handle in the laboratory.

The packed cores were prepared from clean X-231B soil that were spiked with an aqueous TCE solution. Clean X-231B soil was obtained from standard-sized cores (3 in. x 6 in. in length) collected during previous site-characterization activities. The cores were packed such that the final bulk density of the core was approximately equal to the in situ bulk density of X-231B soil (~1.6 to 1.8 g/cm^3).

TCE was chosen as the representative VOC for the following reasons: (1) it was found at highest levels in soil samples collected during X-231B site characterization, (2) it was found at levels above drinking water standards in the aquifer beneath the Unit, and (3) it is the least volatile of all the VOCs found in the Unit.

Core preparation and spiking procedures are described in the following section.

3.3 METHODS

3.3.1 Core Preparation, Spiking, and Pretreatment Characterization

Since the annular soil remained fairly intact during mixing in the core (see Fig. 2.5), only the soil in the single mixing zone was repacked between treatment runs. Because of the tight soil structure and thickness of the intact annular region (~1.5 in.), it was reasonable to assume that TCE added to the mixing region of the packed cores during spiking did not have sufficient time to diffuse into the surrounding intact region, given that spiking and treatment were performed within 2 h. The reaction lysimeter was sealed immediately after core preparation in order to reduce VOC losses.
Soil core preparation and spiking were performed in a fume hood using the following procedure:

1. An aqueous TCE solution (220 mg/L) was prepared by adding 40 uL of pure liquid TCE to 250 mL of distilled water. To ensure complete dissolution of TCE in the water, the solution was mixed by a magnetic stirrer for at least an hour before it was used for spiking the cores. A fresh aqueous TCE solution was made for each batch of cores that was prepared.

2. Soil was extracted from the 3 in. x 6 in. cores and broken up until the largest soil aggregates were ~0.5 in. in diameter. Three batches of 580 g each of broken-up field-moist soil were weighed out and set aside. This mass of soil (~1740 g) was sufficient to pack a single core.

3. The reaction lysimeter with the intact annular region was set on a core preparation stand. The annular intact soil in the lysimeter that was unaffected by the mixing (see Fig. 2.5) formed a "hole" that was eventually filled by re-packed soil. The bottom stainless steel end cap was attached to the reaction lysimeter prior to core preparation, while the top stainless steel end cap was left off.

4. One-half of a 580 g. batch of soil was spread loosely at the bottom of the "hole." Using a syringe, 12.5 mL of TCE solution was distributed as uniformly as possible on the soil surface. The other half of the soil batch was then spread on top of the soil surface and tamped with a hammer and a 4 in. x 4 in. wooden block. After compaction, the soil surface was scarified to ensure structural transition with the overlying soil layer.

5. Step 4 was repeated for the other two batches of soil except that the topmost layer did not have to be scarified.

6. The reaction lysimeter was then sealed by installing the top end cap, and the prepared soil core was allowed to equilibrate for at least an hour at room temperature before the treatment run. The 1-h equilibration time was largely dictated by the need to conduct as many runs as possible within a short time frame for the packed core experiments (see Sect. 1.1). However, this equilibration time was judged adequate for TCE to diffuse throughout the packed soil region. If diffusion time into a porous sphere is on the order of $a^2/D_{(l)eff}$ [Cussler, 1984] where a = radius of the porous sphere and $D_{(l)eff}$ = effective diffusion coefficient, then 1 h will have been sufficient for TCE to diffuse into the soil aggregates assuming that the average soil chunks were 10 mm in diam and that the effective diffusion coefficient of TCE in the pore water is ~10^{-6} cm^2/sec.[a]

Prior to conducting treatment, soil samples were taken from the soil core for pretreatment characterization of VOC levels. The samples were collected using three 1-in. OD stainless steel sampling probes that were inserted into the packed-soil volume (i.e., samples were not taken from the intact annular region). Between one and two soil plugs (5–10 g) were taken from each probe and placed in 40-mL VOA vials, resulting in a total of between three to six pretreatment samples. These samples were analyzed within 5 h of sampling using the heated headspace technique described in Sect. 3.3.3.

3.3.2 Treatment Procedures and Posttreatment Characterization

Table 3.1 summarizes the process conditions used during the packed core experiments. The treatment runs included four different sets of conditions: (1) mixing, vapor stripping

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[a] Most diffusion coefficients in liquids fall close to 10^{-5} cm^2/sec.[11] Assuming a tortuisity factor of 10, then the effective diffusion coefficient of TCE in a soil particle is 10^{-6} cm^2/sec.

with heated air, and vacuum extraction (HA1, HA2, HA3, HA4); (2) mixing, vapor stripping with ambient air, and vacuum extraction (IA3, IA4, IA5); (3) mixing only in an open reaction lysimeter (C2,C3); (4) mixing and vapor stripping with ambient air in an open reaction lysimeter (IA7). Supplementary packed-core runs are described in Appendix B or this report.

The treatment procedure for the packed core experiments is as follows:

1. After the packed core had equilibrated for 1 h, the reaction lysimeter was installed onto the treatability system. In the open lysimeter runs (C2, C3, and IA7), the top end cap of the reaction lysimeter was removed before the lysimeter was placed in the treatability system.

2. The mixer was turned on, and the mixing shaft was lowered into the soil until that the end of the mixing shaft was at the bottom of the single mixing region in the packed soil core. Air injection began at this point for the runs in which the soil was vapor stripped with either ambient or heated air. Vacuum extraction was also initiated for the runs in which the lysimeters were closed during treatment. Mixing and vapor stripping, where applicable, were conducted for an hour for each core.

3. In runs C2, C3, and IA7 (i.e., the open lysimeter runs), soil samples were taken during treatment to determine the contaminant removal as a function of treatment time. Two soil plugs were taken at 10-min intervals using the 1-in. OD stainless steel sampling probes. These soil samples were placed in 40-mL VOA vials with Teflon-coated septum caps and were analyzed within 5 h of sample collection using the heated-headspace technique described in Sect. 3.3.3.

Immediately after each run, soil samples were taken from the soil core for posttreatment characterization of VOC levels. The samples were collected using three 1-in. OD stainless steel sampling probes that were inserted into the mixed soil volume (i.e., samples were not taken from the intact annular region). Between one and two soil plugs (5 – 10 g) were taken from each probe and placed in 40-mL VOA vials, resulting in a total of between 3 and 6 posttreatment samples. These samples were analyzed within 5 h of sample collection using the heated-headspace technique described in Sect. 3.3.3.

3.3.3 TCE Analysis of Soil Samples

A heated headspace technique was used to determine the TCE content of the soil samples. In this method, soil samples in the 40-mL VOA vials were heated for an hour in an 80°C water bath. After heating the soil, headspace samples were extracted from the vial using a gas-tight syringe. The headspace samples were analyzed using a Perkin Elmer Sigma 2000 gas chromatograph (30 m x 0.53 mm Volco column, carrier gas was N_2, flow rate was 4 mL/min, 80°C oven temperature at isothermal conditions, and injector temperature was 250°C) equipped with an Nickel 63 electron capture detector (detection temperature was 300°C). The amount of TCE present in the vial headspace (40 mL less the volume occupied by the soil sample) was extrapolated from the amount detected by the GC/ECD. The amount of TCE in the soil, expressed in units of µg TCE per kg of wet soil, was calculated knowing the mass of the soil sample and assuming that all the TCE that was originally in the soil had been driven to the headspace by heating. All of the TCE soil levels reported in this section are based on the weight of wet soil (i.e, µg TCE/kg wet soil).

3.4 RESULTS

3.4.1 Pre- and Post-treatment TCE Levels in Soil Samples

Tables 3.2, 3.3, and 3.4 contain the results of pre- and posttreatment analyses of samples taken from heated-air, ambient-air, and mixing-only runs, respectively. The pretreatment levels varied among the different cores, even though the same spiking solution was used for each of these cores. These levels are also greater than the levels measured in the intact soil cores used in the first series of experiments and are closer to levels found in the field.

Average pre- and posttreatment levels for each of the packed-core runs are plotted in Fig. 3.3. Except for run HA2, posttreatment levels from the heated-air runs are lower than the posttreatment levels from the ambient-air runs, suggesting that vapor stripping with heated air may be more effective than vapor stripping with ambient air. Fig. 3.3 also shows that posttreatment TCE levels for all runs were less than or equal to 150 µg/kg. Posttreatment levels were not directly correlated with the pretreatment levels (i.e, higher posttreatment levels were not always associated with higher pretreatment levels).

The posttreatment levels of C2 and C3 are about the same as the posttreatment levels in the vapor-stripping runs, indicating that treatment through mixing only was equally effective as mixing with vapor stripping through air injection and vacuum extraction. Explanations for this obervation are given in the section on modeling and discussion of results (Sect. 4).

3.4.2 Treatment Efficiency

Treatment efficiency is defined as the ratio between contaminant mass that was removed by the treatment and contaminant mass that was initially in the soil. However, because of the variability in the pre- and posttreatment levels for a given core, two methods for calculating treatment efficiency were used. In the first method, treatment efficiency is defined by the following equation:

$$\mathrm{TE1} = \frac{\dfrac{\sum_{i=1}^{n_{pre}} A_i}{n_{pre}} - \dfrac{\sum_{j=1}^{n_{post}} B_j}{n_{post}}}{\dfrac{\sum_{i=1}^{n_{pre}} A_i}{n_{pre}}}, \qquad [3.1]$$

where A_i and B_j are pre- and posttreatment TCE measurements in the soil samples, while n_{pre} and n_{post} are the number of pre- and posttreatment samples, respectively.

The second definition of treatment efficiency is given by

$$\mathrm{TE2} = \frac{\sum_{j=1}^{n_{post}} \sum_{i=1}^{n_{pre}} \left(\dfrac{A_i - B_j}{A_i} \right)}{\left(n_{pre}\right)\left(n_{post}\right)}, \qquad [3.2]$$

where the same definitions for the variables in Eq. 3.1 are used. The term in parentheses in the above equation is a treatment efficiency calculated from a combination of one pretreatment and one posttreatment measurement. If there are n_{pre} pretreatment measurements and n_{post} posttreatment measurements, then the total number of these "paired" treatment efficiencies is $(n_{pre})*(n_{post})$. Thus, TE2 is the average of these "paired" treatment efficiencies calculated from all the possible combinations of pre- and posttreatment measurements.

The treatment efficiencies computed from the above equations are shown in Fig. 3.4 for the heated-air, ambient-air and mixing-only runs. In this figure, the columns represent the treatment efficiencies calculated using Eq. 3.1. The filled circles correspond to the treatment efficiency calculated using Eq. 3.2, with error bars reflecting the standard deviations of the "paired" treatment efficiencies for each run. The figure shows that the difference between treatment efficiencies calculated using Eq. 3.1 and 3.2 is negligible.

On the basis of Fig. 3.4, the treatment efficiencies for the four types of treatment appear to be approximately within the same range, and an advantage of using one treatment over the other is not apparent. Heated-air injection resulted in slightly higher removal efficiencies.

3.4.3 Mass Removal Rates

For the packed cores that were treated in closed lysimeters, only the efficiency of 1 h treatments can be established from the pre- and posttreatment samples. However, for the runs that were conducted in open lysimeters (C2, C3, and IA7), soil samples were taken from the cores during treatment. TCE analyses of these soil samples were conducted using the heated-headspace technique described in Sect. 3.3.4. Analysis results were used to establish the treatment levels of the cores as a function of time.

Fig. 3.5 is a plot of the TCE level versus treatment time for C2 (mixing only in an open lysimeter) and IA7 (mixing, ambient-air vapor stripping in an open lysimeter). All measurements were included in the graph in order to illustrate soil TCE measurement variability. Fig. 3.5 does not show a significant difference between the TCE removal rates in the mixed core and those of the mixed and air-stripped core. The similarity of removal rates in C2 and IA7 is further illustrated in Fig. 3.6 where treatment efficiency (as defined by Eq. 1 in Sect. 3.3.1) is plotted as a function of treatment time. Explanations for this observation are given in the following section.

It is also interesting to compare the TCE removal rates in C2 and C3 since the initial TCE levels and equilibration times (2 h for C2; 71 h for C3) between these two runs were significantly different. In Fig. 3.7, the remaining TCE in the soil is plotted as a function of treatment time for run C3. The residual levels in C2 and C3 both approach the same value (~100 μg/kg), even though the initial amount of TCE in C2 was more than twice the amount of TCE in C3. A plot of treatment efficiency (defined by Eq. 3.1 in Sect. 3.3.1) as a function of treatment time (see Fig. 3.8) suggests a slower removal rate for the core that had less TCE before treatment was begun.

Tailing at a level of ~100 ug/kg was observed in runs IA7, C2, and C3. This may represent a fraction of VOC contamination that is very resistant to stripping. This is also consistent with the observation in the intact core experiments, in which low levels of VOCs in Core 1078 (100 μg/kg or less) were not altered by 1 h of vapor stripping.

Table 3.1. Summary of packed-core experiments

Treatment	Run	Mixing	Air Flow (cfm)	Air Temp. (°C)	Lysimeter	Ave. Initial TCE in soil (μg/kg)[a]
1	HA1	Yes	0.6	121	Closed	1134
	HA2	Yes	"	"	"	963
	HA3	Yes	"	"	"	1720
	HA4	Yes	"	"	"	2166
2	IA3	Yes	0.6	24	"	1162
	IA4	Yes	"	"	"	1960
	IA5	Yes	"	"	"	2347
3	C2	Yes	N/A	N/A	Open	1548
	C3	Yes	"	"	"	615
4	IA7	Yes	0.6	24	Open	1483

[a] Refer to Table 4.2 for individual sample results.

Table 3.2. Pre- and posttreatment TCE levels for vapor stripping with heated air

Run Label	Sample No.[a]	Pretreatment TCE in Soil (µg/kg)	Sample No.[a]	Posttreatment TCE in Soil (µg/kg)
HA1	1	892	1	133
	2	1942	2	92
	3	1180	3	135
	4	1070	4	80
	5	829	5	44
	6	892	6	55
	Ave.	1134	Ave.	90
	S.D.	417	S.D.	38
HA2	1	822	1	201
	2	1138	2	389
	3	1103	3	232
	4	1062	4	303
	5	847	5	426
	6	806	6	540
	Ave.	963	Ave.	349
	S.D.	154	S.D.	128
HA3	1	1542	1	45
	2	1607	2	95
	3	2080	3	124
	4	2722	4	93
	5	855	5	80
	6	1512	6	42
	Ave.	1720	Ave.	80
	S.D.	628	S.D.	31
HA4	1	1716	1	55
	2	1516	2	63
	3	1860	3	40
	4	3386	4	25
	5	2297	5	36
	6	2223	6	59
	Ave.	2166	Ave.	46
	S.D.	668	S.D.	15

[a] Pre- and posttreatment samples are *not* paired by location.

Table 3.3. Pre- and posttreatment TCE levels for vapor stripping with ambient air

Run Label	Sample No.[a]	Pretreatment TCE in Soil (ug/kg)	Sample No.[a]	Posttreatment TCE in Soil (ug/kg)
IA3	1	1509	1	60
	2	787	2	162
	3	1189	3	217
	Ave.	1162	Ave.	146
	S.D.	146	S.D.	80
IA4	1	1963	1	91
	2	1978	2	207
	3	1937	3	154
	Ave.	963	Ave.	151
	S.D.	154	S.D.	58
IA5	1	2272	1	149
	2	2120	2	127
	3	1906	3	70
	4	3671		
	5	1727		
	6	2384		
	Ave.	2347	Ave.	80
	S.D.	691	S.D.	31
IA7[b]	1	1662	1	55
	2	1724	2	74
	3	1356	3	69
	4	1032		
	5	1663		
	6	1463		
	Ave.	1483	Ave.	46
	S.D.	262	S.D.	15

[a] Pre- and posttreatment samples are *not* paired by location.

[b] Open lysimeter run.

Table 3.4. Pre- and posttreatment TCE levels for mixing-only runs

Run Label	Sample No.[a]	Pretreatment TCE in Soil (ug/kg)	Sample No.[a]	Posttreatment TCE in Soil (ug/kg)
C2	1	1958	1	78
	2	1108	2	90
	3	1458	3	87
	4	1590	4	79
	5	1567	5	48
	6	1609	6	126
	Ave.	1548	Ave.	85
	S.D.	274	S.D.	25
C3	1	646	1	46
	2	595	2	71
	3	618	3	43
	4	542	4	53
	5	374	5	88
	6	917		
	Ave.	615	Ave.	60
	S.D.	177	S.D.	19

[a] Pre- and posttreatment samples are *not* paired by location.

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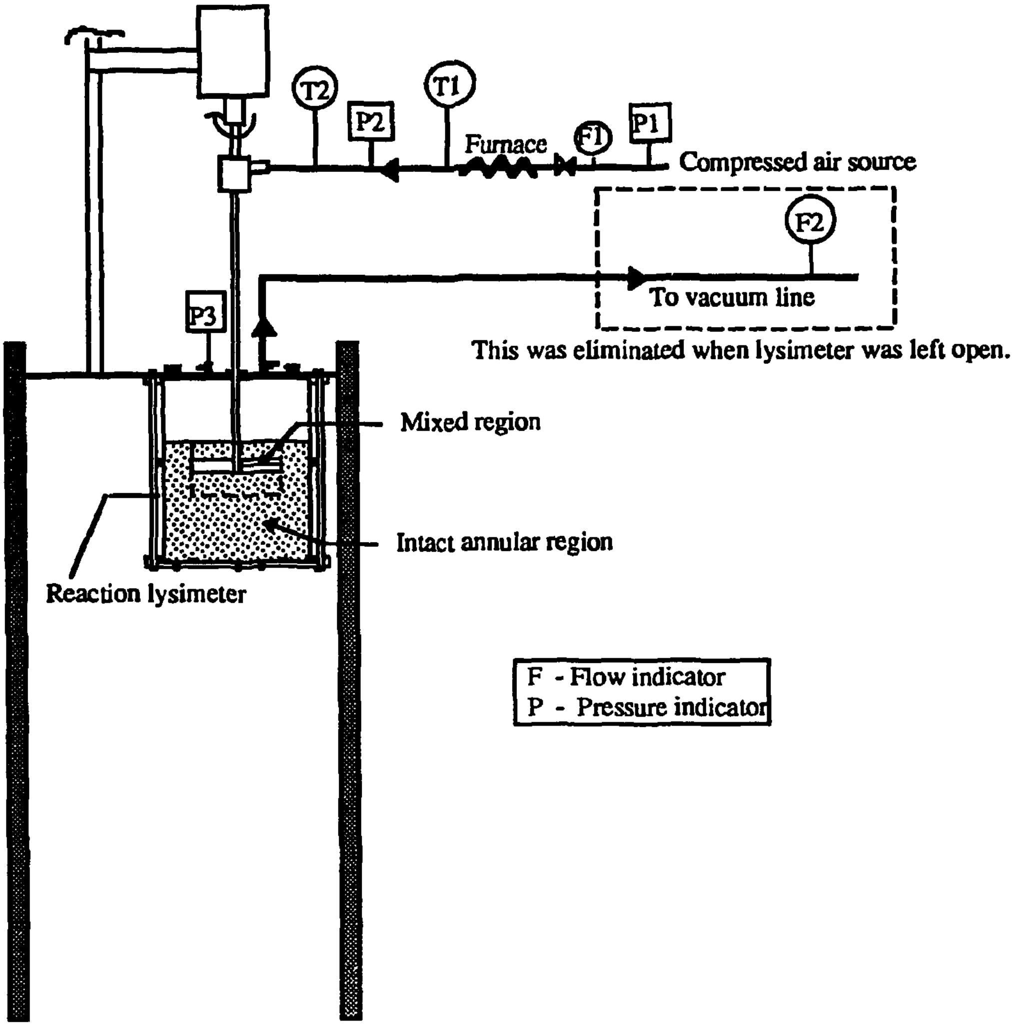

Figure 3.1. Treatability system for packed-core experiments.

ORNL-DWG 93-11773

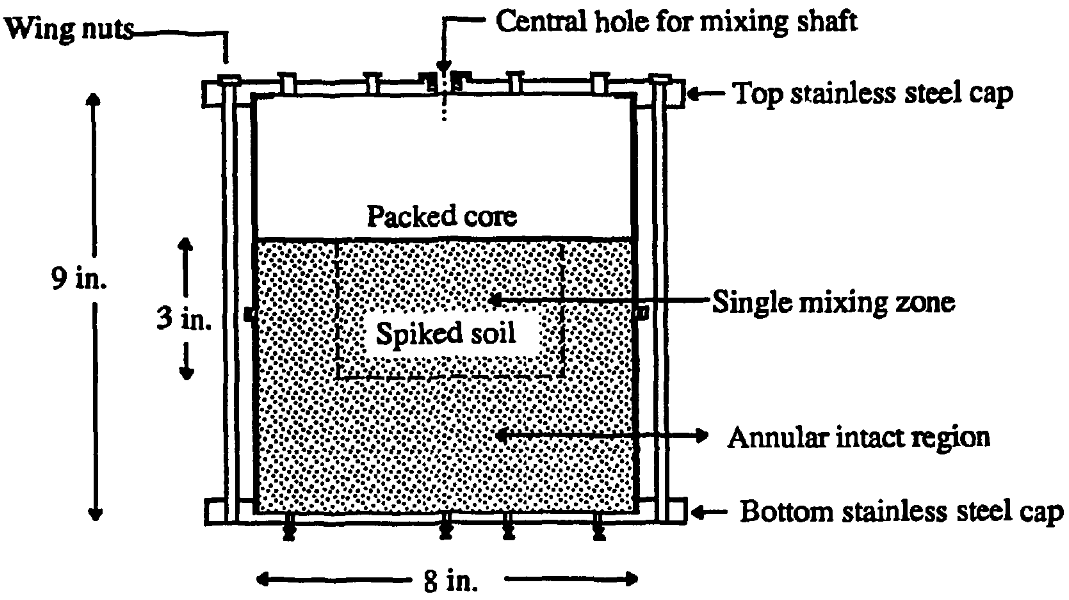

Figure 3.2. Modified reaction lysimeter used for packed-core experiments.

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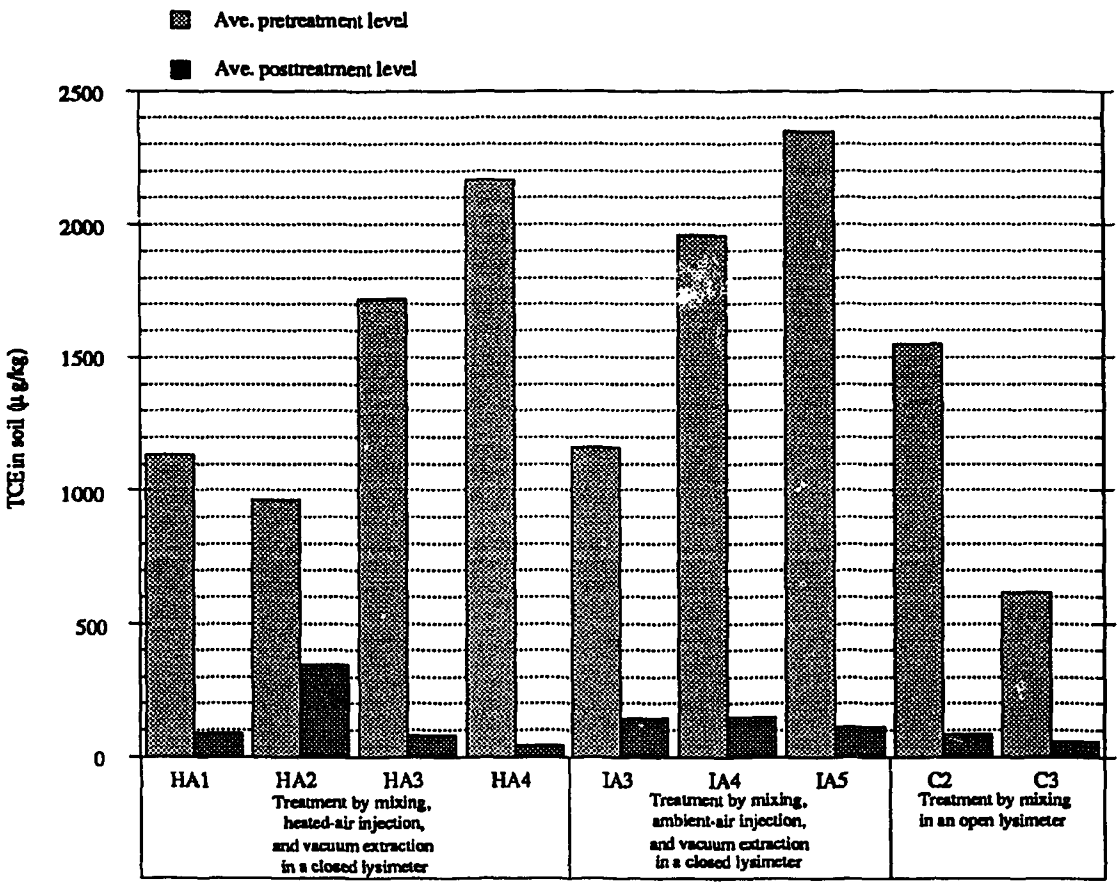

Figure 3.3. Average pre- and posttreatment TCE levels in packed cores.

ORNL-DWG 93-11775

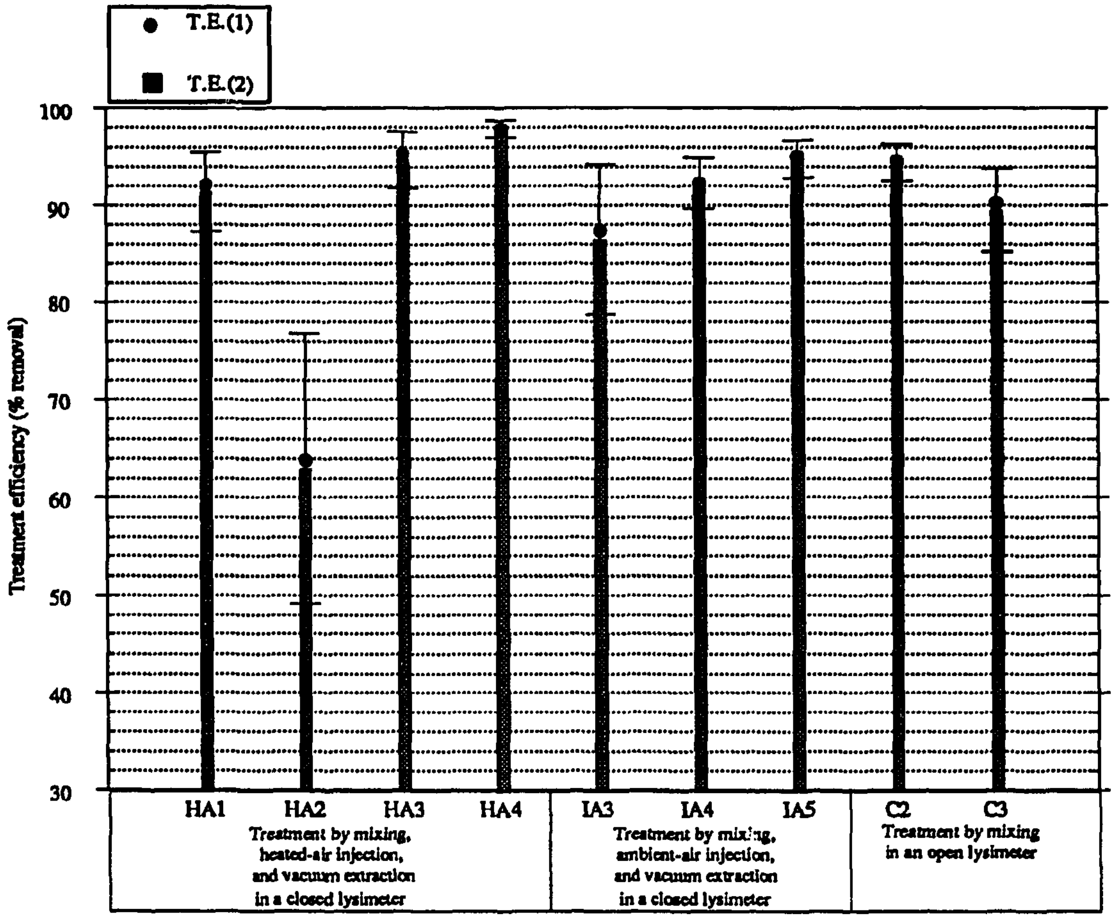

Figure 3.4. Treatment efficiencies calculated from treatment of packed cores. Error bars represent standard deviations of treatment efficiencies calculated using all possible pre- and posttreatment pairs.

ORNL-DWG 93-11776

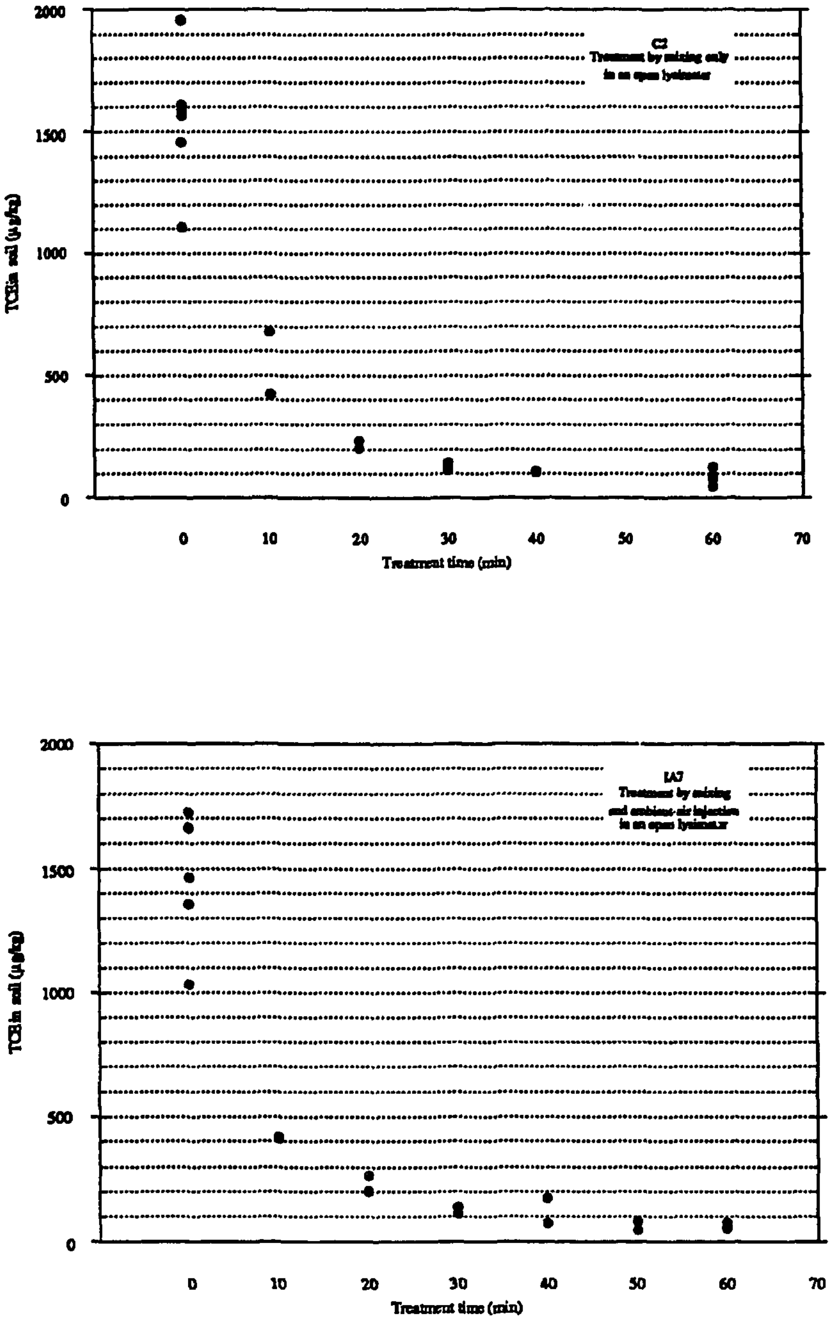

Figure 3.5. **Residual TCE in soil versus treatment time for mixing (C2) and mixing/ambient-air vapor stripping (IA7) runs.**

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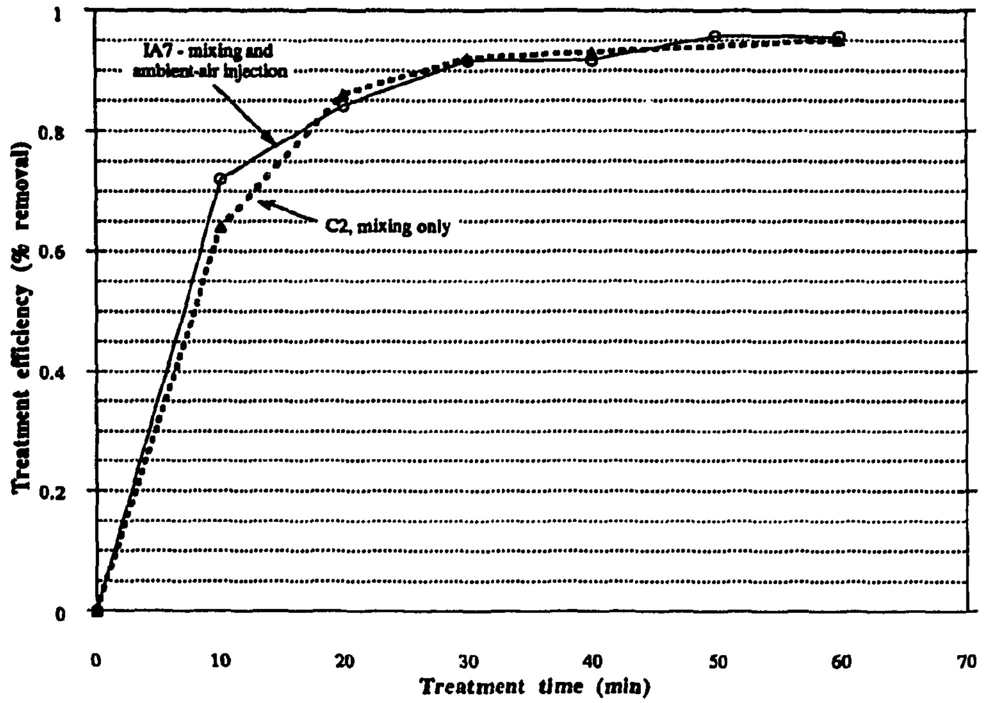

Figure 3.6. Treatment efficiency as a function of treatment time for mixing (C2) and mixing/ambient-air vapor stripping (IA7) runs.

ORNL-DWG 93-11778

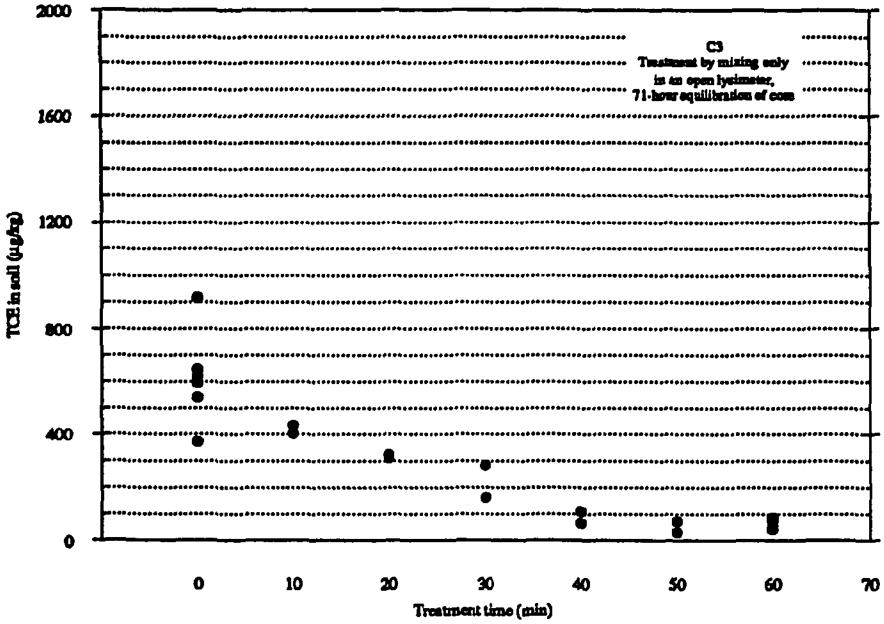

Figure 3.7 **Residual TCE in soil versus treatment time for mixing run C3.**

ORNL-DWG 93-11779

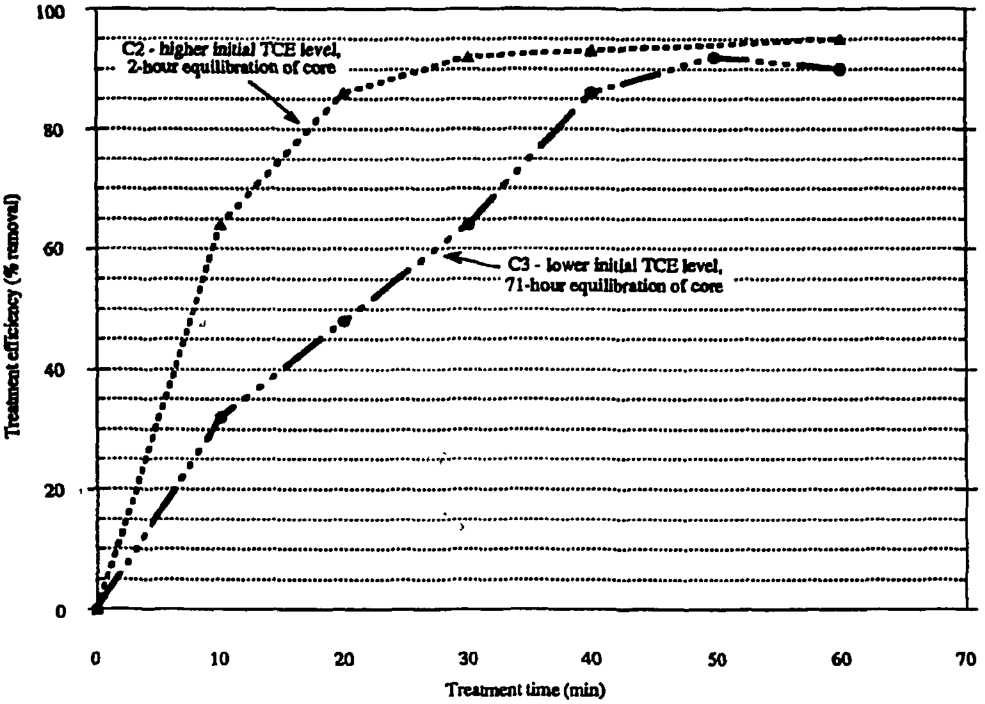

Figure 3.8. Treatment efficiency as a function of treatment time for mixing runs C2 and C3.

4. MODELING AND DISCUSSION OF EXPERIMENTAL RESULTS

4.1 INTRODUCTION

Two batch-type models for mass removal during vapor stripping were formulated in order to predict field performance from the results of treatability studies. The first model was formulated based on the assumption that concentrations of contaminants in the vapor and sorbed phases are always in equilibrium (i.e., it is assumed that the transfer of contaminants from the sorbed to the vapor phase occurs instantaneously). In the second model, the equilibrium assumption was relaxed by incorporating kinetic mass transfer in the form of contaminant diffusion through soil aggregates. The adequacy of these models for simulating clean-up processes during vapor stripping was tested by comparing model predictions against the treatment efficiency curves measured in the packed-core experiments (Sect. 5). The kinetic mass transfer model was much more effective in simulating measured removal efficiencies, and was then used to extrapolate treatment efficiency to X-231B field scale conditions.

4.2 AN EQUILIBRIUM MODEL FOR CONTAMINANT REMOVAL

Applying a mass balance to a unit volume of mixed soil, and assuming a linear equilibrium contaminant partitioning between vapor and sorbed phases, the following equation for mass removal during vapor stripping as a function of time can be derived (see Appendix A):

$$\frac{M}{M_o} = \exp\left(-\frac{qt}{\varepsilon_t R}\right), \tag{4.1}$$

where M is the contaminant mass remaining after time t, M_o is the initial amount of contaminant in the soil, q is the volumetric flow rate per unit volume of mixed soil (i.e., if a "reactor volume" is defined as the volume of the mixed soil, then q is the number of reactor volumes of stripping air per unit time), ε_t is the porosity of the mixed soil, and R is the retardation factor given by

$$R = 1 + \frac{\rho_t K_d'}{\varepsilon_t}. \tag{4.2}$$

In the above equation, K_d' is the partition coefficient between the vapor and sorbed phase contaminant concentrations, and ρ_t is the dry bulk density of the mixed soil. Eq. 4.1 can also be restated as follows:

$$\frac{M}{M_o} = \exp\left(-\frac{\tau}{\varepsilon_t R}\right) \qquad [4.3]$$

where $\tau = qt$ = number of reactor volumes that have been injected into the soil.

Eq. 4.3 implies that given two treatments with different stripping air flow rates, the same removal efficiency will be achieved in each treatment when the same number of reactor volumes of air have been injected into the soil. This also implies a given level of removal efficiency will be reached after a shorter treatment time using higher air flow rates. Such a trend was not observed in runs IA7 (ambient-air injection and mixing) and C2 (mixing alone), where the removal efficiencies were almost identical even though the stripping air flow rate in C2 was nominally equal to zero. To further illustrate this point, the removal rates in IA7 and C2 were predicted using the equlibrium model (see Fig. 4.1 and 4.2). The parameters used for each of these runs are given in Tables 4.1 and 4.2 for simulating IA7 and C2, respectively. In order to account for the uncertainty in estimating the effective flow rate in C2, three values for q were used in the simulations (see Fig. 4.2). The value for K_d', the vapor sorption coefficient, was taken from laboratory measurements made on PORTS soil as well as values reported by Ong and Lion, 1991.[9] A comparison between Figs. 4.1 and 4.2 shows that the equilibrium model predicted a significant decrease in removal rate when the flow rate is decreased from 17.4 r.v./min (IA7) to ~0.1–1 r.v./min (C2). This prediction is not consistent with the observed removal rates. Furthermore, the equilibrium model overestimates the removal rate in IA7 using the parameters listed in Table 4.1. A better fit between the predicted and observed removal rates in IA7 would have been achieved if K_d' were set to 100 ml/g. However, using the same K_d' and a lower flow rate in the equilibrium model would significantly underestimate removal rates measured in C2.

4.3 A KINETIC MODEL FOR MASS REMOVAL

The local equilibrium assumption made in arriving at Eq. 4.1 may be relaxed by accounting for the diffusion of the contaminants within the soil aggregates when deriving the equations for mass transport. In this kinetic model, the mixed soil is assumed to contain two types of porosities: one type of porosity refers to the pores that exist within the soil aggregates (intra-aggregate porosity), and a second type of porosity refers to voids that are produced after the soil has been broken up into aggregates by mixing (interaggregate porosity, see Fig.4.3). Even though contaminants exist in both porosities, only the contaminants in the interaggregate voids are swept away by the stripping air. Contaminants in the intra-aggregate pores diffuse through the soil aggregates and are carried away once they reach the interaggregate voids. A rigorous mathematical modeling of the mass transfer process schematically shown in Fig. 4.3 would include application of the diffusion equation within the soil aggregates, as well as a continuity condition that equates the vapor-phase contaminant concentration on the surface of the aggregate and in the inter-aggregate voids. Another more simple approach would be to use a first-order transfer relation between the inter- and intra-aggregate pore concentrations:

$$F_c = \alpha\left(C_a - C_c\right), \tag{4.4}$$

where F_c is the mass flux on the surface of the aggregates, α is a mass transfer coefficient, and C_a and C_c are the inter- and intra-aggregate vapor-phase contaminant concentrations, respectively. This implies that the intra-aggregate pores are assumed to be unsaturated, which is not entirely unreasonable given that the unmixed soil was obtained from the unsaturated zone. In this approach, C_c is assumed to be constant throughout the soil aggregate. The coefficient α can be derived from more fundamental parameters using the following expression:[12]

$$\alpha = \frac{15\varepsilon_c D_{eff}}{r_c^2}, \tag{4.5}$$

where ε_c is the intra-aggregate porosity, D_{eff} is the effective intra-aggregrate gaseous diffusion coefficient, and r_c is the aggregate radius. The use of this expression for the mass transfer coefficient will more closely approximate the rigorous mathematical modeling of diffusion through the aggregates, while avoiding the complexities of solving equations produced by the latter.

When a mass balance to a unit volume of mixed soil is applied, and the first order mass-transfer relationship given in Eq. (4.4), the following kinetic model for mass removal during vapor stripping as a function of time can be derived (see Appendix A):

$$\frac{M}{M_o} = \left(\frac{-\xi_2}{\xi_1 - \xi_2}\right)\exp\left(\xi_1 t\right) + \left(\frac{\xi_1}{\xi_1 - \xi_2}\right)\exp\left(\xi_2 t\right), \tag{4.6}$$

where α and ε_c have been defined before, R_c is the aggregate retardation coefficient, and ξ_1 and ξ_2 are roots of the following equation:

$$\xi^2 + \left(\frac{q}{\varepsilon_s} + \alpha\left(\frac{1}{\varepsilon_s} + \frac{1}{\left(1-\varepsilon_s\right)\varepsilon_c R_c}\right)\right)\xi + \left(\frac{\alpha q}{\left(1-\varepsilon_s\right)\varepsilon_s \varepsilon_c R_c}\right) = 0,$$

where q is the flow rate (in r.v. per unit time), and ε_s is the porosity of the mixed soil (defined as volume of interaggregate voids / volume of mixed soil). The aggregate retardation factor can be determined as follows:

$$R_c = 1 + \frac{\rho_c K_d'}{\varepsilon_c}, \qquad [4.7]$$

where K_d' is the vapor-phase partitioning coefficient, and ρ_c is the dry bulk density of the aggregates (equal to the bulk density of the unmixed soil).

As in Eq. 4.1, Eq. 4.6 may be expressed in terms of dimensionless time τ = number of reactor volumes injected into the soil. However, in contrast to the equilibrium model of Eq. 4.1 and 4.3, the kinetic mass removal rate determined by Eq. 4.6 is not a function of injected reactor volumes of air alone, since the coefficients of the exponential terms in the latter equation are also functions of the flow rate q. Therefore, unlike the equilibrium model, the kinetic model predicts the existence of a threshold flow rate above which no improvements in removal efficiencies can be achieved. This is illustrated in Fig. 4.4 where the treatment time necessary to remove 50% of the contaminant mass ($t_{50\%}$) as predicted by the kinetic model is plotted against the air flow rate, q. At flow rates greater than 0.5 r.v./min, the mass removal becomes "diffusion-controlled", and the treatment efficiency becomes insensitive to q.

The kinetic model described above was used to simulate the removal rates measured in run IA7 (see Fig. 4.5), with model parameters listed in Table 4.3. The same vapor-sorption coefficient, K_d', utilized in the equilibrium model simulation was applied to the kinetic modeling of IA7. The aggregate radius was estimated to be 0.5 cm, and the effective intra-aggregate diffusion coefficient, D_{eff} was adjusted so that the simulated removal rate approximated the measured values (see Fig. 4.5). The same set of parameters except for lower flow rates was used to predict mass removal in C2. Three values for the flow rate were used in order to account for uncertainty in estimating the air flow rate in the open-lysimeter, mixed-only runs. The prediction shown in Fig. 4.6 shows that the kinetic model is better able to simulate the relative removal efficiencies in runs C2 and IA7, particularly the observed insensitivity of mass removal rates to the air flow rate.

The match between the measured removal efficiencies and kinetic model simulations gradually deteriorate with increasing treatment time (see Fig. 4.5 and 4.6). Whereas a removal efficiency of almost 100% at t = 60 minutes is determined by the kinetic models for both runs IA7 and C2, the measured removal efficiencies for both runs are closer to 95%, and the kinetic model is unable to duplicate the "tailing" in measured data.

The kinetic model is also unable to account for the difference in removal rates that was seen between runs C2 and C3. Faster removal rates were determined for C2 which had a higher initial amount of TCE in the soil and shorter equilibration time. This trend can not be predicted by the kinetic model, since the functional form of Eq. 4.6 implies that removal efficiency (= $1 - M/M_0$) is independent of the initial amount of contaminant M_0. The simple kinetic model of Eq. 4.6 has probably not accounted for all mass transfer mechanisms that occur during vapor stripping of mixed, fine-textured soils. For example, "tailing" of breakthrough curves has been simulated previously by using multiple sorption sites with different kinetic characteristics, e.g., two-site models where rapid mass removal is from sites where local equilibrium applies and tailing is a result of mass-transfer from "less available" sites.[16]

Due to lack of soil TCE data *during* treatment, the kinetic model cannot predict the removal efficiencies measured during the intact-core experiments described in Sect. 2. However, the pretreatment levels of VOCs in the intact cores were on the same order as the posttreatment levels of VOCs in the packed cores. Therefore, consistent with results from C3 and the "tailing" observed in IA7, C2, and C3, it is possible that the long treatment times for the intact cores were due to the very low levels of VOCs in the soil.

It is difficult to determine whether the kinetic model can simulate mass removal from the closed lysimeter runs where only pre- and (1-h) posttreatment samples were collected (i.e., HA1, HA2, HA3, IA3, etc). It is possible that tailing in these runs had started earlier than the open lysimeter runs IA7, C2, and C3; for example, removal in the former runs may have been more rapid than the latter. However, since the 1-h removal efficiencies from these cores were approximately the same as the open lysimeter runs, a conservative estimate of removal efficiency as a function of time for the closed lysimeter runs will result from assuming that intermediate removal efficiencies in these cores followed the same trends as the open lysimeter runs.

The similarity in removal efficiency between mixing alone and mixing coupled with air injection should not be interpreted as an indication that air injection is an unnecessary component of vapor stripping. As will be shown in the succeeding section, air injection enhances mass removal when aggregates produced by mixing are small enough such that the vapor-stripping process is no longer diffusion controlled. In addition, the treatment volumes of the intact cores were very shallow (~3 in.),so the interaggregate pathway of the contaminant is very short. For deeper treatment columns (e.g., 15 ft in the field vs 3 in. in the laboratory) where interaggregate pathways for VOC transport are much longer, removal efficiencies can be improved by higher flow rates.

4.4 DISCUSSION OF MODELING RESULTS

4.4.1 Predicting Field-Scale Removal Efficiencies

The kinetic model described previously can be used as a means for estimating field-scale removal efficiencies from laboratory experiments. The flow rate used in the field demonstration ranged from 1000 to 1300 scfm for most of the vapor-stripping treatment columns.[5] Since the volume of soil in a 10-ft diameter, 15-ft deep treatment column is ~1178 ft^3, then between 0.85 and 1.1 r.v./min were injected into each column. Fig. 4.7 shows predictions of mass removal as a function of time for a flow rate of 1 r.v./min, and with estimated aggregate radii of 0.5 and 1.5 cm. The rest of the model parameters were set to values given in Table 4.4. K_d' was set to 0.9 mL/g, the same value used in modeling removal rates in the packed-core experiments. A removal efficiency of 90% (corresponding to a residual mass ratio of 0.1) was achieved after 30 and 240 minutes for estimated aggregate radii of 0.5 and 1.5 cm, respectively. Fig. 4.7 also contains simulations at a lower air flow rate of 0.1 r.v./min. For an aggregate radius of 1.5 cm, vapor-stripping efficiency is not improved significantly by increasing the air flow rate from 0.1 to 1 r.v./minute. For a smaller aggregate size of 0.5 cm, flow rates have a greater impact over removal efficiency. This is not surprising given that VOC intra-aggregate diffusion pathways are longer in large aggregates, and vapor stripping becomes more diffusion controlled as aggregate sizes increase. The simulations shown in Fig. 4.7 also highlight the importance of breaking up the soil matrix during vapor stripping, since a significant improvement in removal efficiencies was calculated by reducing aggregate size.

The kinetic model uses a batch-type (i.e., completely mixed) assumption in simulating mass removal. Therefore, removal efficiencies predicted by the model are insensitive to the length of interaggregate transport pathways or the length of the treatment column. As mentioned previously, higher flow rates will improve removal efficiencies in deeper columns much more than the batch-type kinetic model will predict.

4.4.2 Thermal Enhancement

Early modeling efforts for vapor stripping focussed on modeling the thermal response of soil to steam injection.[14] Thermal enhancement of VOC mass removal during vapor stripping was calculated based on an equilibrium mass removal model similar that given by Eq. 4.1 with temperature-dependent vapor-sorption partition coefficients. According to these early modeling results, steam injection will not produce a significant improvement in VOC mass removal over air injection primarily because treatment times required to remove contaminants from the soil using air injection alone was less than the time it took for the steam to heat up the soil. However, treatment times under isothermal air injection may have been grossly underestimated, in light of the results presented in Sect. 3 as well as modeling described in preceding subsections. For example, the equilibrium model would have predicted a treatment time of ~2 min for contaminant mass to be reduced to 10% of its initial value at a stripping air flow rate of 17 r.v./min using a $K_d' = 10$ ml/g. The latter value of K_d' was used in the early simulations.[14] Results from IA7 clearly show that more than 2 min was required to achieve a removal efficiency of 90%.

The kinetic model of Eq. 4.6 may be used as a basis for determining improvements due to thermal enhancements by using temperature dependent parameters such as K_d' and D_{eff}. Temperature measurements from the intact core experiments described in Sect. 2 did not indicate effective soil heating through heated-air injection. Therefore, it is difficult to assess using the kinetic model alone, whether or not heated air resulted in improved removal efficiencies.

Table 4.1. Model parameters fitted to removal rates measured in run IA7

Model Parameter	Value
ε_t, mixed soil porosity	0.3
ρ_t, dry density of mixed soil	1.6 g/mL
K_d', vapor sorption partition coefficient	0.9 mL/g
q, air flow rate	17.4 r.v./min

Table 4.2. Equilibrium model parameters used to predict removal rates measured in run C2

Model Parameter	Value
ε_t, mixed soil porosity	0.3
ρ_t, dry density of mixed soil	1.6 g/mL
K_d', vapor sorption partition coefficient	0.9 mL/g
q, air flow rate	0.1, 0.5, 1 r.v./min

Table 4.3 Kinetic model parameters used to model removal rates measured in run IA7 (ambient-air vapor stripping and mixing)

Model Parameter	Value
ε_c, intra-aggregate porosity	0.3
ε_s, inter-aggregate porosity	0.2
ρ_c, dry density of unmixed soil	1.8 g/mL
K_d', vapor sorption partition coefficient	0.9 mL/g
D_{eff}, intra-aggregate effective vapor phase diffusion coefficient	0.008 cm^2/min
r_c, aggregate radius	0.5 cm
q, air flow rate	17.4 r.v./min

Table 4.4 Kinetic model parameters used to predict removal rates measured in run C2 (mixing only)

Model Parameter	Value
ε_c, intra-aggregate porosity	0.3
ε_s, inter-aggregate porosity	0.2
ρ_c, dry density of unmixed soil	1.8 g/mL
K_d', vapor sorption partition coefficient	0.9 ml/g
D_{eff}, intra-aggregate effective vapor phase diffusion coefficient	0.008 cm^2/min
r_c, aggregate radius	0.5 cm
q, air flow rate	0.1, 0.5, 1 r.v./minute

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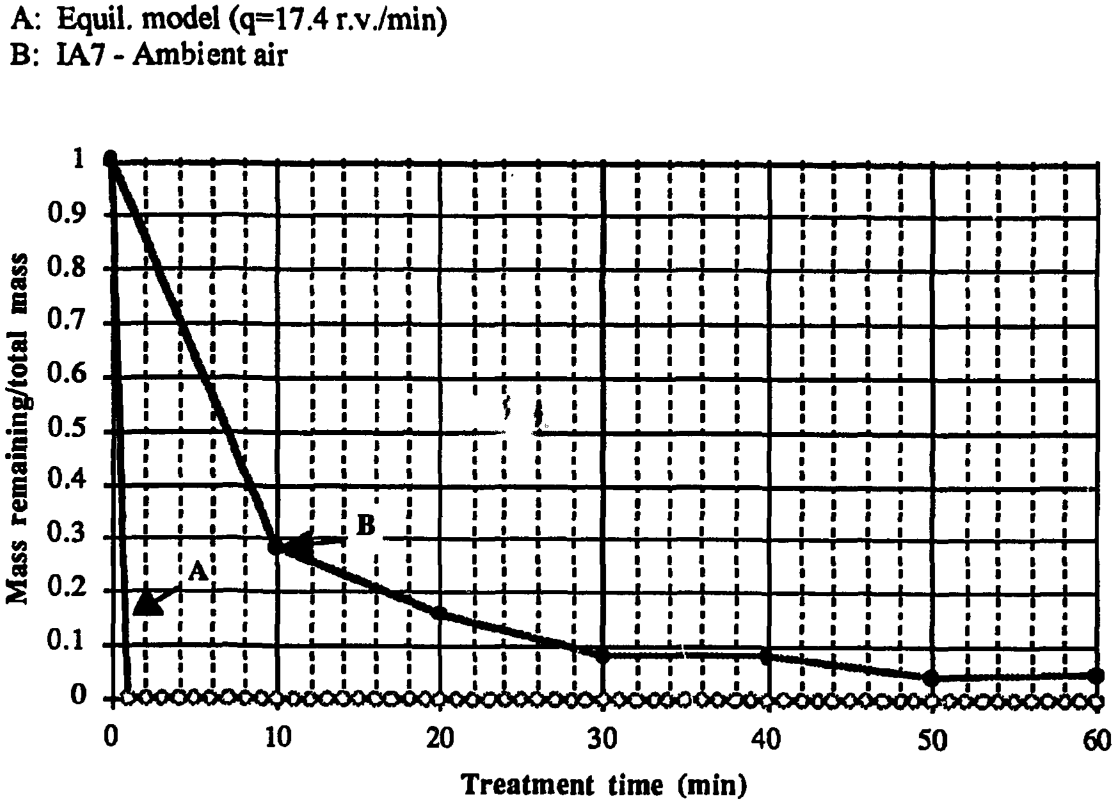

Figure 4.1. Measured versus modeled mass removal rates using the equilibrium model for run IA7 (ambient-air vapor stripping and mixing).

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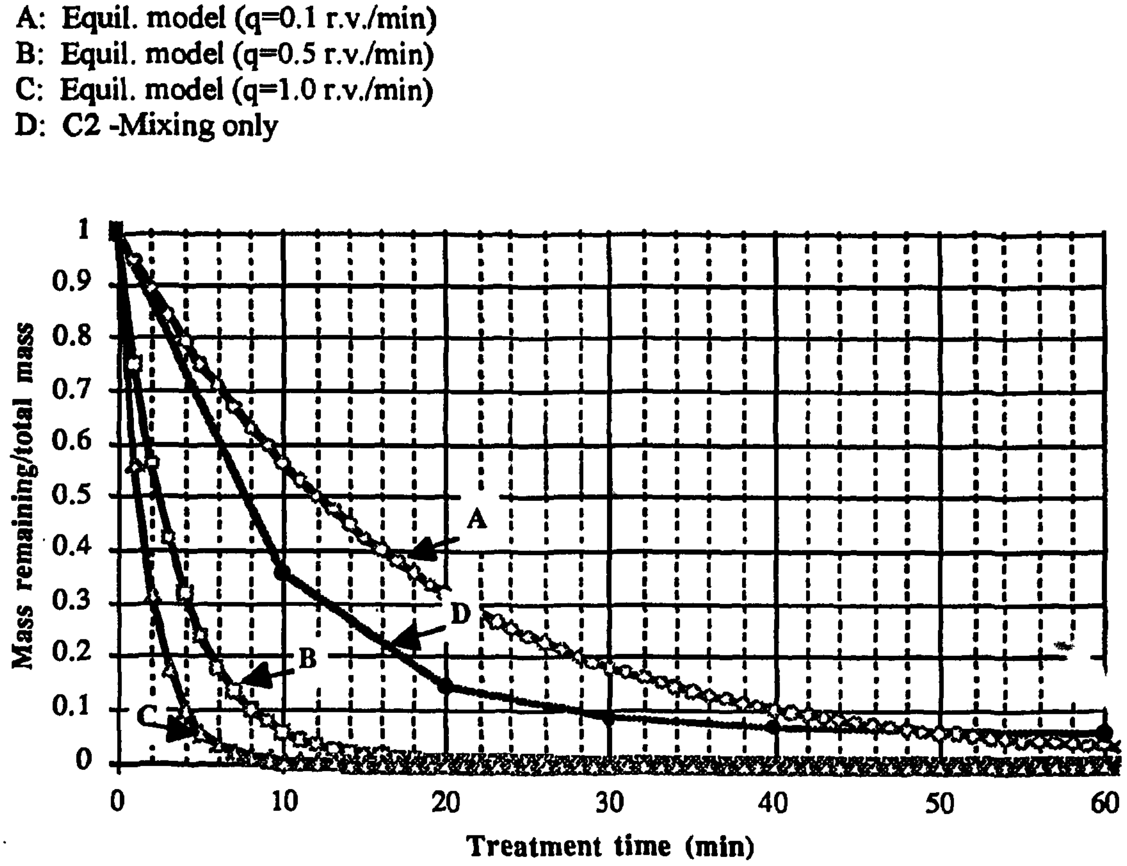

Figure 4.2. Measured versus predicted mass removal rates using the equilibrium model for run C2 (mixing only). Predictions based on Kd' = 0.9 ml/g.

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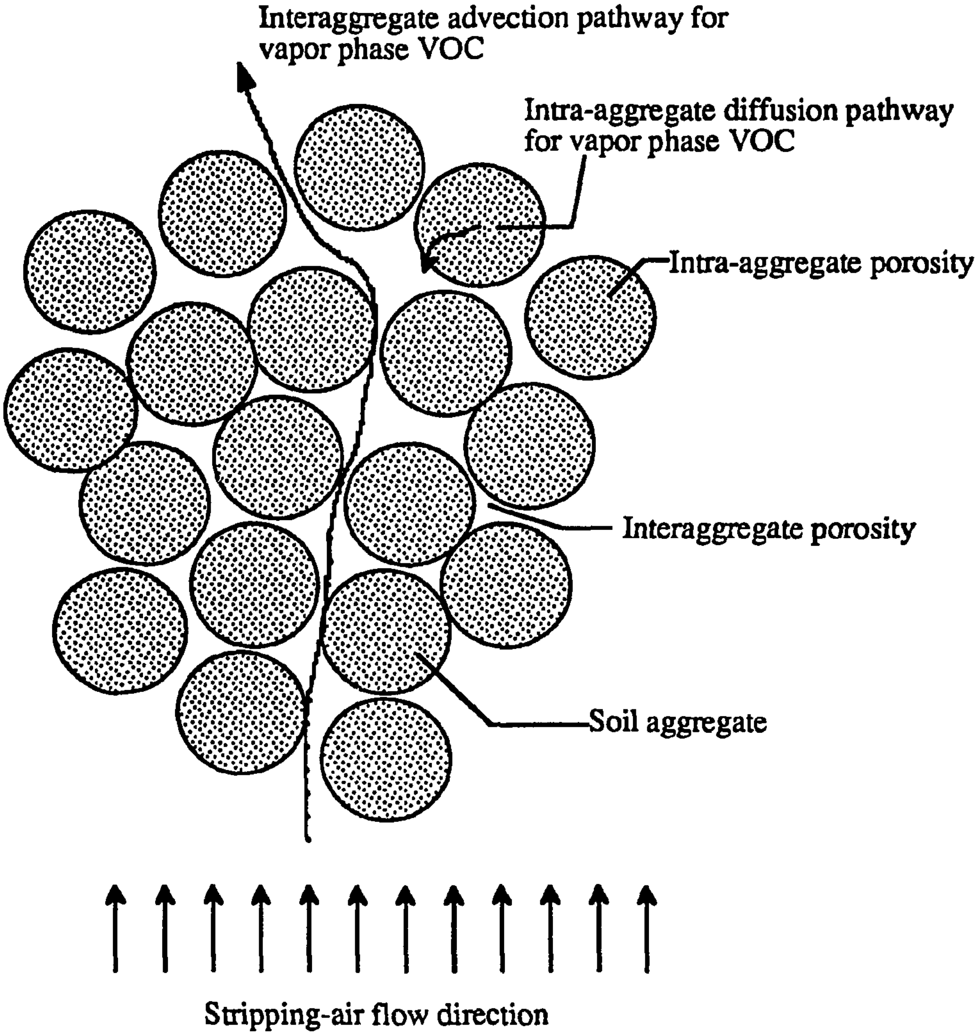

Figure 4.3. Pathways for VOC transport in mixed, fine-textured soils during vapor stripping.

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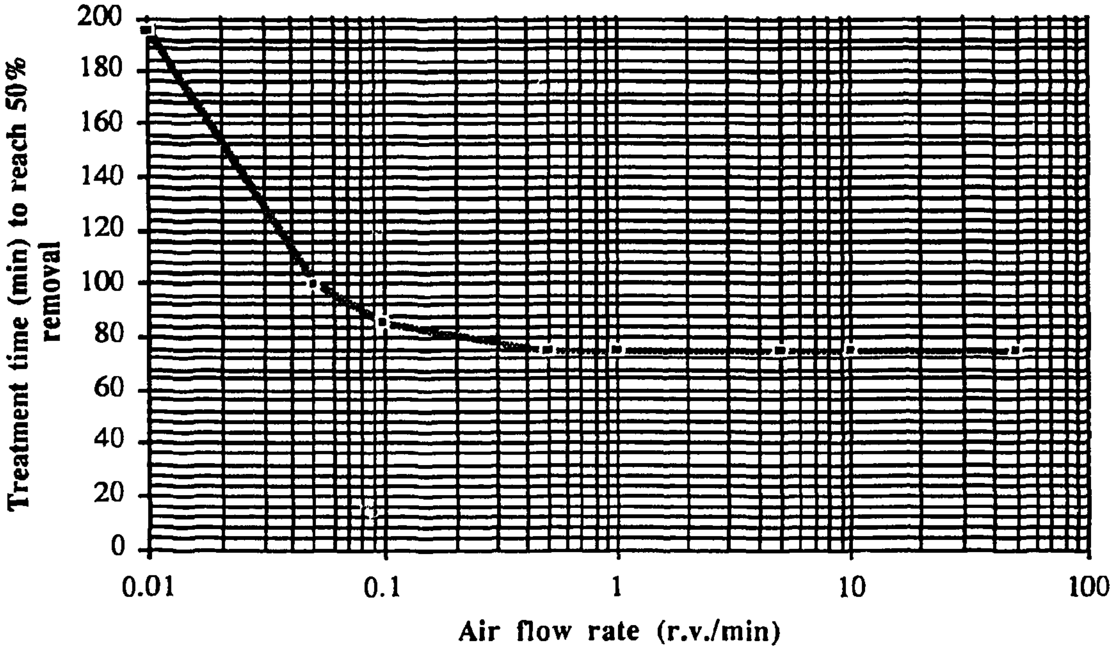

Figure 4.4. Treatment time to reach 50% removal versus air flow rate as predicted by the kinetic model. Treatment time is unaffected by increased air flow rate when q > 0.5 r.v./min.

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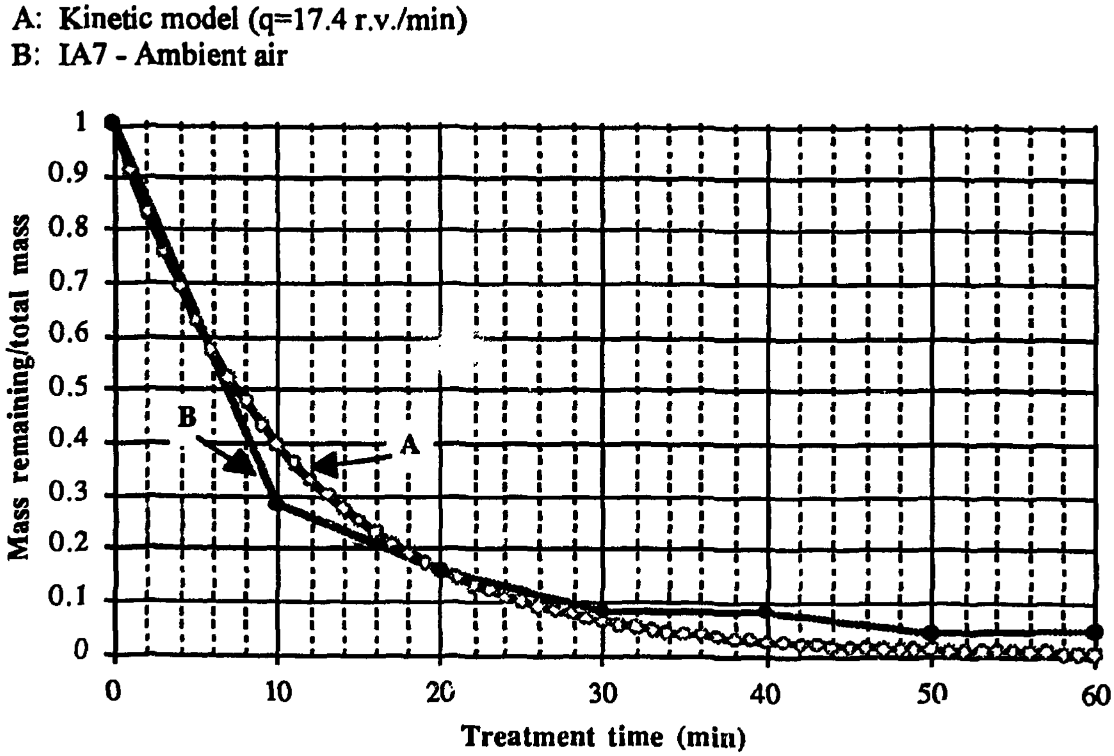

Figure 4.5. Measured versus predicted mass removal rates using the kinetic model for run IA7 (ambient-air vapor stripping).

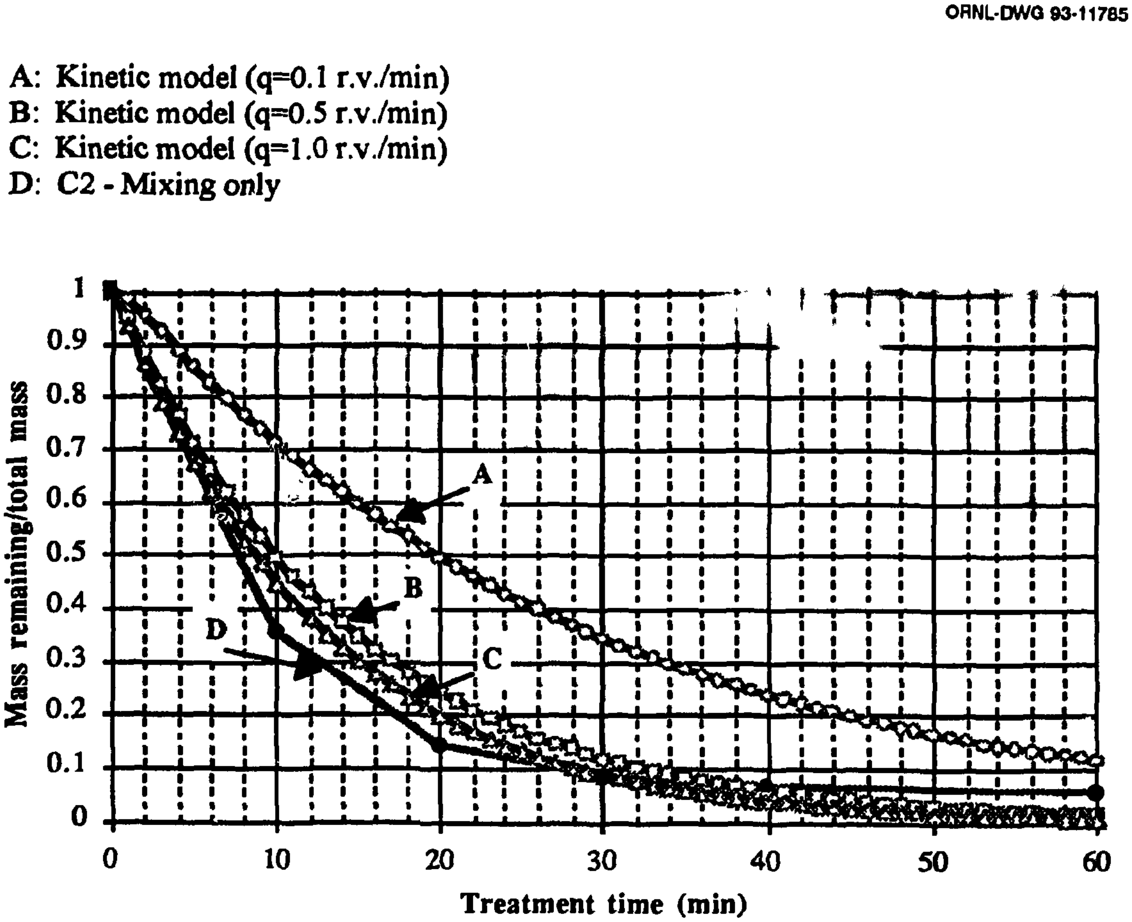

Figure 4.6. Measured versus predicted mass removal rates using the kinetic model for run C2 (mixing only).

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A: q = 1 r.v./minute, r_c = 1.5 cm
B: q = 0.1 r.v./minute, r_c = 1.5 cm
C: q = 1 r.v./minute, r_c = 0.5 cm
D: q = 0.1 r.v./minute, r_c = 0.5 cm

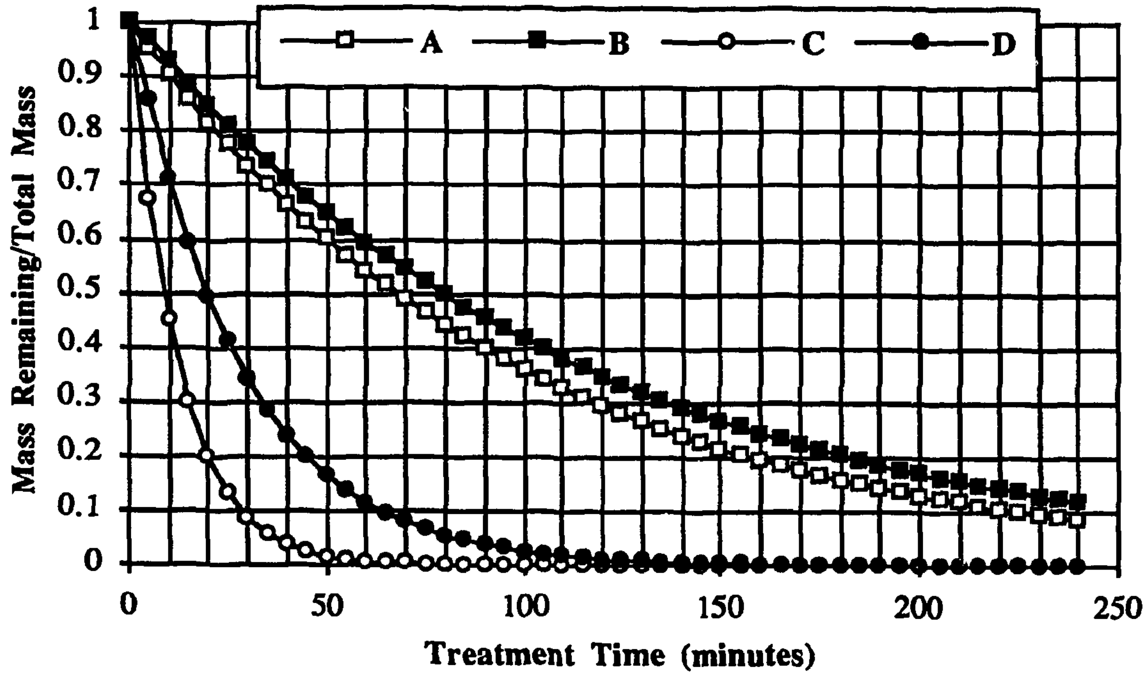

Figure 4.7. Predicted field mass removal rates for different sets of flow rates and estimated aggregate radii using a kinetic mass transfer mode! D_{eff} = 0.008 cm²/minute

5. CONCLUSIONS

The treatability studies described in this report were conducted to assess the feasibility of vapor stripping coupled with soil mixing as a means for removing VOCs from fine-textured soils such as those that underlie the PORTS X-231B Unit. These experiments and subsequent modeling of collected data led to the following conclusions:

1. Mixing of large intact cores collected from the PORTS X-231B Unit resulted in soil that was more granular in appearance. The soil structure adjacent to but outside of the treatment region was minimally affected by mixing.

2. Vapor stripping and mixing of large intact cores collected from the PORTS X-231B Unit achieved low levels of VOCs in the soil, provided that treatment time was sufficient. Monitoring the off-gas VOC concentration was not successfully used for treatment process control. However, this may have been due mainly to experimental difficulties.

3. Small cores packed with clean soil from PORTS X-231B Unit and spiked with known amounts of TCE were successfully treated using vapor stripping and mixing, as well as using mixing alone. Removal efficiencies after 1-h of treatment by mixing and air injection at 17.4 r.v./min and by mixing alone were between 64 and 98%, and most treatment efficiencies were >85%.

4. There was only a slight indication that vapor stripping with heated air resulted in improved removal efficiencies.

5. Removal efficiency as a function of time was quantified by sampling a subset of the small packed cores during treatment. Measured trends between vapor stripping and mixing, and mixing alone were very similar. This observation was successfully simulated using a kinetic mass transfer model that incorporated contaminant diffusion through soil aggregates.

6. Tailing at a residual level of 100 μg/kg or less was observed in packed cores that were sampled during treatment. The residual TCE levels for all the cores appeared to be independent of the initial TCE level.

7. The kinetic model was used to extrapolate field-scale performance of vapor stripping from measured laboratory removal efficiencies. With flow rates used in the field demonstration, 90% removal can be achieved in 240 min if the aggregate size is 1.5 cm. This level of removal can be achieved within 30 min if the aggregate size is reduced to 0.5 cm, which highlights the importance of physical disruption in vapor stripping of fine-textured soils.

8. With larger aggregate sizes, the kinetic model predicts that vapor stripping becomes diffusion controlled and removal efficiency is not improved significantly with increasing flow rates. However, since the kinetic model neglects the effects of interaggregate transport pathways on mass removal, it probably underestimates the benefits of higher flow rates for treating deep soil columns (e.g., 15 ft) in vapor stripping under field conditions.

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APPENDIX A: FORMULATION OF MASS TRANSFER MODELS

A. FORMULATION OF MASS TRANSFER MODELS

A.1 EQUILIBRIUM MASS TRANSFER MODEL

The equilibrium model for mass removal is based on the assumption that volatile organic compound (VOC) concentrations in the vapor and sorbed phases are always in equilibrium; for example, it is assumed that mass transfer between the two phases occurs instantaneously. Consider a unit volume of mixed soil with an air-filled porosity of ε_t. Let C_a = VOC concentration in the vapor phase, and S = VOC concentration in the sorbed phase expressed in terms of mass of sorbed phase VOC per unit mass of dry soil. The equilibrium assumption dictates that C_a and S are related by the following equation:

$$S = K_d' C_a, \qquad [A.1]$$

where K_d' is the vapor-phase partitioning coefficient. Following Ong and Lion (1991)[13], S includes mass that is directly sorbed onto the soil, as well as mass that is dissolved in the pore water.

A mass balance in a unit volume of mixed soil will result in the following equation:

$$-qC_a = \frac{d(C_a\varepsilon_t)}{dt} + \frac{d(\rho_t S)}{dt}, \qquad [A.2]$$

where q = air flow rate per unit volume of mixed soil (in reactor volumes/unit time), ε_t and ρ_t are the air-filled porosity and dry density of the mixed soil, respectively. Substituting Eq. A.1 into Eq. A.2, the latter is reduced to a single-variable differential equation:

$$-qC_a = \varepsilon_t\left(1 + \frac{\rho_t K_d'}{\varepsilon_t}\right)\frac{dC_a}{dt}. \qquad [A.3]$$

Defining R as the term in parenthesis in the above equation, the solution to Eq. A.3 is given by the following

$$\frac{C_a}{C_{ao}} = \exp\left(-\frac{qt}{\varepsilon_t R}\right), \qquad [A.4]$$

where C_{ao} = initial vapor-phase concentration. Given that the total VOC mass per unit volume of soil is:

$$M = \varepsilon_t C_a + \rho_t S = C_a \varepsilon_t R, \tag{A.5}$$

then the residual mass ratio M/M_o is given by

$$\frac{M}{M_o} = \exp\left(-\frac{qt}{\varepsilon_t R}\right), \tag{A.6}$$

where M_o is the initial mass of VOC in the soil.

A.2 KINETIC MODEL FOR MASS REMOVAL

The kinetic model for mass removal formulated below is based on the conceptual model of mixed soil shown in Fig. 4.3. Let C_a and C_c be the interaggregate and intra-aggregate VOC vapor-phase concentrations, respectively. Let S be the VOC mass per dry unit mass of soil that is sorbed onto the soil within the aggregates. As in Sect. A.1, S includes VOC mass that is sorbed onto the soil as well as dissolved in the intra-aggregate pore water.

Applying a mass balance to the interaggregate pores of a unit volume of mixed soil, the following equation is arrived at

$$\frac{d(\varepsilon_s C_a)}{dt} = -qC_a + \alpha(C_c - C_a), \tag{A.7}$$

where q is the air flow rate per unit volume of mixed soil (in reactor volumes per unit time), ε_s is the interaggregate air-filled porosity of the mixed soil, and α is a mass transfer coefficient which defines the mass transfer rate between the inter- and intra-aggregate voids. Note that the formulation of Eq. A.7 assumes that the VOC is no longer sorbed or retarded once it reaches the interaggregate pores. This is not unreasonable for conditions in which diffusion within the aggregates dominates the mass transfer process.

When a mass balance is applied to the aggregates in a unit volume of mixed soil, the following equation is arrived at

$$(1-\varepsilon_s)\left[\frac{d(\varepsilon_c C_c)}{dt} + \frac{d(\rho_c S)}{dt}\right] = -\alpha(C_c - C_a), \tag{A.8}$$

where ε_c is the intra-aggregate porosity (also equal to the porosity of the unmixed soil), and ρ_c is the dry density of the aggregates (also equal to the dry density of the unmixed soil). Assuming local equilibrium within the aggregates, Eq. A.1 can be applied to Eq. A.8 as follows

$$(1-\varepsilon_s)\varepsilon_c R_c \frac{dC_c}{dt} = -\alpha\left(C_c - C_a\right), \qquad [A.9]$$

where R_c is defined by

$$R_c = 1 + \frac{\rho_c K_d'}{\varepsilon_c}. \qquad [A.10]$$

The term R in Eq. A.4 is different from R_c because properties of the aggregates (or unmixed soil) are used in the latter.

The solutions to the coupled Eqs. A.7 and A.9 can be derived analytically following methods described in Hildebrand (1976).[16] By applying the initial conditions $C_a(0) = C_c(0) = C_{ao}$, the following equation for C_c is arrived at

$$\frac{C_c}{C_{ao}} = \left(\frac{-\xi_2}{\xi_1 - \xi_2}\right)\exp(\xi_1 t) + \left(\frac{\xi_1}{\xi_1 - \xi_2}\right)\exp(\xi_2 t), \qquad [A.11]$$

where ξ_1 and ξ_2 are roots of the following equation:

$$\xi^2 + \left(\frac{q}{\varepsilon_s} + \alpha\left(\frac{1}{\varepsilon_s} + \frac{1}{(1-\varepsilon_s)\varepsilon_c R_c}\right)\right)\xi + \left(\frac{\alpha q}{(1-\varepsilon_s)\varepsilon_s \varepsilon_c R_c}\right) = 0.$$

Since equilibrium was assumed within the aggregates and using the same argument in arriving at Eq. A.6, M/M_0 is equal to C_c/C_{ao}, and Eq. A.11 can be used to determine the residual mass ratio.

The kinetic model defined by Eq. A.11 assumes that only the vapor-phase VOCs are mobile, and intra-aggregate pores are not completely saturated.

APPENDIX B. ADDITIONAL PACKED-CORE EXPERIMENTS

APPENDIX B. ADDITIONAL PACKED CORE EXPERIMENTS

Four additional packed cores were treated by mixing and vapor stripping with ambient air in open lysimeters under operating conditions similar to run IA7 described in Sect. 3. These supplementary runs were performed in order to observe the effects of a lower spiking level (IA8 and IA9), a higher spiking level (IA10) and longer equilibration time (IA11) on mixing/vapor stripping treatment efficiencies. Characteristics of these runs as well as average pretreatment TCE levels in the packed cores are summarized in Table B.1.

The treatment efficiencies for each of the supplementary runs are plotted against treatment time in Fig. B.1. Treatment efficiencies among the cores were not significantly different from each other or from the treatment efficiency measured in IA7. The results from IA8, IA9 and IA11 indicate that pretreatment TCE levels do not affect treatment efficiency. The slower removal rate during the first 20 minutes of treatment in IA11 may be an effect of the longer equilibration time, however, the final removal efficiency achieved in IA11 after 60 minutes of treatment is the same as the rest of the runs.

Table B.1 Characteristics of supplementary packed core experiments

Run[a]	TCE concentration of spiking solution (mg/L)[b]	Ave. initial TCE in soil (ug/kg)	Equilibration time (h)
IA8	78	345	~2 h
IA9	78	645	~2 h
IA10	374	2533	~2 h
IA11	234	746	~15 h

[a] All cores were mixed and vapor-stripped with ambient air in open lysimeters. Air flow rate was equal to 0.6 cfm for all runs.

[b] Spiking solution used in cores described in Sect. 3 had a TCE concentration of 234 mg/L.

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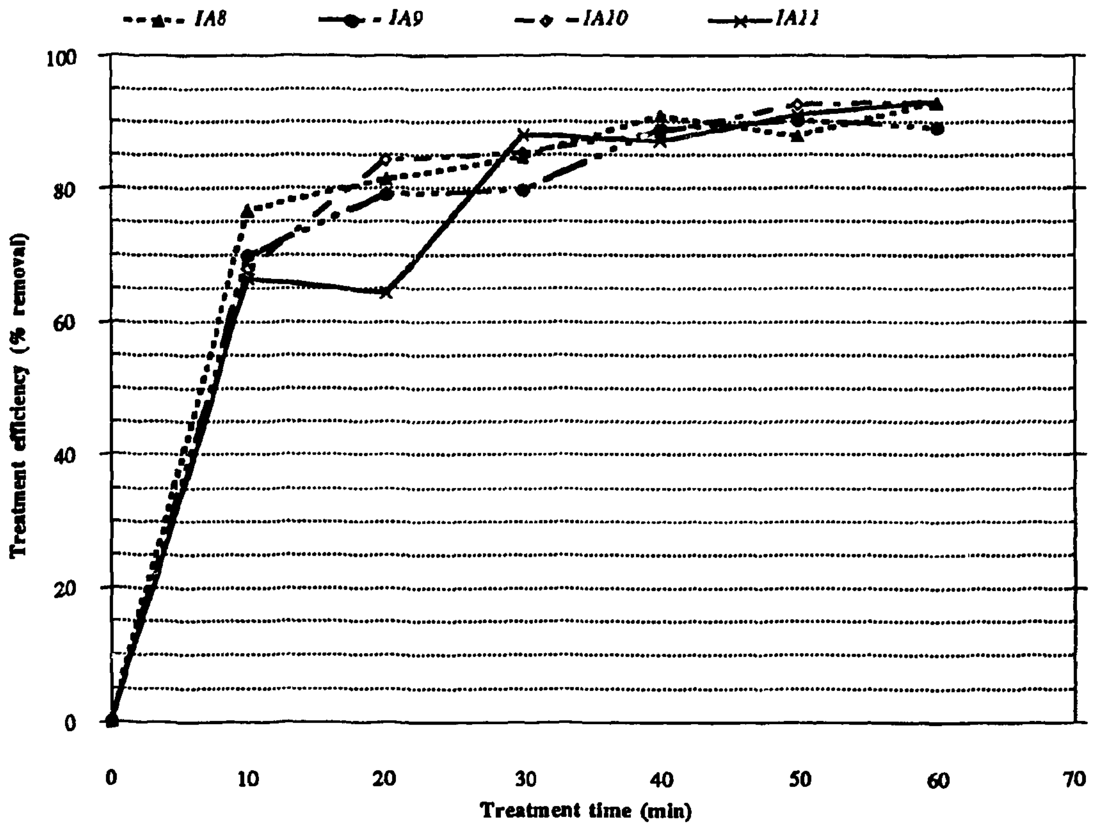

Figure B.1. Treatment efficiencies for mixing/ambient-air vapor stripping runs IA8, IA9, IA10, IA11. All runs were performed in open lysimeters. Packed cores in IA8 and IA9 were spiked at lower levels of TCE compared to packed cores described in Sect. 3. Packed core in IA10 was spiked at a higher level of TCE. Packed core in IA11 was equilibrated for 15 hours.

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