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OPTIMIZATION OF SOIL MIXING TECHNOLOGY THROUGH METALLIC IRON ADDITION*

by

Lawrence P. Moos
Environment, Safety and Health
Argonne National Laboratory-East
9700 South Cass Avenue
Argonne, Illinois 60439

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DISCLAIMER

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NOTATION

The following is a list of the acronyms, initialisms, and abbreviations (including units of measure) used in this document. Some acronyms used in tables or equations only are defined in the respective tables or equations.

ACRONYMS, INITIALISMS, AND ABBREVIATIONS

ANL-E	Argonne National Laboratory-East
bgs	below ground surface
CO_2	carbon dioxide
DO	dissolved oxygen
DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
HEPA	high-efficiency particulate air (filter)
ISF	In-Situ Fixation
ORP	oxidation reduction potential
OVA	organic vapor analyzer
PLFA	phospholipid fatty acid
RCRA	Resource Conservation and Recovery Act
RFI	RCRA Facility Investigation
SM/TESVE	soil mixing with thermally enhanced soil vapor extraction
SVOC	semivolatile organic compound
TKN	total kjeldahl nitrogen
VOC	volatile organic compound
XRF	x-ray fluorescent analyzer

UNITS OF MEASURE

°C	degree(s) Celsius
cm	centimeter(s)
eV	electron volt(s)
°F	degree(s) Fahrenheit
ft	foot (feet)
ft^2	square foot (feet)
in.	inch(es)
kg	kilogram(s)
kv	kilovolt
L	liter(s)
m	meter(s)
µg	microgram(s)
mg	milligram(s)
min	minute(s)
mL	milliliter(s)
oz	ounce(s)
pmol	picomole(s)
ppm	part(s) per million
ppmv	part(s) per million (volume)
rpm	revolution(s) per minute
s	second(s)

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SUMMARY

Enhanced soil mixing is a process used to remove volatile organic compounds (VOCs) from soil. In this process, also known as soil mixing with thermally enhanced soil vapor extraction, or SM/TESVE, a soil mixing apparatus breaks up and mixes a column of soil up to 9 m (30 ft) deep; simultaneously, hot air is blown through the soil. The hot air carries the VOCs to the surface where they are collected and safely disposed of. This technology is cost effective at high VOC concentrations, but it becomes cost prohibitive at low concentrations. Argonne National Laboratory-East conducted a project to evaluate ways of improving the effectiveness of this system.

The project investigated the feasibility of integrating the SM/TESVE process with three soil treatment processes — soil vapor extraction, augmented indigenous biodegradation, and zero-valent iron addition. Each of these technologies was considered a polishing treatment designed to remove the contaminants left behind by enhanced soil mixing. The experiment was designed to determine if the overall VOC removal effectiveness and cost-effectiveness of the SM/TESVE process could be improved by integrating this approach with one of the polishing treatment systems.

Three experimental areas and one control area were first treated with the SM/TESVE soil process. The polishing treatment technologies were then deployed in the mixed soil. The soil vapor extraction system was deployed by installing two slotted vertical pipes into the mixed area. A vacuum system then pulled air through the mixed soil, thereby removing contaminants. The biodegradation experiment was implemented by injecting bionutrients and a supplemental carbon source (methanol) into the treated area with the soil mixing equipment. The iron-addition experiment was deployed by injecting a water slurry containing metallic iron particles (<50 mesh particle size)

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into the soil with the soil mixing equipment. The effects of the three polishing treatment systems on VOCs were then monitored for up to 90 days.

Monitoring of VOC concentrations in the soil vapor extraction and biodegradation areas indicated that these technologies had no discernable effect on contaminant levels. The iron particles, on the other hand, resulted in rapid reduction of chlorinated VOC concentrations. Within two weeks of the addition of iron, the residual concentrations of carbon tetrachloride, chloroform, 1,2-dichloroethene, and trichloroethene decreased to below analytical detection limits (<100 μg/kg). Chloride concentrations increased, which indicated that chlorine atoms were removed from the contaminants, thereby resulting in less toxic materials. Nonchlorinated volatile organics were not affected by the iron as much as the chlorinated organics. Several follow-up experiments were performed that verified the effectiveness of the iron-addition process. Integrating the iron addition into the soil mixing operation improved the cost-effectiveness of the enhanced soil mixing process.

INTRODUCTION

The 317 Area of Argonne National Laboratory-East (ANL-E) is an active radioactive waste staging area. During the 1950s, this area was used for the disposal of various liquid chemical wastes. The liquids were placed into one or more units called French drains, which consisted of gravel-filled trenches or similar structures into which the chemical waste was poured. An undetermined amount of liquid chemical waste was placed in these units. As a consequence of this past practice, organic chemicals were detected in the soil and groundwater beneath the 317 Area.

In late 1997, ANL-E began removing the organic contaminants from the soil near the original French drain sites. Because the soil at the ANL-E site consists of highly impermeable clay, common techniques for removing the contaminants, such as soil vapor extraction, would not have been effective. After evaluating numerous technologies, ANL-E chose to use a process known as soil mixing with thermally enhanced soil vapor extraction (SM/TESVE).

The SM/TESVE process utilizes a soil mixing apparatus, a hydraulically powered auger-like assembly, to break up and mix a column of soil up to 9 m (30 ft) deep. At the same time the soil mixing is occurring, a mixture of steam and hot air is pumped down the hollow stem of the auger assembly where it exits at the tip of the auger. The steam and hot air cause the volatile organic compounds (VOCs) in the soil to diffuse into the air stream where they are carried to the surface. The off-gas is then captured and treated in an off-gas treatment system.

Treatability studies of this technology for ANL-E were performed by Kiber Environmental Services, Inc., of Atlanta, Georgia, in 1996 (Kiber 1997). These studies indicated that the SM/TESVE process could economically remove approximately 70 to 80% of the VOCs present at the 317 Area. However, the initial contaminant concentrations were high enough that over 95% removal of VOCs was necessary to meet cleanup objectives. To achieve this further removal, ANL-E proposed the use of polishing treatment in addition to SM/TESVE. Several soil treatment processes were evaluated to determine their suitability as a polishing step. The intent of this evaluation was to compare several viable polishing treatment systems that would be integrated with the SM/TESVE process to optimize the cost-effectiveness of this approach. On the basis of results of the initial treatability studies, three polishing techniques — soil ventilation, augmented indigenous biodegradation, and metallic iron addition — were selected for a field trial. The field trial indicated that the addition of metallic iron was by far the most effective treatment technique of the three tested. Four additional short-term follow-up studies were conducted to verify the results of the initial iron experiment and to explore various ways in which the iron addition could be integrated with the SM/TESVE process. This report describes the results of these field trials.

Following completion of the field trials, the zero-valent iron polishing technique was utilized during the full-scale remedial action rather than the conventional soil vapor extraction (soil ventilation) that had originally been proposed. This change in the treatment approach resulted in a significant improvement in treatment effectiveness; the residual VOC concentrations were reduced by more than a factor of 10, as compared with the SM/TESVE process alone.

2 PROJECT BACKGROUND

2.1 SITE BACKGROUND INFORMATION

The 317 Area contains a small waste-processing building (Baler Building), two in-ground radioactive waste storage vaults (North Vault and Deep Vault), and a storage area for containers of radioactive and hazardous waste (Mixed Waste Storage Pad). Four former storage structures (Map Tube Vault, and Southwest, South Middle, and Southeast Vaults), which have been decontaminated and demolished, were also present in the area. The northern half of the area has been used extensively for aboveground storage of containers of radioactive waste. Figure 2.1 shows the current layout of the 317 Area.

The French drains were actively used from the mid to late 1950s and possibly into the early 1960s. No documentation is available on the amount or types of wastes placed in this unit. The locations and configurations of the former French drains are not well documented. It appears that at least one drain was constructed along a gravel-filled former drainage ditch. Liquid wastes were poured into the gravel where they then soaked into the underlying soil. This unit is thought to have been located north or northwest of the North Vault. A second unit, which appears to have consisted of two small tanks that may have drained into an open pipe driven into the soil, existed on the eastern side of the 317 Area, northeast of the Deep Vault.

2.2 SITE GEOLOGY

The soil underlying the 317 Area consists of a mixture of glacially deposited clays, sand, and gravel and is approximately 21 m (70 ft) thick. This soil overlies weathered dolomite bedrock. The glacial till material consists primarily of dense clay with interbedded layers of silt, sand, and gravel. The silt, sand, and gravel layers are thought to be typically discontinuous, but in many cases, could be interconnected to varying degrees. Measurement of the clay layers indicated a hydraulic conductivity of approximately 1×10^{-8} cm/s. This very low permeability greatly impedes the movement of water through the soil. Downward movement of groundwater is thought to occur through a series of microfractures and cracks in the clay layers. There is some evidence of a fairly contiguous layer of saturated sand and gravel approximately 6 to 8 m (20–25 ft) deep in the French Drain area. The groundwater present in this and other sand and gravel zones above the dolomite appears to be perched and is not hydraulically connected to underlying saturated zones.

The first truly contiguous aquifer is located in the upper portion of the dolomite bedrock. This layer lies approximately 21 m (70 ft) below the surface. Thus far, it has not been affected by the VOCs present in the overlying soil and perched groundwater.

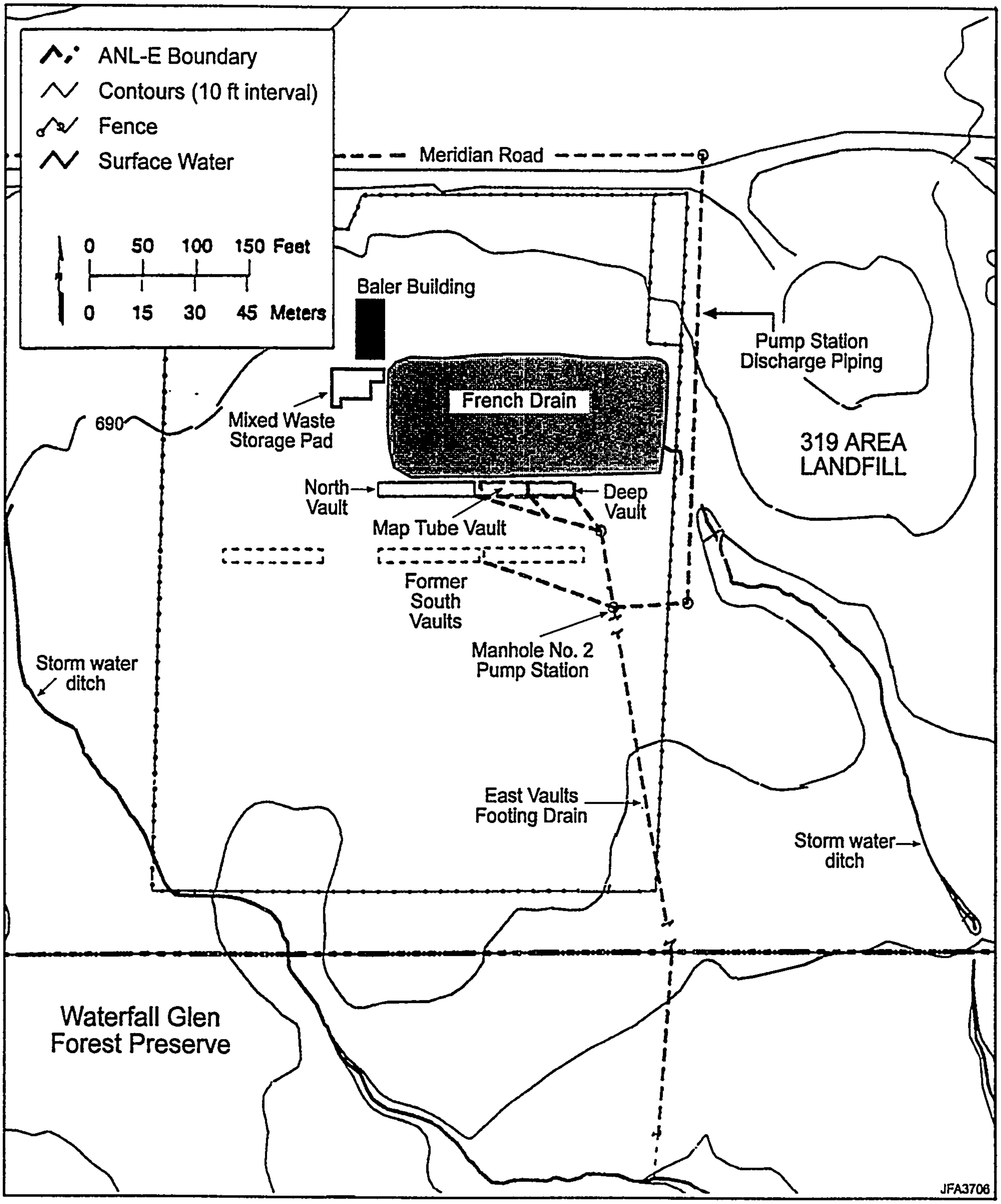


FIGURE 2.1 Location of the 317 Area French Drain and Adjoining Units

2.3 DESCRIPTION OF CONTAMINATION

The nature and extent of contamination in the 317 French Drain area have been studied extensively since 1990. Figure 2.2 shows the distribution of total VOCs within the 317 Area. The results of the various investigations indicate that soil contamination extends from the surface to a depth of approximately 9 m (30 ft). The area used for the field studies, experimental area A, is situated approximately 5 m (15 ft) north of the North Vault.

Contaminants detected in this area were almost exclusively VOCs. Only one semivolatile organic compound (SVOC), nitrobenzene, was detected in significant concentrations in this area. Table 2.1 shows the principal contaminants detected and the maximum concentration present in the soil in the test area prior to the start of the experiments.

Because of the multiple release points and highly heterogeneous nature of the soil, the distribution of contaminants is also highly heterogeneous. Contaminant concentrations were found to vary by orders of magnitude within a few inches of vertical or horizontal distance. The mixture of contaminants at a given location also varied greatly.

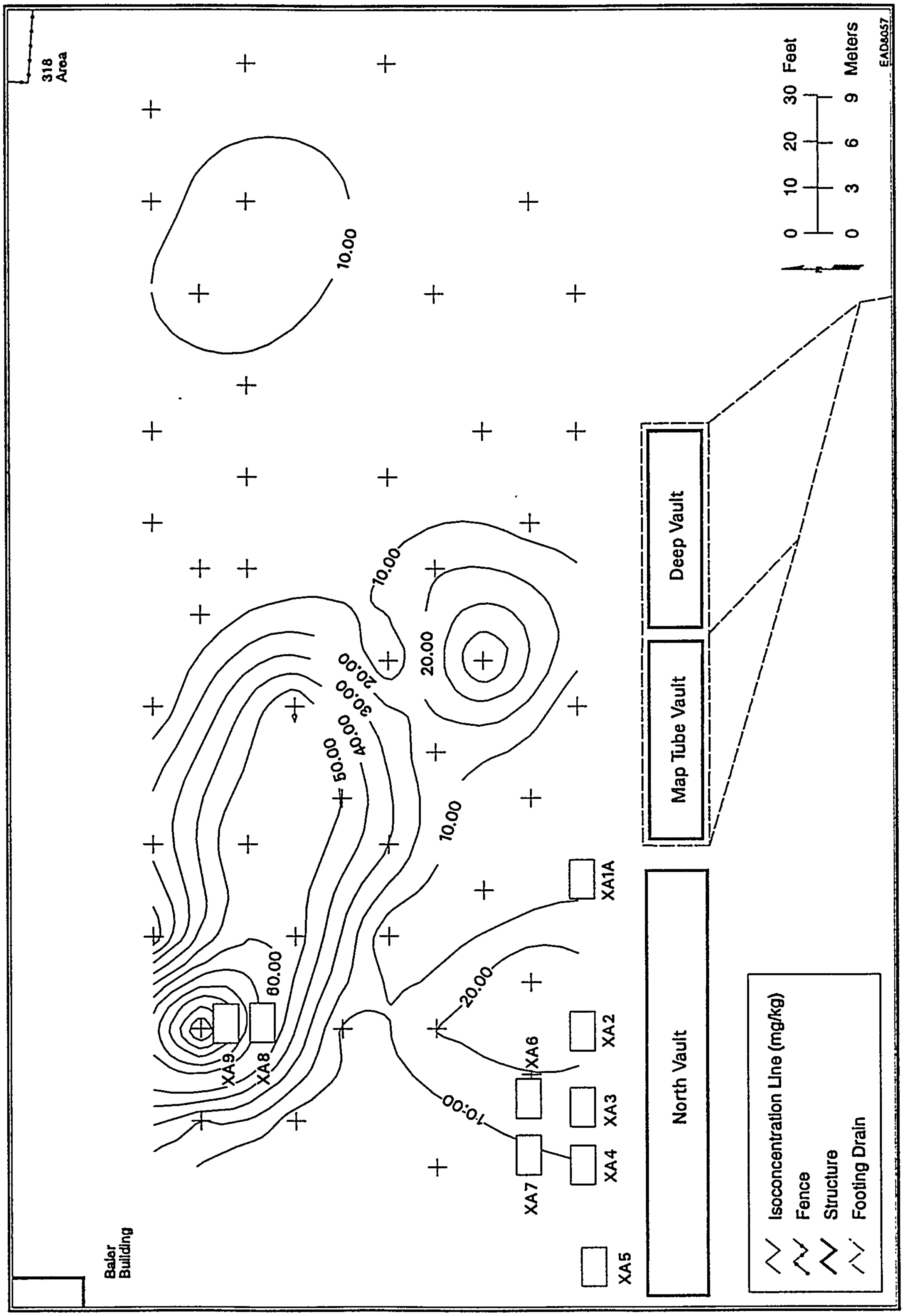


FIGURE 2.2 Average VOC Concentrations in the Area of the 317 French Drain

TABLE 2.1 Highest Concentrations of Principal Contaminants Detected in Experimental Area A

Constituent	Concentration (μg/kg)
Acetone	3,300
Benzene	19,000
Carbon disulfide	450
Carbon tetrachloride	180,000
Chlorobenzene	190
Chloroform	51,000
1,2-Dichloroethene (total)	3,200
Ethyl benzene	2,600
Isobutyl alcohol	39,000
4-Methyl 2-pentanone	8,000
Methylene chloride	3,000
Tetrachloroethene	71,000
Toluene	4,400
1,1,1-Trichloroethane	110
Trichloroethene	180,000
Xylene (total)	37,000

3 PROJECT DESCRIPTION

3.1 TECHNOLOGY SELECTION

The soil treatment method used for the full-scale remediation project, SM/TESVE, was selected because of its capability to remove contaminants from highly impermeable clay soil without the need to excavate and treat the soil above ground. It also has the capability of removing a wide spectrum of organic constituents from the soil. The process utilizes a pair of augers, approximately 2 m (5½ ft) in diameter, that counter rotate at approximately 5 rpm as they move into the soil. The augers break up the soil, while a mixture of steam and hot air is simultaneously injected into the ground near the tips of the augers. The steam condenses on the soil, thereby heating the soil and associated contaminants. The hot air moves up the mixed soil column and carries away organic constituents that diffuse out of the soil and groundwater. The off-gas is treated in an activated-carbon absorption system prior to discharge to the atmosphere. Figure 3.1 is a process schematic of this system. Figures 3.2 through 3.4 are photographs of the equipment in use during this project.

Use of the SM/TESVE process is limited in that it cannot economically remove low concentrations of contaminants or produce low residual concentrations. The laboratory-scale treatability studies conducted by Kiber Environmental Services, Inc., of Atlanta, Georgia, in 1996 (Kiber 1997) indicated that contaminant removal in the range of 70 to 80% was feasible with this technology. This degree of treatment would leave 20 to 30% of the original contaminant mass in the soil, which would result in exceeding the proposed cleanup objectives determined for the 317 Area (ANL 1997b). Therefore, removal of residual contamination following the SM/TESVE process would be necessary to further reduce the contaminant concentrations. Several options for achieving this residual treatment were considered. An important criterion for selection of the polishing system was compatibility with the soil mixing process.

During the Kiber treatability studies (Kiber 1997), six polishing treatment systems were also evaluated. The systems studied included soil vapor extraction, metallic iron addition, augmented indigenous biodegradation (using three types of organic compound additives to serve as elector donors — methanol, formate, and phenol), chemical oxidation (using potassium permanganate [$KMnO_4$]), a proprietary humic acid-based treatment compound known as Humasorb (manufactured by ARTECH Inc., Sterling, Virginia), and Daramend, a proprietary treatment compound (manufactured by Grace Dearborn, Mississauga, Ontario). Table 3.1 summarizes the results of the Kiber Environmental Services, Inc., treatability studies (Kiber 1997).

On the basis of these studies and the expected cost of each system if deployed in the 317 Area, ANL-E decided to proceed with the field evaluation of three of these treatment systems — soil vapor extraction (referred to in this report as soil ventilation to prevent confusion with the

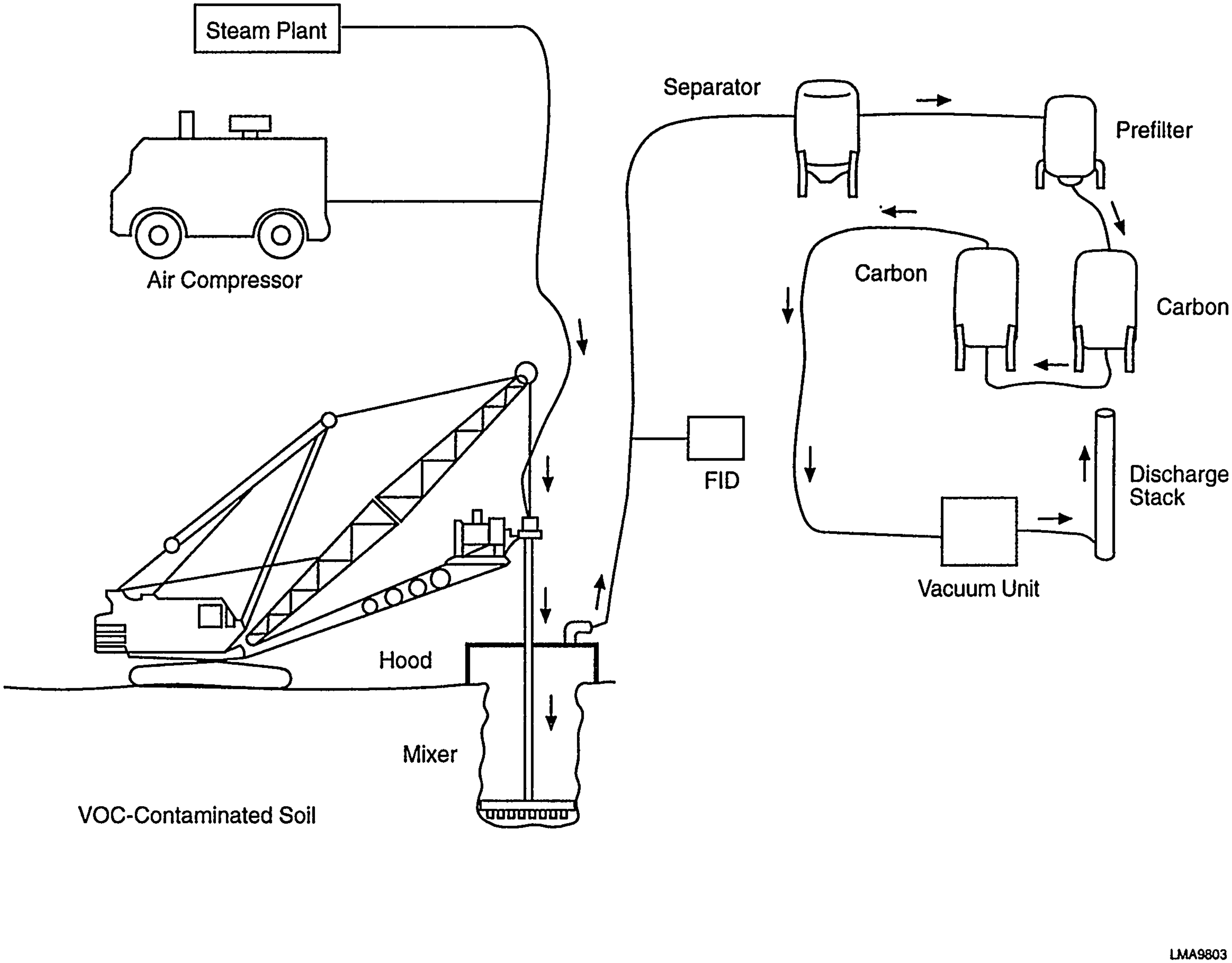


FIGURE 3.1 Process Schematic of SM/TESVE

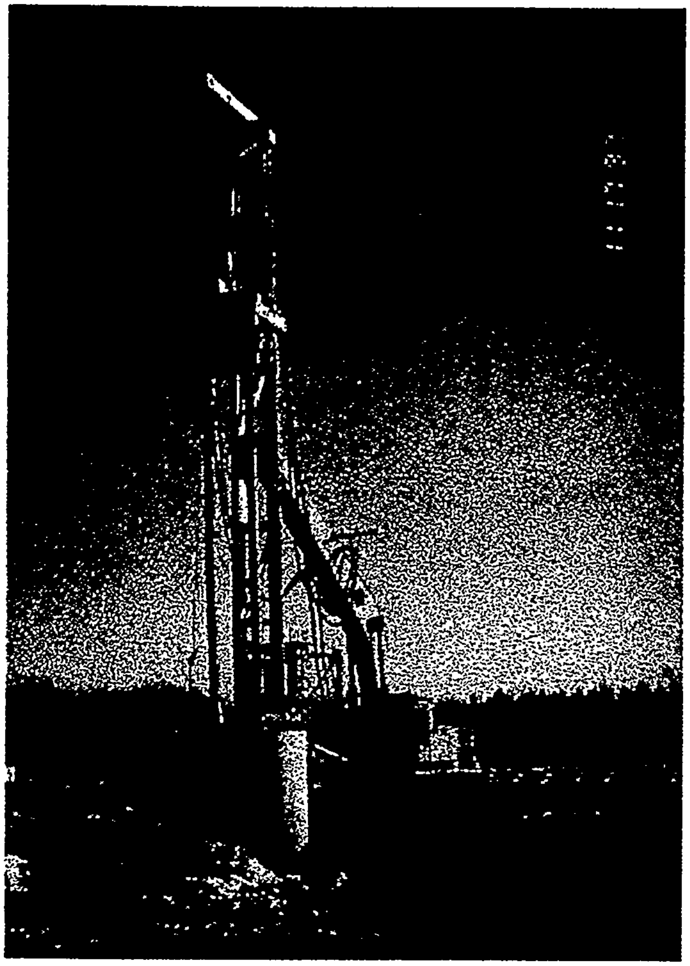


FIGURE 3.2 Soil Treatment Rig

thermally enhanced soil vapor extraction part of the overall process), iron addition, and augmented indigenous biodegradation.

3.2 PROJECT OBJECTIVES

The objective of the field evaluation of these three treatment methods was to determine the most effective soil polishing treatment process of the three. The most effective polishing process would then be integrated with SM/TESVE to produce an integrated treatment approach capable of removing 95% or more of the contaminants present. By combining SM/TESVE and a polishing treatment, the best qualities of both processes would produce an optimal treatment process from the standpoint of efficient utilization of treatment funds.

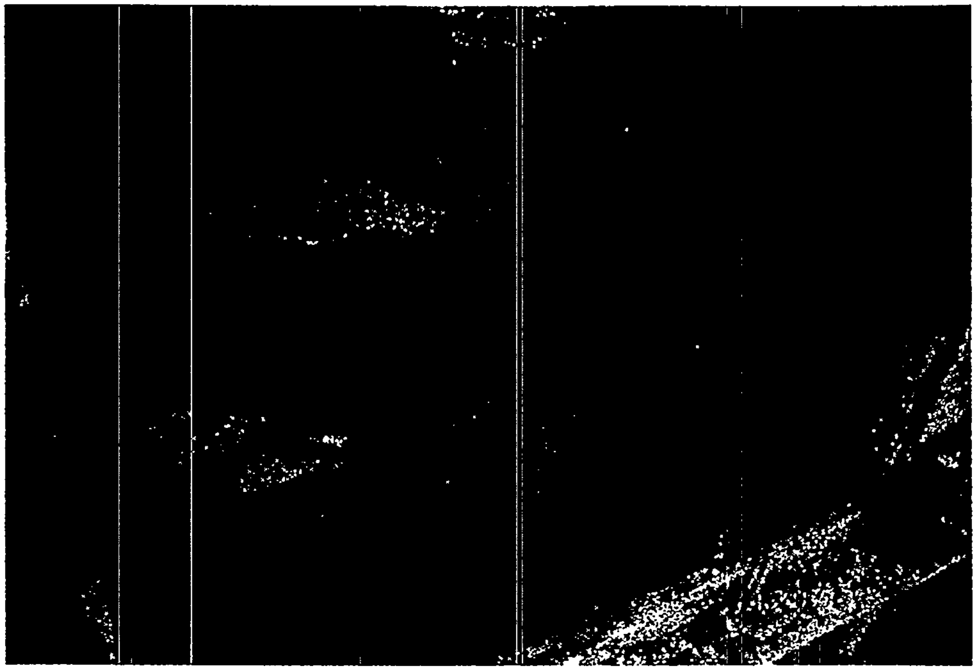


FIGURE 3.3 Closeup View of the Augers inside the White Enclosure

FIGURE 3.4 Mounded Soil following Treatment

TABLE 3.1 Kiber Environmental Services, Inc., Treatability Study Results

Treatment Method	Aggregate VOC Removal Efficiency (%)	Observations
No polishing - SM/TESVE only	69–74	Following 90 minutes of mixing.
SM/TESVE followed by potassium permanganate ($KMnO_4$) addition	78–79	5% and 10% $KMnO_4$ were added.
SM/TESVE followed by soil ventilation (soil vapor extraction)	92–98	Soil ventilation was performed for 2 to 7 days prior to analysis.
SM/TESVE followed by iron addition	84–99	2.5–8.5% iron was added in several trials.
SM/TESVE followed by Humasorb	69–94	Various Humasorb products were tested with varying results.
SM/TESVE followed by Daramend	73–87	Various Daramend formulas were tested, but none was optimized for this site.
SM/TESVE followed by enhanced biodegradation	69–84	Methanol, formate, and phenol were used as cometabolites. The test was 14 days in duration.

3.3 EXPERIMENT DEPLOYMENTS

The experiment deployments, as well as the subsequent full-scale treatment of the 317 French Drain soils, were performed by In-Situ Fixation (ISF), of Chandler, Arizona. This company used a mobile dual-auger soil mixing system equipped with special soil mixing blades designed by ISF for clay soil.

The three polishing treatments plus one control area were deployed in four test areas located north of the North Vault. The areas were located in a portion of the 317 French Drain area containing a large number of contaminants at concentrations typical of the site as a whole. The soil was native clay soil overlain by approximately 61 cm (24 in.) of compacted gravel. Geological logging of the area indicated that the upper 3 m (10 ft) of soil may have been previously disturbed during the construction of the North Vault in the early 1950s. The contaminants in this area were limited primarily to the upper 6 m (18 ft) of soil depth. The saturated sand and gravel layer observed in other parts of the 317 Area was not found in these experimental areas. Figure 3.5 shows the locations of the test areas within the 317 Area. The test areas were labeled sequentially from XA1A to XA10. The first attempt to mix soil at XA1 was terminated when a buried boulder was encountered. The second attempt, labeled XA1A, was successful. Test Area XA5 was mixed but was never used in the study.

All three polishing processes were designed to be integrated with the SM/TESVE process and would be deployed during or following the SM/TESVE operation. For this investigation, the normal SM/TESVE process was first performed in each of the four test areas. The soil mixing loosened and homogenized the soil; the steam added heat and moisture. The hot air carried away approximately 70 to 95% of the chemicals originally present. Following treatment, each experimental area consisted of a well mixed, slightly mounded area of wet clay-rich soil. Figure 3.6 is a photograph showing one of the experimental areas immediately following the SM/TESVE treatment.

The experimental systems were deployed soon after the SM/TESVE treatment. To establish an experimental control, one area (XA2), immediately adjacent to the experimental areas, was treated only with SM/TESVE. No further treatment was performed in this area.

The soil ventilation system (XA1A) was constructed by installing two polyvinylchloride (PVC) well screens in the mixed soil column with a hollow stem auger rig. A vapor extraction system was attached to one of the wells. The other well then served as an air inlet pipe. The air extraction system was fitted with flow and pressure monitoring devices, a high-efficiency particulate air (HEPA) filter and a modular activated-carbon absorber unit. The HEPA filter was installed to prevent contamination of the carbon by dust or radioactive particles that may have been picked up by the ventilation system. Figure 3.7 is a schematic of the soil ventilation system. Figure 3.8 is a photograph of the completed system.

The augmented indigenous biodegradation test (XA4) was deployed by using the soil mixing apparatus to inject and mix a solution containing a nutrient mixture and methanol. The nutrient solution was a combination of a commercial growth-enhancing product (Humega) and ammonium polyphosphate. Laboratory grade methanol was also added. The nutrients and methanol were mixed with water in a holding tank. The mixture was then pumped into the soil through the hollow auger stem (Kelly bars).

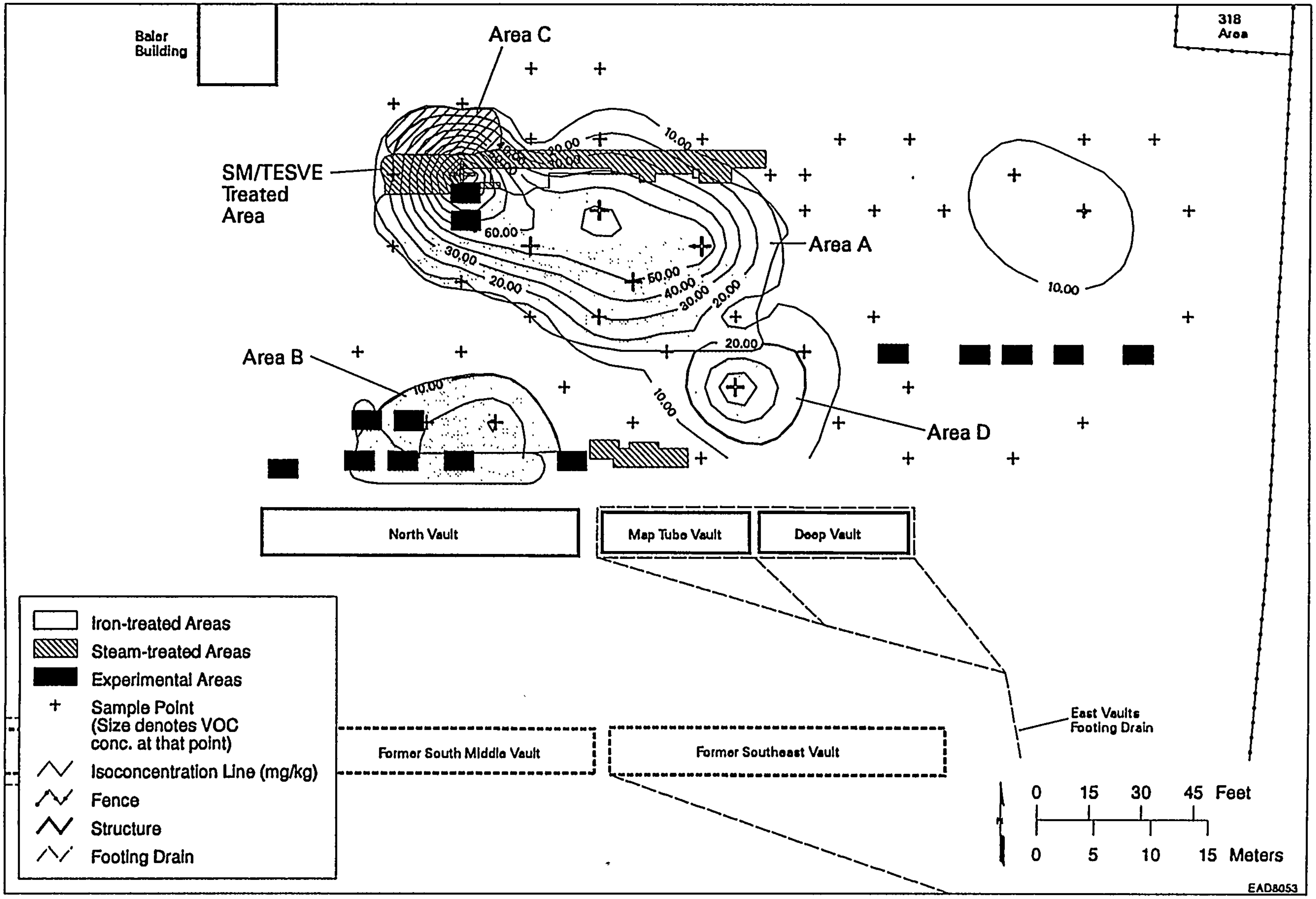


FIGURE 3.5 Final Treated Areas for the 317 Area French Drain

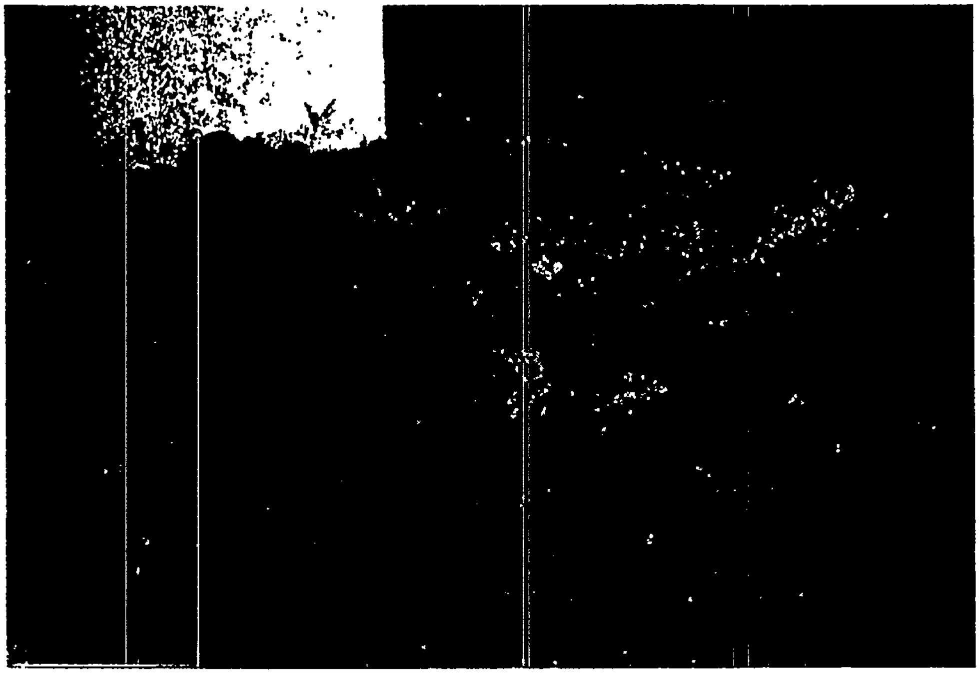


FIGURE 3.6 Closeup of Soil following Treatment (Note the saturated appearance and the presence of steam, which indicates high temperatures.)

The iron-addition experiment (XA3) was deployed by using the soil mixing apparatus to inject and mix a slurry of iron powder and guar gum (50% iron, 50% water with a small amount of guar gum powder added) into the test area. Sufficient iron slurry was injected to achieve 5% metallic iron concentrations. The iron was a commercially available iron powder that had been cleaned and size classified into a less than 50 mesh particle size range by the manufacturer (the material specification was –50 mesh particle size iron aggregate purchased from Connelly-GMP Inc., Chicago, Illinois). This size range represents the smallest iron particle size commercially available and includes all particles that will pass through a 50-mesh sieve. The iron was visually free of oil or other contaminants. No cleaning or other treatment of the iron was performed prior to injection. The material was poured directly out of shipping bags into the slurry mixer, which prepared the slurry and pumped it into the hollow Kelly bars. The slurry exited the Kelly bars near the tips of the augers, which mixed the slurry with the soil.

Figure 3.9 shows the iron-addition process schematic. Figure 3.10 is a photograph of the iron slurry mixing and injection equipment.

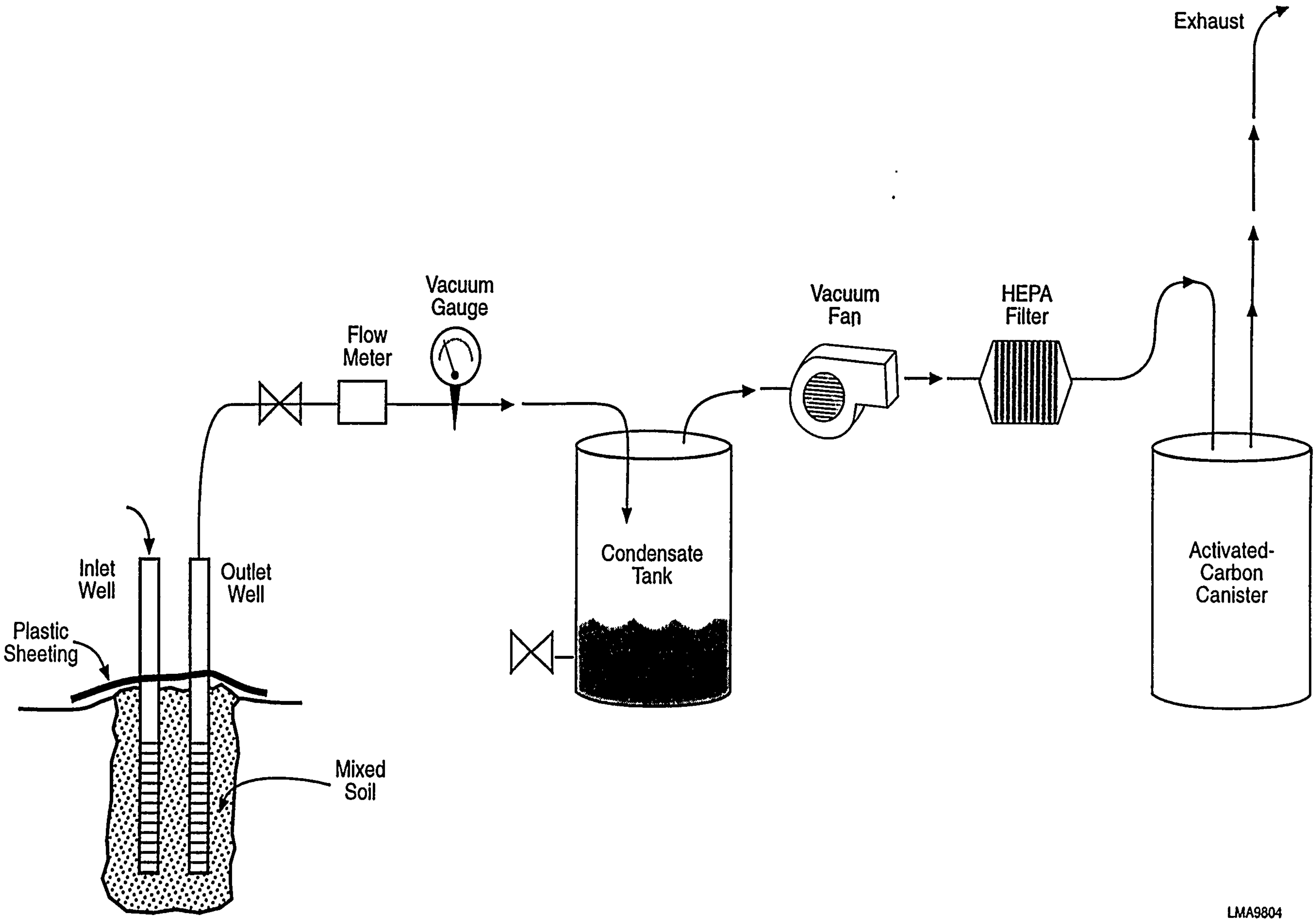


FIGURE 3.7 Soil Ventilation System

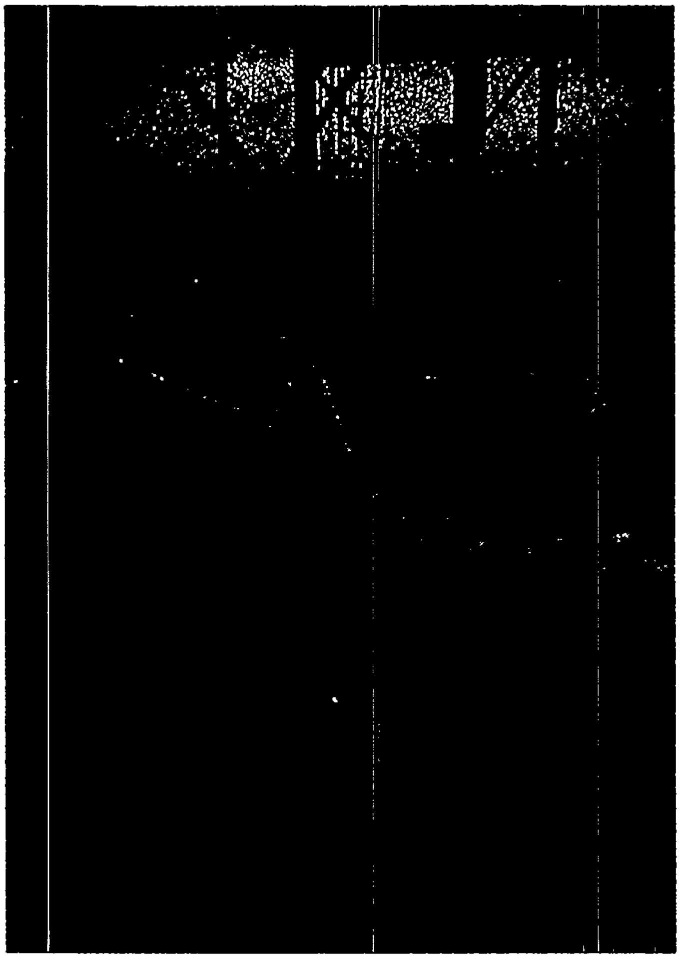


FIGURE 3.8 Soil Ventilation System at Experimental Area XA1A

Following preliminary analysis of the results of the performance monitoring samples, it was decided to perform further iron-addition experiments. These experiments (XA6 through XA10) were intended to confirm the results of the earlier experiment and to investigate several ways of integrating the iron addition with the SM/TESVE process. These supplemental experiments were performed in much the same way as the original, except that the amount of iron was reduced, and the amount of steam and air stripping of the soil used with the SM/TESVE process varied.

Temporary groundwater monitoring wells were installed in the iron-addition and biodegradation experimental areas. These wells were standard stainless-steel groundwater monitoring wells fitted with 3-m (10-ft) long screens. They were installed into boreholes drilled through the mixed soil by a hollow stem auger rig. Filter pack sand was placed approximately 0.30 m (1 ft) above the screen section; the remainder of the hole was filled with bentonite pellets and hydrated. Following completion of data collection efforts, the wells were removed.

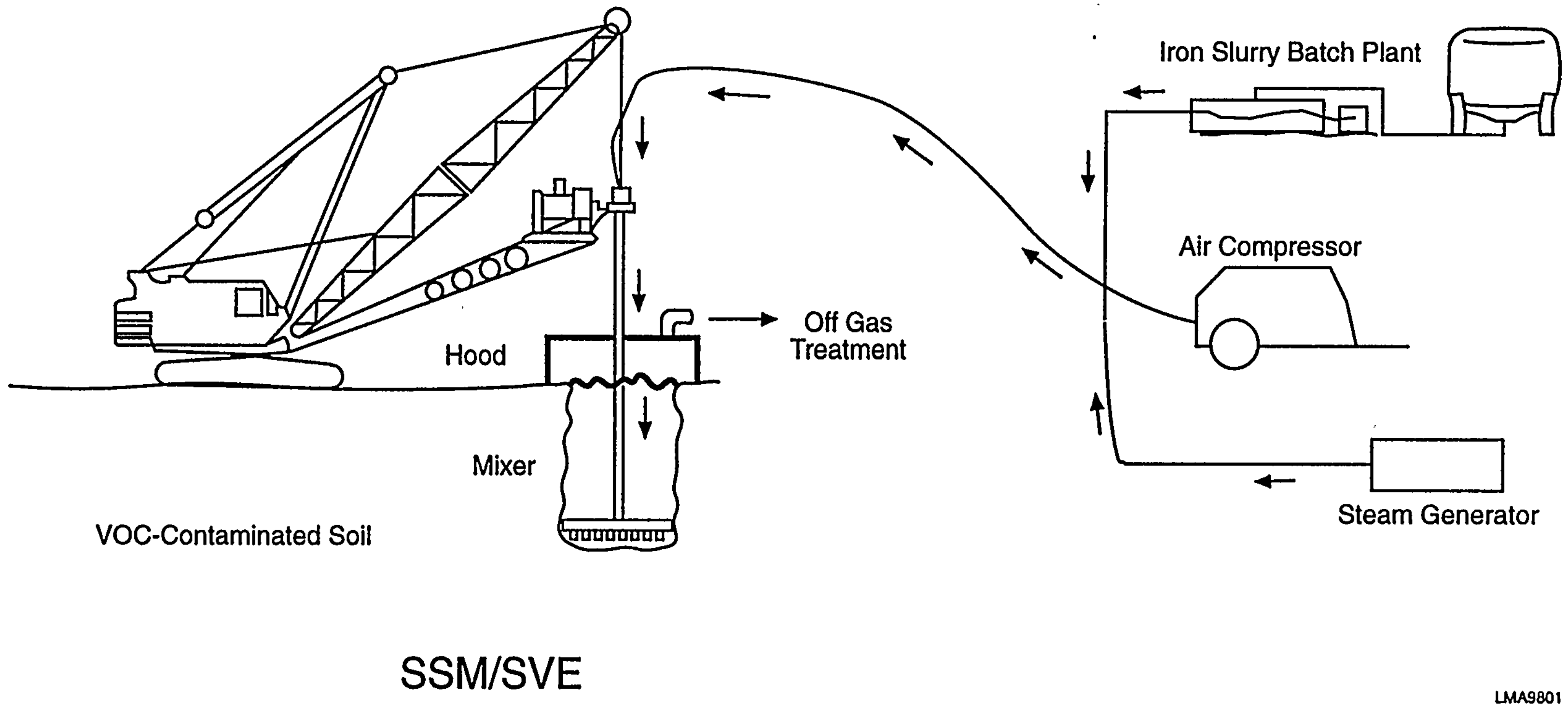


FIGURE 3.9 Iron-Addition Schematic

FIGURE 3.10 Iron Powder Being Added to the Mixing Unit in the Iron Batch Plant

3.4 INVESTIGATIVE APPROACH

The three experiments were designed as controlled, side-by-side comparisons in which the only factor intentionally varied was the type of treatment material or technique used. The intention was that the initial conditions of each experimental area would be very similar. The relative effectiveness would then be monitored by measuring the effects on the target compound concentrations over time. Because the majority of the compounds present were VOCs, this class of compounds was selected as the target of the study. Therefore, the bulk of the investigation is based on VOC measurements of soil samples. Other analyses, in addition to VOC analysis, were also performed to monitor the progress of the investigation. These analyses included analysis of water samples from four wells and analysis of off-gas samples; these analyses are discussed in Sections 4.2 and 4.3, respectively. Table 3.2 is a summary of the measurements performed and the samples collected and analyzed from the experimental areas.

The data generated by this study were to be used to decide which technology would be used in the full-scale treatment of the 317 French Drain area before such treatment was implemented. Therefore, it was important that the data be collected and analyzed rapidly. In addition, the length of the performance monitoring period was limited by the accessibility of the experimental areas prior to full-scale treatment. Because the data gathering effort was geared toward rapid development of relative VOC removal effectiveness and was not intended to provide an academic-quality research

TABLE 3.2 Summary of Analytical Measurements for Experimental Areas

Initial Characterization Samples	Pretreatment Characterization Samples	Performance Monitoring Samples
Soil - Field VOC screening	*Soil* - Field VOC screening	*Soil* - Field VOC screening
Field VOC analysis	Field VOC analysis	Field VOC analysis
Lab VOC analysis	Lab VOC analysis	Lab VOC analysis
Phospholipid fatty acid (PLFA)	Soil pH	Temperature
pH	PLFA (XA2 and XA4)	Soil pH
Nutrients	Chloride	Chloride
Chloride	Total iron	Nutrients
	Hydrocarbons	PLFA (XA2 and XA4)
	SVOCs (XA10)	Total iron
		Hydrocarbons
		SVOCs (XA10)
		Methanol
		Groundwater - pH
		Depth
		ORP
		DO
		Lab VOC analysis
		Gas - Composition
		Trace organics
		Flow

project, rapid turnaround VOC field analytical methods were used whenever possible. The field methods were confirmed by submitting split samples for conventional VOC analysis. Two field methods of VOC measurements were used. The first method, called VOC field screening, was designed to give an initial indication of the presence of contamination. The second method used was called field VOC analysis. In this method, a mobile laboratory was used to rapidly generate concentration values for specific contaminants in soil samples by using a head space/gas chromatography vapor analysis method. A subset of these samples was submitted to a conventional laboratory for standard VOC analysis (SW-846 Method 8260A [EPA 1986]).

Because of time limitations, none of the treatment systems was optimized prior to deployment. Treatability studies performed by Kiber Environmental Services, Inc., of Atlanta, Georgia, in 1996 (Kiber 1997) provided the basis for air flow rates for the soil ventilation study and dosage amounts for the iron and augmented indigenous biodegradation experiment.

3.4.1 Initial Characterization

The experiments were initiated by performing an initial characterization of each experimental area. This was performed by collecting soil samples (pretreatment characterization samples) from each area to a depth of approximately 6 m (18 ft). The samples from each depth interval (0.6-m [2-ft] increments) were analyzed by field VOC screening, field VOC analysis (in the mobile laboratory), and confirmatory VOC analysis in a fixed laboratory. Other parameters, such as chloride and pH, were also measured prior to deployment of the polishing treatment systems.

Following the SM/TESVE treatment phase, an additional set of samples (initial characterization samples) was collected and analyzed in a similar manner. Because the soil mixing process disturbs the soil structure and adds a large amount of moisture to the soil, the load-bearing capacity of the mixed soil is initially very low. To prevent the drilling rig from sinking into the mixed soil, it was mounted on a mobile steel platform that was placed onto the surface by a long-reach forklift truck. Figure 3.11 shows the sampling device.

3.4.2 Performance Monitoring

Once the three treatment systems and control were deployed, the performance monitoring period was begun. This consisted of collecting soil core samples at periodic intervals and analysis of the samples for headspace organic vapor concentrations (field screening), VOC analysis in the field (mobile laboratory), and confirmatory VOC analysis in a conventional fixed laboratory. In addition, from time to time other parameters were measured in the soil, including pH, chloride, temperature, nutrients, methanol, and total iron concentration. Groundwater was sampled and analyzed on several occasions in those test areas equipped with a groundwater monitoring well. As discussed later in Section 4.3, gas emanations were also captured and analyzed. The analyses performed during this period are shown in Table 3.2.

The sample collection intervals varied somewhat during the experiment. Initially, samples were collected more frequently because the rate of VOC removal was not known. However, once it was determined how quickly VOC concentrations were changing, the sampling intervals were extended. The sampling intervals are shown in the data tables discussed in Section 4.

Sample collection continued until the target compound concentrations approached analytical detection limits, until no further changes were noted for three or more sampling periods, or until the approximately 90-day sampling period was completed.

FIGURE 3.11 Sampling Rig Suspended from a Forklift Boom over a Treated Area to Collect Posttreatment Samples

4 SAMPLING AND ANALYSIS METHODS

Three types of samples were collected during this study — soil, groundwater, and gas emanations. The measurements and analyses were performed with field instruments, a mobile analytical laboratory, and several on- and off-site fixed analytical laboratories. Descriptions of the sample collection techniques and analytical procedures follow.

4.1 SOIL SAMPLING

Soil samples were collected using a push-point sampling device driven into the ground by a hydraulic sampling tool. The push-point sampler consisted of a split-spoon sampler into which a transparent acetate liner was placed. After retracting the sampler, the spoon was opened and the liner was removed. The liner was then cut into segments and marked to indicate the sampling location and depth. The samples were cut in lengths approximately 15 cm (6 in.) long, transferred to an iced cooler and from there to a sample refrigerator in the mobile laboratory.

Because of the extreme heterogeneity of the soil and contaminant characteristics, special procedures were used to develop representative data. To compensate for the heterogeneity, samples were selected from four arbitrary depth intervals (typically 0 to 0.6, 1.2 to 1.8, 2.4 to 3.0, and 3.7 to 4.3 m [0–2, 4–6, 8–10, and 12–14 ft] below the ground surface [bgs]). Samples were consistently collected from near the bottom of each depth interval. The data from these four depths were then averaged to minimize the effects of heterogeneity.

4.2 GROUNDWATER SAMPLING

Temporary groundwater monitoring wells were installed in experimental areas XA3, XA4, XA6, and XA7 and were sampled on several occasions. In addition, XA2, the soil ventilation experiment, had an air inlet well which, as it turned out, also served as a groundwater monitoring well. This well was also sampled several times, and depth-to-groundwater measurements were also taken.

Prior to collecting samples from these wells, standing water in the well casing was removed with a clean baler. All these wells recharged very slowly; all water was removed during purging Once the wells recharged with sufficient water to sample (often several days after purging), the samples were collected using a clean baler. Samples were then placed directly into the precleaned sample containers. Field measurements such as temperature, pH, and oxidation reduction potential (ORP) were taken immediately after the baler was removed from the well.

4.3 GAS EMANATIONS

As the experiment progressed, a small amount of gas was noted to be moving to the surface above the experimental areas where iron had been added. To capture some of this gas for analysis, an inverted funnel device was fabricated. The device consisted of a translucent plastic tray to which an inverted graduated plastic container was affixed. A vent with a flexible hose was mounted to the top of the inverted container. Figure 4.1 is a photograph of this system.

The area where gas had been observed to emerge at the surface was flooded with water to a depth of several inches. The gas discharge then appeared as bubbles rising through the ponded water. The inverted funnel was placed in the water over the gas bubbles. The water served as a seal to exclude air from the sampling device. A hand vacuum pump was then used to evaluate the air from the funnel and graduated container; the vacuum pulled water up into the container from the ponded area. When all of the air had been removed and replaced with water, pumping of air from the device was stopped. Gas emanating from the soil was captured by the inverted funnel and flowed into the graduated container. The rate at which the container was filled with gas was measured, thus allowing for calculation of the gas emanation rate.

After the graduated container filled with gas, a sample of the gas was collected by attaching an evacuated gas collection sphere (Summa canister) to the vent hose. The inlet valve on the sphere was slowly opened, thus allowing gas from the graduated container to enter the sphere. The filled sphere was then submitted to an on-site analytical laboratory for analysis by gas chromatography.

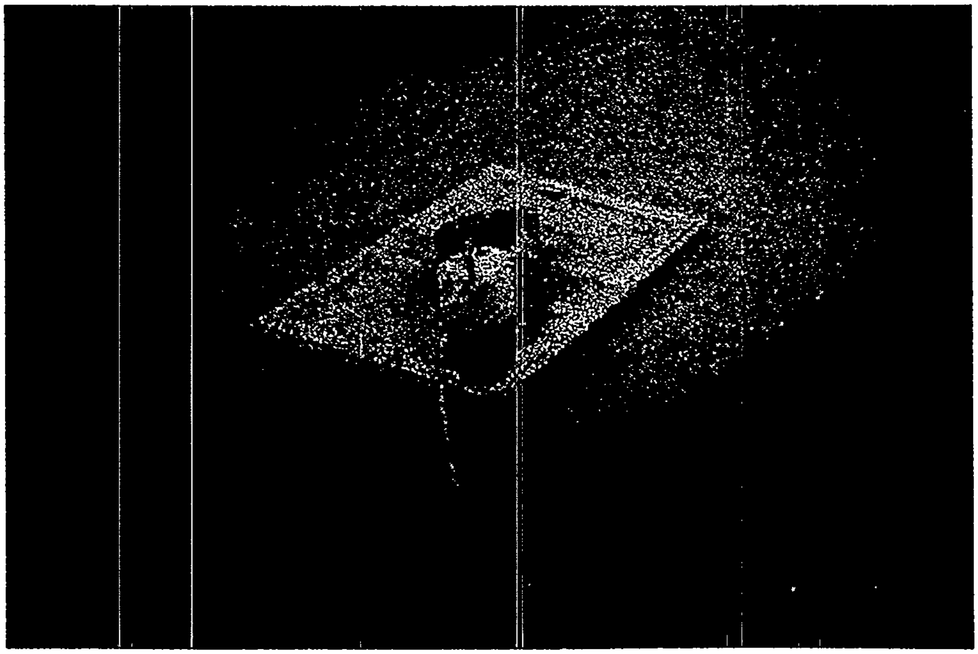


FIGURE 4.1 Gas Sample Apparatus Being Used to Measure the Gas Emanation Rate

5 ANALYTICAL METHODS

A variety of analytical methods were used to collect the data discussed in this report. These methods are presented below; Table 5.1 summarizes the methods used.

5.1 FIELD ORGANIC VAPOR SCREENING

Every soil core sample collected was screened for the presence of organic vapors with a field organic vapor analyzer (OVA) (Microtip Model MP-1000 with a 10.6-eV lamp). The soil was screened by measuring the amount of organic vapors in the headspace above the soil placed in a sealed glass jar. To prepare the headspace sample, approximately 200 g (7 oz) of soil was removed from the end of a sample tube and immediately placed in a 118-mL (4-oz) glass jar. The jar was covered with aluminum foil and placed in a 32°C (90°F) oven for a minimum of 15 minutes. The samples were then removed from the oven, and the probe of the OVA was inserted through the aluminum foil. As soon as the OVA reading stabilized, the reading was recorded and the sample was discarded.

The OVA was calibrated at least daily by using zero gas and isobutylene gas in accordance with the manufacturer's requirements.

5.2 GROUNDWATER PH, ORP, AND TEMPERATURE MEASUREMENTS

Groundwater pH and ORP were measured with a portable pH meter equipped with a combination pH/ORP electrode and a temperature probe. Water samples taken immediately after removal from the well were placed in a plastic sample cup, and the probe was inserted. When readings stabilized, the values were recorded, and the sample was discarded.

The pH meter was calibrated before each use in accordance with the manufacturer's specifications. The ORP and temperature probes did not require calibration.

TABLE 5.1 Sample Analytical Methods and Detection Limits

Analysis	Analytical Method	Detection Limits
Field organic vapor screening	Organic Vapor Meter	1.0 ppm
Field VOC analysis	3810[a]	100 μg/kg (approx)
Laboratory VOC analysis	Meter (Microtip OVA with 10.2-kV bulb)	5–200 μg/kg[b]
Chloride	300.0 (modified)[c]	2.0 mg/kg
Nitrate/nitrite nitrogen	353.1 (modified)[c]	0.5 mg/kg
Total kjeldahl nitrogen (TKN)	351.2[c]	5.0 mg/kg
Total phosphorous	365.1 (modified)[c]	10.0 mg/kg
Sulfate	300.0 (modified)[c]	5.0 mg/kg
Semivolatile organic compounds	3550A Prep. 8270B Anal.[a]	330–3,300 μg/kg[b]
Total iron	X-ray fluorescent analyzer (XRF) meter	
Soil pH	9045C[c]	0.1 pH units
Soil moisture	SL 4005[c]	1%
Bacterial abundance	Phospholipid fatty acid (PLFA)[d]	1.0 pmol PLFA/g soil
pH, oxidation/reduction potential (ORP), and temperature in groundwater	pH meter	Various
Dissolved oxygen in groundwater	4,500–0C[e]	0.05 mg/L
Gas compositional analysis	Mass spectrometry[f]	Varies by compound
Gas trace organics analysis	Gas chromatography[f]	Varies by compound

[a] *Test Methods for Evaluating Solid Waste*, EPA-530-SW-846: 3rd ed., Nov. 1986 and subsequent updates, U.S. Environmental Protection Agency, Office of Solid Waste, Washington, DC.

[b] Detection limit range depends on individual compounds (see Laboratory Quality Assurance Plan for details).

[c] *Methods for Chemical Analysis of Water and Waste*, EPA-600/4-79-020, Environmental Monitoring Systems Laboratory, Cincinnati, OH (EMSL-CI), U.S. Environmental Protection Agency, Revised March 1983 and 1979 where applicable.

[d] Method for PLFA adapted from *Handbook of Methods in Aquatic Microbial Ecology*, P.F. Kemp, et al., editors, Lewis Publishers, Boca Raton, FL, 1993, Chapter 32, "Quantitative Description of Microbial Communities Using Lipid Analysis."

[e] *Standard Methods for the Examination of Water and Wastewater*, 14th ed., M.A. Franson, American Public Health Association, Washington, DC, 1976.

[f] Gas analytical methods were developed in-house by the ANL-E Analytical Chemistry Division. No standard method or recognized method number exists.

5.3 LABORATORY METHODS

The primary data gathering effort associated with this project was the measurement of specific VOCs. This was conducted in two ways. Because of the importance of rapid data generation, and because the chemical reactions involving the contaminants and the soil treatment additives were expected to continue after sample collection and prior to analysis of the samples, a rapid analytical method was chosen. Most VOC analyses were performed by using a field analytical method (SW-846 Method 3810 [EPA 1986]). This method involves placing weighed amounts of soil into sealed glass vials, heating the vials to 90°C (194°F) with an auto sampling device, and injecting the headspace gas into a gas chromatograph. The resulting chromatogram was then used to calculate the concentrations of VOCs in the soil. The precision, accuracy, and minimum detection limits for this method were evaluated by using known quantities of contaminants added to clean sand. Detection limits were found to be approximately 0.1 mg/kg (100 µg/kg).

In addition, occasionally samples were split, and part of the sample was sent to an off-site analytical laboratory that performed VOC analysis by using the standard VOC analytical method (SW-846 Method 8260A [EPA 1986]). Split samples for this purpose were collected from the section of the split-spoon liner immediately adjacent to the first sample. This was performed to check the field VOC method and to provide data on other analytes that the field method was not intended to measure.

All VOC results are reported on a dry weight basis.

The methods used for the other parameters measured or analyzed are shown in Table 5.1. Whenever possible, standard EPA SW-846 methods (EPA 1986) were used. Nonstandard methods used included measuring iron with a portable x-ray fluorescent meter calibrated by using site soils to which various amounts of iron powder had been added. Analysis for PLFA was performed to provide an indication of the mass of viable microorganisms in the soil and the composition of the population present. This is a special method adopted from a procedure used for assessing bacteria in aquatic environments. The analysis for off-gas composition and trace organic constituents was performed at the ANL-E analytical chemistry laboratories with methods derived from standard procedures.

6 INITIAL SOIL CONDITIONS

To determine the initial conditions of the soil prior to any treatment, soil sampling was performed at various depths within the contaminated portion of the soil column. Once the experiments were underway, samples were routinely collected from intervals of 0 to 0.61, 1.2 to 1.8, 2.4 to 3.0, and 3.7 to 4.3 m (0–2 ft, 4–6 ft, 8–10 ft, and 12–14 ft) bgs.

Table 6.1 shows the contaminant concentrations in the four experimental areas and five supplemental iron-addition experiments prior to any treatment. Average VOC concentrations as high as 125 mg/kg were found in this area. Individual sample results included concentrations as high as 315 mg/kg. The most abundant contaminants were chloroform, carbon tetrachloride, trichloroethene, and tetrachloroethene. The individual sample results indicated that a general zone of contamination existed to a depth of about 6 m (18 ft). The individual contaminant concentrations within this zone varied by an order of magnitude or more within just a few feet.

The five supplemental iron-addition experiments focused on VOC removal by iron addition integrated with the SM/TESVE process. Thus, the initial sampling was more limited than that of the main experiments. The performance was measured by monitoring VOC concentrations as measured by the field laboratory (and confirmed by the fixed laboratory). The only other parameters measured were soil moisture, pH, iron concentration, and chloride concentration. For these experiments, the initial conditions were determined by soil core analysis prior to any soil disturbance. The iron-addition experiments were considered underway as soon as the iron was mixed into the soil during SM/TESVE treatment. Because SM/TESVE was not performed as a separate step in the supplemental iron-addition experiments, only one set of initial samples was collected rather than the two sets collected in the first experiments.

TABLE 6.1 Summary of Initial Average Field VOC Concentrations (mg/kg) in Experimental Areas

Compound	Experimental Area/Sample Date XA1A (10/22/97)	XA2 (9/29/97)	XA3 (9/30/97)	XA4 (9/30/97)	XA6 (12/4/97)	XA7 (12/4/97)	XA8 (12/11/97)	XA9 (12/11/97)	XA10 (3/4/98)
Acetone	0.36	0.28	<0.1U[a]	1.78	1.82	2.56	<0.10U	<0.10U	0.48
Benzene	0.59	5.94	1.39	4.00	8.19	4.47	<0.10U	0.24	1.14
Carbon tetrachloride	31.22	125.37	5.10	119.86	8.48	17.36	<0.10U	<0.10U	9.34
Chloroform	6.57	21.79	1.19	8.49	17.65	23.8	<0.10U	<0.10U	5.85
1,2-Dichloroethene	<0.1U	1.03	3.57	0.26	<0.1U	1.28	1.27	2.72	<0.10U
Isobutanol	1.66	0.28	4.18	0.71	6.42	0.47	<0.10U	<0.10U	1.27
4-Methyl 2-pentanone	2.61	2.23	0.62	0.52	5.41	1.63	<0.10U	<0.10U	1.20
Methylene chloride	0.21	0.39	1.06	2.88	1.76	5.35	<0.10U	<0.10U	0.52
Nitrobenzene	4.30	1.23	<0.1U	<0.1U	11.72	0.32	0.10	0.10	<0.10U
Tetrachloroethene	9.13	3.83	0.23	1.51	1.24	0.87	115.68	96.62	0.71
Toluene	2.55	1.70	1.04	7.36	9.91	1.8	0.73	0.55	2.48
Trichloroethene	17.41	13.99	7.77	60.11	28.03	38.49	3.74	4.74	34.40
m/p Xylene	0.42	0.30	0.29	11.34	0.23	0.3	0.20	0.20	0.35
o Xylene	0.25	0.34	0.27	6.67	0.19	0.27	0.23	0.23	1.44

[a] Definition of data qualifier: U = compound not detected (the value shown is the analytical detection limit).

7 SOIL CONDITIONS FOLLOWING SM/TESVE TREATMENT

The soil sampling was repeated following the SM/TESVE treatment of the main study areas to determine the effects of this phase of the treatment process and the nature and magnitude of residual contamination. Table 7.1 shows the results of this sampling and analysis as well as the pretreatment samples discussed in Section 6. Figure 7.1 shows the posttreatment VOC concentrations in experimental areas XA1A through XA4 as measured by the field screening method plotted against depth. For ease of comparison with the pretreatment concentrations, these initial data have been plotted along with the pretreatment concentrations on the same scale. A comparison of these charts shows that the removal of VOCs from experimental areas XA2 and XA3 by SM/TESVE was highly effective; however, in XA1A and XA4, little VOC removal occurred, as evidenced by the elevated field screening results.

Table 7.1 compares average field VOC concentrations before and after SM/TESVE treatment and gives VOC removal efficiencies for the most significant contaminants. Removal efficiency varied significantly and ranged from 22 to 99%. Most of the removal values fell in the 75 to 95% range. These removal efficiencies compared well with the bench-scale testing of this technology.

The SM/TESVE treatment was not performed for the supplemental iron-addition experiments — XA6, XA7, XA8, XA9, and XA10. Consequently, no data are available on the effectiveness of SM/TESVE alone in these experiments.

TABLE 7.1 Summary of Average VOC Removal Efficiencies during SM/TESVE Process

	Experimental Area XA1A			Experimental Area XA2		
Compound	Pretreatment Samples (10/22/97) (mg/kg)	Initial Characterization Samples (10/31/97) (mg/kg)	Removal Efficiency (%)	Pretreatment Samples (9/29/97) (mg/kg)	Initial Characterization Samples (11/1/97) (mg/kg)	Removal Efficiency (%)
Benzene	NA[a]	NA	NA	5.94	0.62	**89.6**[b]
Carbon tetrachloride	31.22	20.70	**33.7**	125.37	1.63	**98.7**
Chloroform	6.57	3.14	**52.2**	21.79	4.60	**78.9**
1,2-Dichloroethene	NA	NA	NA	1.03	<0.1	BDL[c]
Isobutanol	1.66	1.22	**26.8**	NA	NA	NA
4-Methyl 2-pentanone	2.61	2.04	**21.7**	2.23	0.42	**81.3**
Nitrobenzene	4.30	3.22	**25.0**	1.23	0.59	**52.4**
Tetrachloroethene	9.13	1.56	**82.9**	3.83	0.70	**81.8**
Toluene	2.55	<0.1	BDL	1.70	0.36	**78.8**
Trichloroethene	17.41	7.81	**55.1**	13.99	1.68	**88.0**

	Experimental Area XA3			Experimental Area XA4		
Compound	Pretreatment Samples (9/30/97) (mg/kg)	Initial Characterization Samples (11/1/97) (mg/kg)	Removal Efficiency (%)	Pretreatment Samples (9/30/97) (mg/kg)	Initial Characterization Samples (11/4/97) (mg/kg)	Removal Efficiency (%)
Acetone	NA	NA	NA	1.78	0.33	**81.5**
Benzene	1.39	0.26	**81.1**	4.00	0.52	**87.0**
Carbon tetrachloride	NA	NA	NA	119.86	4.29	**96.4**
Chloroform	1.19	0.54	**54.7**	8.49	3.87	**54.4**
1,2-Dichloroethene	3.57	0.46	**87.0**	NA	NA	NA
Isobutanol	4.18	<0.1	BDL	NA	NA	NA
4-Methyl 2-pentanone	NA	NA	NA	NA	NA	NA
Methylene chloride	1.06	0.55	**48.1**	2.88	0.39	**86.5**
Tetrachloroethene	NA	NA	NA	1.51	0.25	**83.4**
Toluene	1.04	<0.1	BDL	7.36	0.49	**93.3**
Trichloroethene	7.77	1.47	**81.1**	60.11	8.00	**86.7**

[a] NA = not applicable; the removal efficiency could not be calculated because this compound was not detected or the concentrations were too low to be meaningful.

[b] Bold indicates that the removal efficiency value was considered reliable because initial concentrations were significant (above 1.0 mg/kg), and concentrations after treatment were above detection limits.

[c] BDL = below detection limit; the concentration after treatment was below detection limits; thus, a removal efficiency could not be calculated.

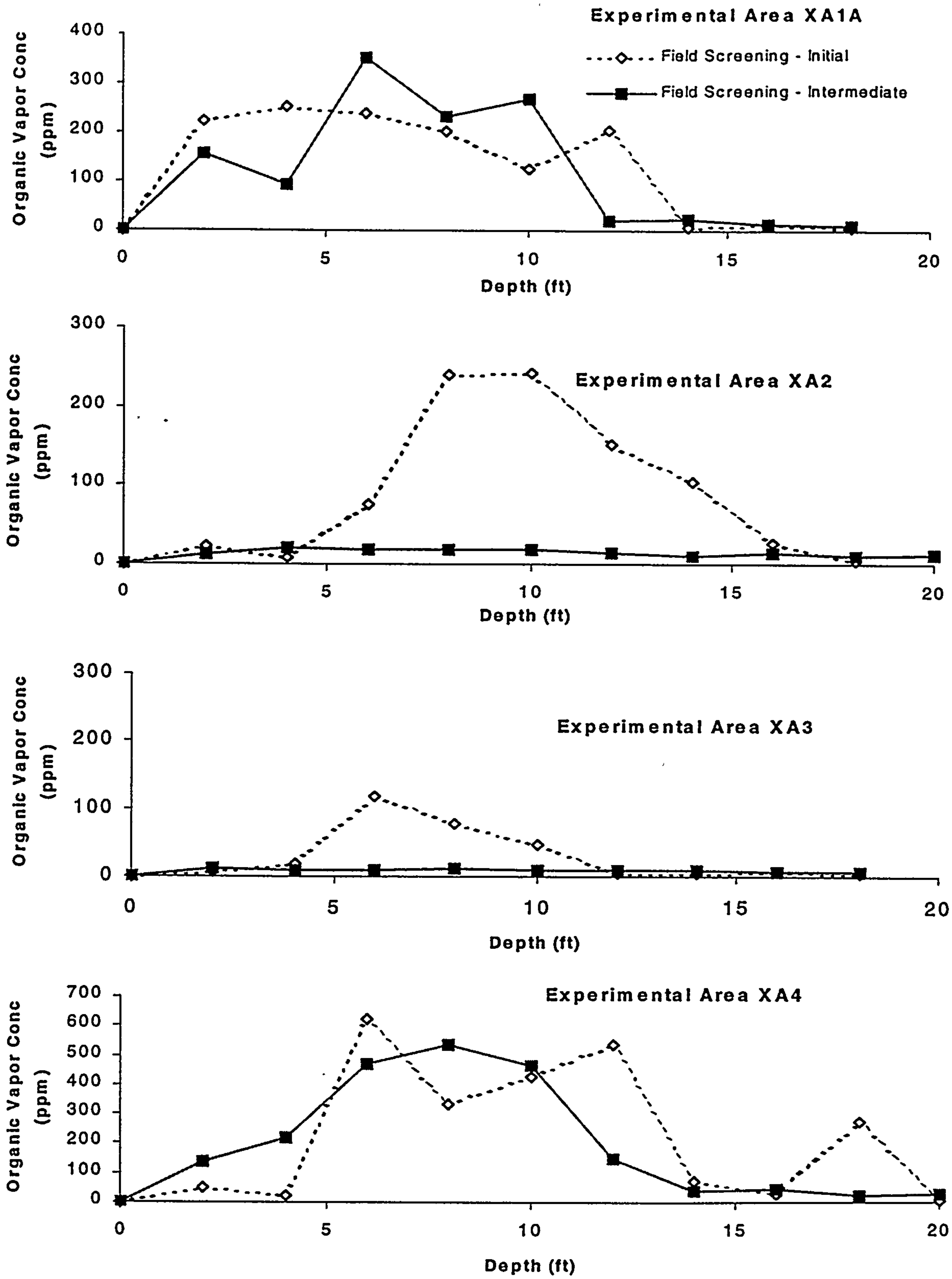


FIGURE 7.1 VOC Distribution in Experimental Areas following SM/TESVE Treatment

Following the completion of the SM/TESVE process, the three main experiments plus the control were deployed. In XA1, the soil ventilation experiment, the soil ventilation pipes were installed, and the ventilation fan was started. In XA3, the iron-addition experiment, the soil mixing equipment was used to inject approximately 5% iron into the column in a water slurry. In XA4, the biodegradation experiment, a mixture of nutrients and methanol was injected into the previously mixed soil with the soil mixing equipment. In XA2, the control, no further treatment or disturbance of the soil occurred. Because of the disturbance of the soil during deployment of the three experiments, it was thought that the posttreatment contaminant concentrations would not accurately reflect the initial conditions of the soil column at the start of the experiment. As a result, initial soil conditions were measured by collecting additional soil core samples as soon as possible following deployment of each system. The date of the deployment of the various treatment systems was considered time zero. The conditions prior to time zero were taken as those measured by the posttreatment samples. These data are shown in the data tables in Section 8, Performance Monitoring Results.

In addition to contaminant concentrations, other parameters were measured prior to the experiments. The results of the analyses for these parameters are also discussed in the following sections.

8 PERFORMANCE MONITORING RESULTS

Performance monitoring of the experimental areas varied from experiment to experiment. Sampling was performed until key contaminant concentrations were reduced to below the analytical detection limits or until approximately 90 to 100 days had elapsed.

8.1 CONTROL EXPERIMENT XA2

The analytical results of the performance monitoring of the experimental control are contained in Tables 8.1 through 8.3. Table 8.1 contains the average field VOC results (i.e., the average of four samples collected at intervals of 0 to 0.61, 1.2 to 1.8, 2.4 to 3.0, and 3.7 to 4.3 m [0–2, 4–6, 8–10, and 12–14 ft] bgs) for the 104-day monitoring period as well as average field screening results, total hydrocarbons (designated as diesel), and average moisture content.

Figure 8.1 shows the average field VOC concentrations for selected contaminants during the monitoring period. As expected, the field VOC measurements in the control area did not show a consistent trend of decreasing VOC concentrations during the monitoring period. The variability in sample concentrations was significant and reflects the highly heterogenous soil conditions; however, no overall trend in VOC concentrations was evident.

A sampling of fixed laboratory data for this experimental area, as compared with the field VOC method, is shown in Table 8.2. The results were similar, although the field method reported concentrations significantly higher (i.e., the average ratio of field VOCs divided by lab VOC results ranged up to a factor of 4) than the fixed laboratory method. The reason for the higher values with the field method is likely related to the more rapid analysis of the field VOC samples. They were typically prepared and analyzed within 24 to 48 hours of collection, as compared with the fixed laboratory method, which has a holding time of up to 14 days. It is possible that the VOCs could have volatilized from the samples during storage. Such a comparison was made with the data from each of the experimental areas with similar results. The other comparisons are not discussed in this report.

Periodically during the monitoring period, soil chloride concentrations and soil pH were also measured. Chloride concentrations, which are shown in Table 8.3, did not change appreciably during the experiment. Likewise, soil pH did not change appreciably.

TABLE 8.1 Summary of Average Field VOC Measurements in Experimental Area XA2 (Control: Treatment Date 11/1/97)

Constituent (mg/kg)	Pretreatment Samples (9/29/97)	Initial Characterization Samples Day 0 (11/1/97)	Performance Monitoring Samples						
			Day 30 (12/1/97)	Day 37 (12/8/97)	Day 44 (12/15/97)	Day 66 (1/6/98)	Day 79 (1/19/98)	Day 94 (2/3/98)	Day 104 (2/13/98)
Acetone	0.28	0.46	0.43	0.55	0.48	0.67	0.40	0.43	0.53
Benzene	5.94	0.62	0.56	0.57	1.27	0.86	0.80	0.45	0.57
Carbon tetrachloride	125.37	1.63	0.28	1.42	0.48	0.65	0.65	0.25	1.08
Chloroform	21.79	4.60	1.27	0.91	7.49	5.22	5.90	2.18	3.47
1,1-Dichloroethane	<0.10U[a]	<0.10U	<0.10U	<0.10U	0.11	<0.10U	<0.10U	<0.10U	<0.10U
1,2-Dichloroethane	0.19	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
1,1-Dichloroethene	0.30	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
1,2-Dichloroethene	1.03	<0.10U	0.23	0.21	1.07	0.48	0.41	0.15	0.23
Isobutanol	0.28	0.54	0.19	0.24	0.28	0.25	0.24	0.18	0.23
4-Methyl 2-pentanone	2.23	0.42	0.20	0.34	0.38	0.49	0.42	0.29	0.38
Methylene chloride	0.39	<0.10U	0.97	1.56	0.38	0.42	0.28	0.42	0.78
Nitrobenzene	1.23	0.59	0.19	0.27	0.41	0.42	0.54	0.50	0.35
Tetrachloroethene	3.83	0.70	0.26	0.25	0.47	0.39	0.29	0.23	0.27
Toluene	1.70	0.36	0.17	0.22	0.27	0.21	0.23	0.17	0.16
1,1,1-Trichloroethane	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
Trichloroethene	13.99	1.68	1.11	1.36	2.93	2.23	2.31	1.11	1.69
m/p Xylene	0.30	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
o Xylene	0.34	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
Total VOC	179.18	11.58	5.85	7.89	16.02	12.27	12.44	6.34	9.72
Diesel[b]	NA[c]	85	<1U	<1U	1U	1	<1U	1	1
Field screening	111	14.9	14.4	7.1	48.5	35.1	27.5	7.4	8.8
Water content (%)	14.5	34.6	25.4	29.5	22.3	26.4	31.3	28.0	27.7

[a] Definition of data qualifier: U = compound not detected (the value shown is the analytical detection limit).

[b] Constituent labeled diesel is an estimated value based on the peak area of a series of straight chain and branched hydrocarbons.

[c] NA = not applicable; a diesel concentration was not determined for this sample.

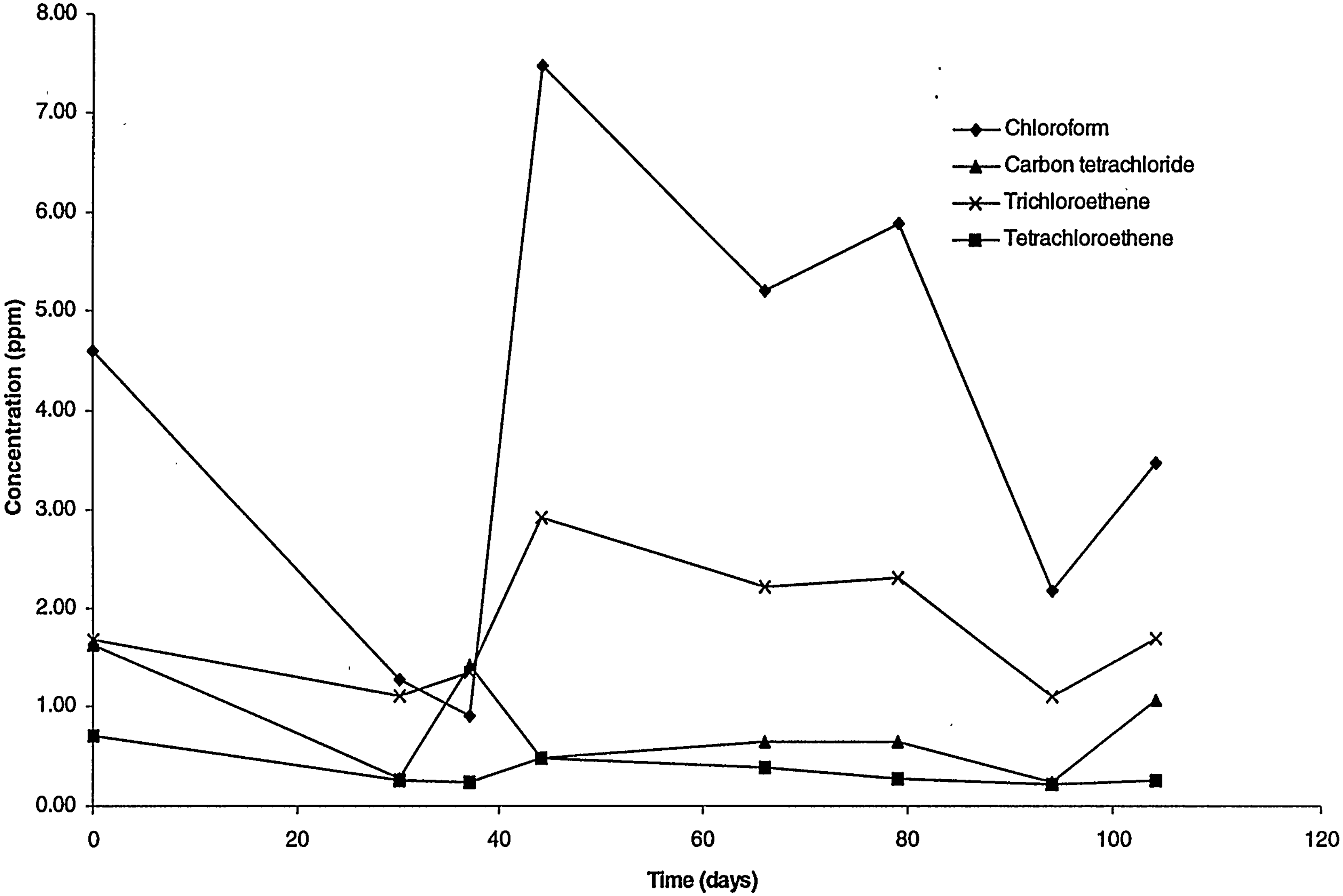


FIGURE 8.1 **Average VOC Concentrations in Experimental Area XA2 (Control)**

TABLE 8.2 Comparison of Field VOC and Laboratory VOC Analytical Results in Experimental Area XA2 (Control: Treatment Date 11/1/97)

	XA2-SB01 (1/6/98) (8–10)			XA2-SB01 1/19/98 (4–6)			XA2-SB01 (1/19/98) (8–10)		
Constituent (mg/kg)	Field	Laboratory	Ratio (field/lab)	Field	Laboratory	Ratio (field/lab)	Field	Laboratory	Ratio (field/lab)
Field VOC Compounds									
Acetone	0.77	4DB[a]	0.19	0.22	0.29	0.76	0.52	2.8BJ	0.19
Benzene	1.08	0.87D	1.24	0.60	0.08	7.50	1.27	0.42J	3.02
Carbon tetrachloride	0.11	0.027	4.07	0.76	0.078	-[b]	0.27	<0.80U	-
Chloroform	8.73	7.1D	1.23	2.38	0.31	7.68	8.46	2.9	2.92
1,2-Dichloroethene[c]	0.46	0.031 (trans) 0.13 (cis)	-	0.44	0.012 (trans) 0.052 (cis)	-	0.71	<0.40 (trans) 0.24 (cis)J	-
Isobutanol	0.14	<0.26U	-	<0.1U	<1.3U		0.16	<32U	-
4-Methyl 2-pentanone	0.63	0.9DJ	0.70	0.30	0.14	2.14	0.65	0.49J	1.33
Methylene chloride	<0.1U	0.15B	-	<0.1U	0.037	-	0.14	1.5B	-
Nitrobenzene	0.43	NA[d]	-	<0.1U	NA	-	<0.1U	NA	-
Tetrachloroethene	0.48	0.17	2.82	0.17	0.039	4.36	0.36	0.29J	1.24
Toluene	0.25	0.12	2.08	<0.1U	0.021	-	0.21	<0.80U	-
Trichloroethene	2.80	3.2D	0.88	2.17	0.37	5.86	2.97	1.3	2.28
Other Compounds[e]									
Acetonitrile		0.006J			<0.63U			1.4BJ	
Acrolein		<0.13U			<0.65U			0.78J	
2-Butanone		0.03B			0.023			<3.2U	
Carbon disulfide		0.17			<0.032U			<0.80U	
1,2-Dibromo-3-chloropropane		<0.013U			<0.065U			0.22J	
Ethyl benzene		0.01			<0.032U			<0.80U	
1,1,2-Trichloroethane		0.002			<0.032U			<0.80U	

[a] Definitions of data qualifiers: B = compound detected in the method blank; D = result from diluted sample; J = estimated concentration; U = compound not detected (the value shown is the analytical detection limit).

[b] A hyphen indicates that the field VOC/lab VOC ratio could not be calculated because one or both analyses were below detection limits.

[c] Field VOC analysis reports 1,2-dichloroethene as total (cis plus trans isomers), while the laboratory analysis provides individual results for both isomers.

[d] NA = not applicable; lab VOC analysis does not measure nitrobenzene.

[e] These compounds were detected in the laboratory VOC analyses but were not measured in the field VOC analysis.

TABLE 8.3 Summary of Miscellaneous Measurements for Experimental Area XA2 (Control: Treatment Date 11/1/97)

Soil Temperature		Soil pH		Soil Chloride Ions			Nutrient Concentration (mg/kg)		
Value (°F)	Date Measured	Value (pH Units)	Date Measured	(mg/kg)	Date Measured	Nutrient	8/7/97[c]	1/19/98	2/13/98
>120	11/6/07	7.0–8.0	8/7/97[a]	130[b]	8/7/97[a]	Sulfate	NA[d]	52.7	58.7
67	12/8/97	7.2–7.7	12/15/97	114[e]	1/19/98	TKN	330	224	13U
72	12/11/97	6.9–7.3	1/8/98	104[e]	2/12/98	Total phosphorous	31	513	251
63	12/16/97	7.3–7.4	1/19/98			Nitrate	<1.0U[f]	<0.64U	<0.65U
55	1/5/98								

[a] Samples collected on 8/7/97 were collected during the experiment planning stage from a location near the eventual site of experiment XA2.

[b] The value shown is the mathematical average of three samples collected from depth intervals of 3–5, 9–11, and 11–13 ft bgs.

[c] The value shown is the mathematical average of two samples collected from depth intervals of 3–5 and 11–13 ft bgs.

[d] NA = not applicable.

[e] The value shown is the mathematical average of four samples collected from depth intervals of 0–2, 4–6, 8–10, and 12–14 ft bgs.

[f] Definition of data qualifier: U = compound not detected (the value shown is the analytical detection limit).

8.2 SOIL VENTILATION EXPERIMENT XA1A

Monitoring of the effectiveness of this system began immediately after the extraction wells were installed and the exhaust fan was started. An air flow rate of approximately 0.25 m^3 (9 ft^3)/min was maintained in the off-gas system. A negative pressure of 83 to 89 cm (33–35 in.) of water was observed at this air flow rate.

Soon after the system was installed, it was noted that water had accumulated in the air inlet well to a depth of less than 0.6 m (2 ft) below the surface. After several weeks of monitoring, no decrease in the water level was noted. Repeated attempts to remove water from the well did not prove effective in lowering water levels in the well.

Apparently, the permeability of the treated soil was so low that it did not permit excess water to drain from the soil into the air outlet well as was hoped. The presence of water in the inlet well meant that the soil immediately outside the well was saturated with groundwater, thus filling the pores in the soil through which the soil gas was to have moved. As a result, very little air was moving through the treated soil.

The source of the water in the soil in the test area was apparently from the steam injected during the SM/TESVE process, as well as groundwater already present in the soil column. In addition, the weather was fairly wet during the experimental period; a combination of melting snow and rain kept the experimental areas wet.

Soil samples were collected from four depth intervals at approximately one-week intervals for the first six weeks and then at approximately two-week intervals. The experiment was monitored for 104 days. One groundwater sample was collected form the air inlet pipe. The monitoring results for this system are shown in Tables 8.4 and 8.5. Figure 8.2 depicts the variations in the average field VOC concentrations of the most significant contaminants in this experiment during the monitoring period.

As shown in Figure 8.2, contaminant concentrations were essentially unchanged throughout the study, which indicates that minimal VOC removal was occurring because of air flow through the soil column. An examination of chloride data in Table 8.6 indicates that chloride levels were stable, which confirms that degradation of chlorinated compounds was also not occurring.

Numerous VOCs were detected in the groundwater at concentrations up to 9.3 mg/L. The species found in the groundwater generally corresponded with the species found in the soil at high concentrations. Table 8.5 gives the groundwater VOC data.

TABLE 8.4 Summary of Average Field VOC Measurements for Experimental Area XA1A (Soil Ventilation: Ventilation Started 11/13/98)

			Performance Monitoring Samples								
Constituent (mg/kg)	Pretreatment Samples (10/22/97)	Initial Characterization Samples Day 0 (10/31/97)	Day 1 (11/12/97)	Day 9 (11/21/97)	Day 19 (12/1/97)	Day 26 (12/8/97)	Day 32 (12/15/97)	Day 55 (1/6/98)	Day 68 (1/19/98)	Day 83 (2/3/98)	Day 92 (2/12/98)
Acetone	0.36	<0.1U[a]	0.25	0.22	0.34	0.31	0.32	0.33	0.29	0.32	0.22
Benzene	0.59	<0.1U	0.38	0.38	0.59	0.41	0.50	0.63	0.67	0.57	0.46
Carbon tetrachloride	31.22	20.70	7.65	8.02	8.76	10.45	10.56	14.01	9.75	7.84	7.32
Chloroform	6.57	3.14	3.57	3.58	5.45	3.18	4.00	5.90	4.78	5.93	4.36
1,1-Dichloroethane	<0.1U	<0.1U	<0.1U	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
1,2-Dichloroethane	<0.1U	<0.1U	<0.1U	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
1,1-Dichloroethene	<0.1U	<0.1U	<0.1U	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
1,2-Dichloroethene	<0.1U	<0.1U	0.14	0.12	0.22	0.14	0.17	0.17	0.17	0.18	0.12
Isobutanol	1.66	1.22	0.61	0.41	0.52	0.38	0.32	0.98	0.64	0.76	0.42
4-Methyl 2-pentanone	2.61	2.04	1.39	1.17	1.48	1.07	1.51	2.17	1.49	1.94	1.33
Methylene chloride	0.21	<0.1U	0.14	0.35	0.69	0.43	<0.1	0.14	0.13	0.32	0.18
Nitrobenzene	4.30	3.22	1.95	1.33	1.47	1.80	3.20	3.15	0.22	1.87	2.70
Tetrachloroethene	9.13	1.56	0.93	0.85	0.92	0.80	1.45	1.71	1.07	1.08	0.90
Toluene	2.55	<0.1U	0.27	0.25	0.38	0.24	0.39	0.49	0.44	0.34	0.28
1,1,1-Trichloroethane	<0.1U	<0.1U	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Trichloroethene	17.41	7.81	4.40	4.14	5.64	4.36	6.37	8.11	6.00	6.17	5.00
m/p Xylene	0.42	<0.1U	<0.1	<0.1	<0.1	<0.1	0.12	0.11	<0.1	<0.1	<0.1
o Xylene	0.25	<0.1U	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Total VOC	55.02	38.57	21.48	18.44	23.39	20.10	21.50	37.44	24.71	26.71	23.09
Diesel[b]	24	<1.0U	1	2	1	<1U	2	3	2	2	2
Field screening	149	201	28	37	23	24	61	136	107	26.7	-[c]
Water content (%)	19	38	37	27	27	34	27	32	34	31	27

[a] Definitions of data qualifiers: B = compound detected in the method blank; D = result from diluted sample; J = estimated concentration; U = compound not detected (the value shown is the analytical detection limit).

[b] Constituent labeled diesel is an estimated value based on the peak area of a series of straight chain and branched hydrocarbons.

[c] A hyphen indicates that field screening data were not available for this sampling event.

TABLE 8.5 Summary of Groundwater VOC Analysis Results for Experimental Area XA1A (Soil Ventilation)

Constituent (mg/L)	Sample Date (12/19/97)
Field VOC Compounds	
Acetone	4.9BD[a]
Benzene	0.55D
Carbon tetrachloride	1.00D
Chloroform	8.20D
1,2-Dichloroethene	<0.028 (trans) 0.170 (cis)
4-Methyl 2-pentanone	9.30D
Methylene chloride	0.62BD
Tetrachloroethene	0.082
Toluene	0.11
Trichloroethene	2.20D
Xylene (total)	0.026U
Other Compounds[b]	
2-Butanone	0.19
Ethyl benzene	0.006
1,1,2-Trichloroethane	0.004J
Trichloroflouromethane	0.015

[a] Definitions of data qualifiers: B = compound detected in the method blank; D = result from diluted sample; J = estimated concentration; U = compound not detected (the value shown is the analytical detection limit).

[b] These compounds were detected in the laboratory VOC analyses but were not measured in the field VOC analyses.

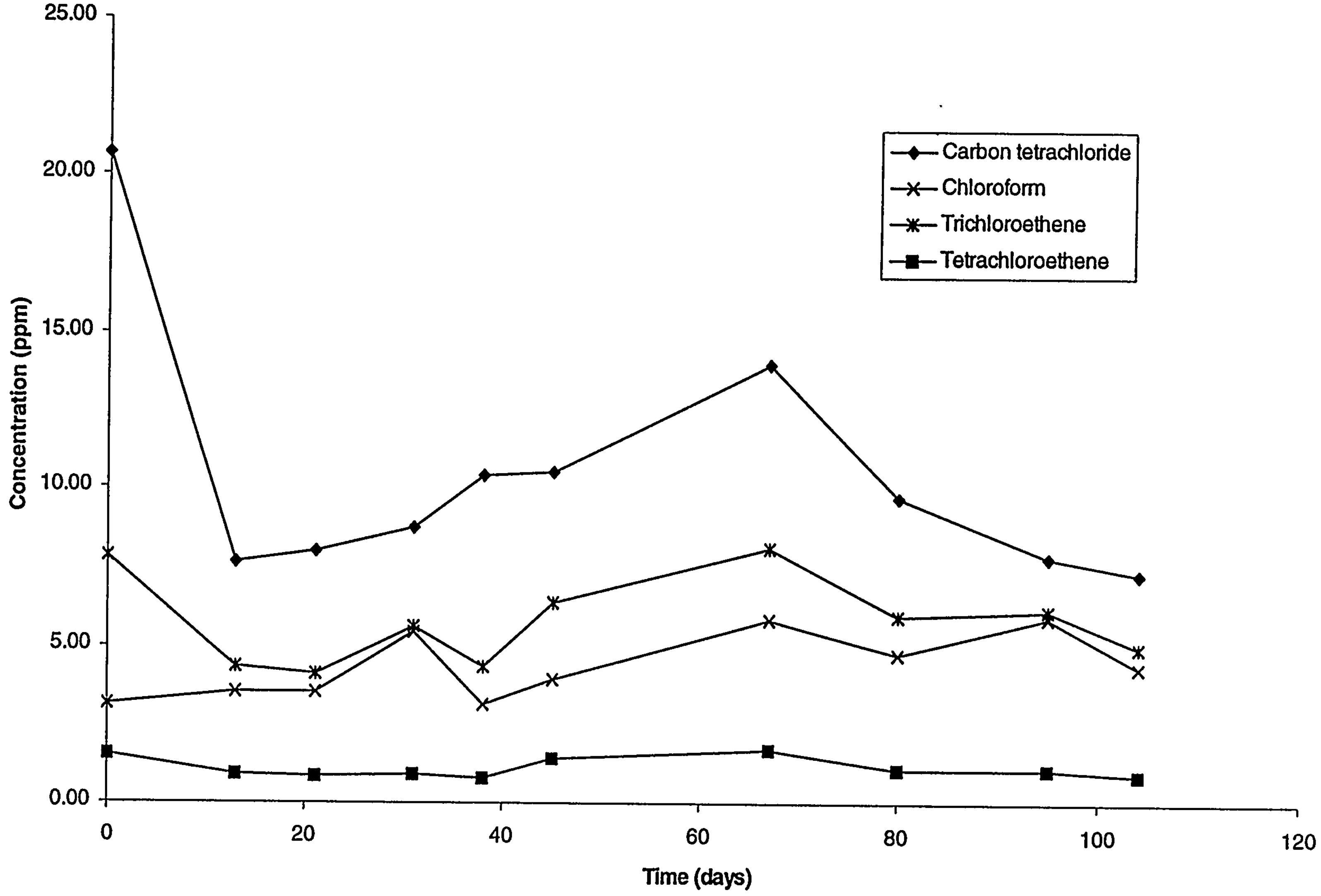


FIGURE 8.2 Average VOC Concentrations in Experimental Area XA1A

TABLE 8.6 Summary of Miscellaneous Measurements for Experimental Area XA1A (Soil Ventilation: Ventilation Started on 11/13/98)

Soil Temperature		Soil pH		Soil Chloride Ions	
Value (°F)	Date Measured	Value (pH Units)	Date Measured	(mg/kg)	Date Measured
100	11/6/97	8	8/7/1997[a]	100[b]	8/7/97[a]
98	11/10/97	5.4–7.5	1/6/98	116[c]	1/19/98
74	11/25/97			92.4[c]	2/12/98
69	12/2/97				
66	12/8/97				
61	12/22/97				

Depth to Groundwater Surface		Groundwater pH		Groundwater Oxidation Reduction Potential	
(ft)	Date Measured	Value (pH Units)	Date Measured	(mV)	Date Measured
4.6	12/4/97	6.85	12/5/97	10.5	12/5/97
4.6	12/11/97				
4.1	12/12/97				
5.2	12/16/97				
10.3	12/17/97[d]				
4.9	1/5/98				
7.7	1/19/98				

[a] Samples collected on 8/7/97 were collected during the experiment planning stage from a location near the final site, experimental area XA1A.

[b] The value shown is the mathematical average of three samples collected from depth intervals of 7–9, 9–11, and 11–13 ft bgs.

[c] The value shown is the average of two samples collected from depth intervals of 4–6 ft and 8–10 ft bgs.

[d] The well was baled dry on 12/16/97; the well depth was 14.3 ft bgs.

8.3 AUGMENTED BIODEGRADATION EXPERIMENT XA4

In this experiment (XA4), a nutrient solution was injected into the soil in the treatment area, along with a small amount of methanol. The nutrients were injected to ensure that bacterial growth would not be nutrient limited. The methanol served as a cometabolite for certain anticipated bacteriologically mediated anaerobic dechlorination reactions. In addition to ammonium polyphosphate solution, which was added to provide nitrogen, phosphorous, and methanol, a commercial biodegradation emanative material called Humega was added. This material, which is manufactured by BioFlora International, Inc., of Goodyear, Arizona, is a mixture of humic acids blended with a biologically active solution of yeasts, molds, bacteria, and enzymes. This material provided micronutrients, potentially beneficial microorganisms, and other materials that may have been absent from the soil. The nutrients and amounts added are shown in Table 8.7..

The amount and types of nutrients were selected on the basis of the 1996 Kiber Environmental Services, Inc., treatability study (Kiber 1997). This study found that the removal of approximately 70 to 80% of residual VOCs present was achieved after 14 days of incubation. Because of schedule constraints for this field investigation, it was not possible to perform further studies to optimize nutrient doses or other factors that may have improved the biodegradation process.

This experiment was monitored for 83 days after nutrient injection. Soil samples were monitored primarily for VOC reductions with the field VOC method, which was confirmed by the laboratory VOC method. These data are shown in Table 8.8.

The average field VOC data in Table 8.8 are shown graphically in Figure 8.3. From the data, it appears that very little VOC removal from the soil took place during the monitoring period.

TABLE 8.7 Augmented Biodegradation Experiment: Soil Amendment Amounts and Sources

Nutrients Supplied	Source	Amount added to Water Injected (mL/gal)	Mass Added to Soil (mg/kg)
Nitrogen (N) and phosphorous (P)	Ammonium polyphosphate	1.3	0.15 as N 0.59 as P
Micronutrients	Humega	114	74.4
Methanol	Reagent-grade methanol	1.5	0.73

TABLE 8.8 Comparison of Field VOC and Laboratory VOC Analytical Results for Experimental Area XA4 (Biodegradation)

Constituent (mg/kg)	XA4-SB01 (9/30/98)(4–6)			XA4-SB01 (1/5/98) (8–10)			XA4-SB01 (2/13/98) (8–10)		
	Field	Laboratory	Ratio (field/lab)	Field	Laboratory	Ratio (field/lab)	Field	Laboratory	Ratio (field/lab)
Field VOC Compounds							0.41	4.6B	
Acetone	<0.1	1.6J[a]	-[b]	0.18	0.14B	1.29	1.00	0.36J	2.78
Benzene	2.93	0.84J	3.49	0.50	0.32DJ	1.56	6.08	2.5	2.43
Carbon tetrachloride	315[c]	41	7.68	6.24	4.8D	1.30	7.76	3.1	2.50
Chloroform	4.67	2.1	2.22	3.90	2.1D	1.86	<0.1U	<0.79U	
1,2-Dichloroethene	0.31U	<0.85U	-	0.24	0.022 (trans) 0.140 (cis)	-	<0.1U	<32U	
4-Methyl 2-pentanone	0.17	<6.8U	-	3.11	2.8DJ	1.11	0.15	0.82B	
Methylene chloride	<0.1U	3.3	-	<0.1U	0.039B	-	<0.1U		
Tetrachloroethene	4.78	0.47J	10.17	0.67	0.9D	0.74	1.05	0.61J	1.72
Toluene	18.44	2	9.22	0.68	0.66DJ	1.03	<0.1U	<0.79U	
Trichloroethene	148.29	26	5.70	12.50	9.6U	1.30	1.47	3.4	
m/p Xylene	31.87	20	-		4.6J	-	0.61	3.4	
o Xylene	12.59	20	-		4.6J	-			
								<16U	
Other Compounds[e]									
Acetonitrile		26J			<0.13U			<16U	
2-Butanone		<6.8U			0.007BJ			0.3J	
Carbon disulfide		<1.7U			0.14			<1.6U	
Ethyl benzene		2.7			0.23			ND	
Tetrahydrofuran[f]		18J			ND			<0.79U	
1,1,2-Trichloroethane		<1.7U			0.006J			<1.6U	

[a] Definitions of data qualifiers: B = compound detected in the method blank; D = result from diluted sample; J = estimated concentration; U = compound not detected (the value shown is the analytical detection limit).

[b] A hyphen indicates that the lab VOC/field VOC ratio was not calculated because the sample was below analytical detection limits, the values were not comparable (such as m/p xylene as compared with total xylene) or, in the case of nitrobenze, lab VOC results were not available.

[c] This concentration value was reported as being above the field VOC analysis upper detection limit; thus, this value was considered an estimate of the minimum concentration.

[d] NA = not applicable; lab VOC analysis does not measure nitrobenzene.

[e] These compounds were detected in the laboratory VOC analyses but were not screened for in the field VOC analyses.

[f] Tetrahydrofuran is not on the standard list of VOCs. It was detected in the tentatively identified compound (TIC) scan. No minimum detection limit was provided by the lab.

[g] ND = not detected.

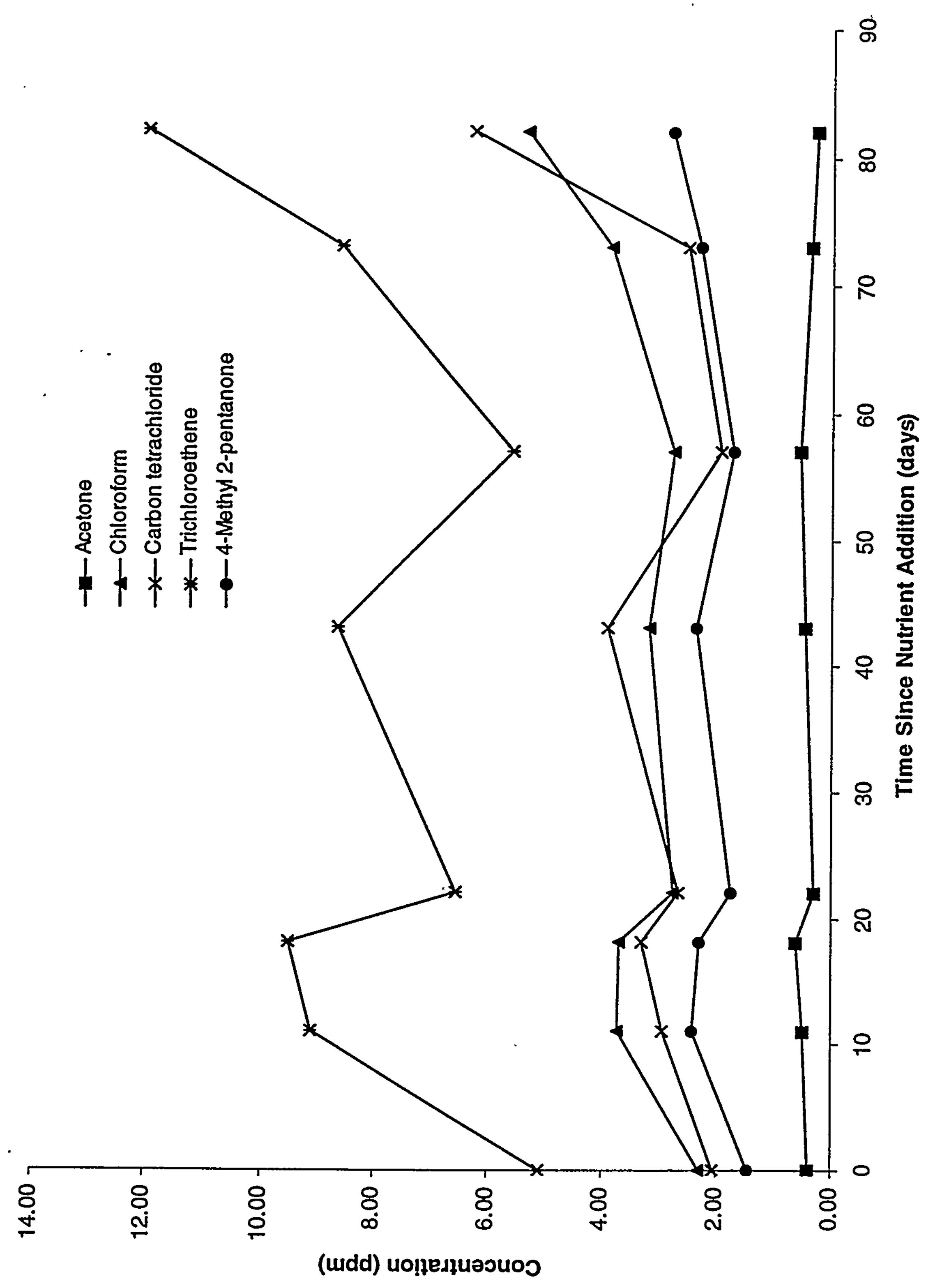


FIGURE 8.3 Average VOC Concentrations in Biodegradation Experimental Area XA4

The results of the comparison of the field and laboratory VOC concentrations were similar to the other experiments. Field VOC measurements were similar but usually higher than laboratory methods by a factor of up to 2 to 2.5. Nine compounds, which were not detected in the field method, were detected in the laboratory VOC method. Most of these were found at very low concentrations, well below 1.0 ppm. Tetrahydrofuran and acetonitrile were found at 18 and 26 ppm, respectively, in one sample. Neither of these compounds was detected in subsequent samples from this location.

Table 8.9 contains the pH, chloride, nutrient, and methanol data. Methanol was never detected in any of the samples. Chloride concentrations did not increase, but rather decreased slightly.

A nutrient profile of the soil was measured at several points during the performance monitoring period. Methanol concentrations in the soil were also measured. In addition, soil temperature, chloride, and pH of soil were measured on several occasions, as well as groundwater pH, VOCs, ORP, and dissolved oxygen (DO) concentrations.

An attempt was made to determine the effect of the soil mixing and nutrient addition process on the population of bacteria present in the soil. This was accomplished by using the phospholipid fatty acid (PLFA) analysis, as discussed in Section 5. Samples for PLFA analysis were collected from this area, as well as the control area, on four occasions. A comparison of the total number and relative abundance of bacteria between these sets of samples would then give an indication of the success of these organisms at surviving the soil mixing process and the impact of the nutrients and methanol.

Soil nutrient concentrations following treatment indicated that nitrogen concentrations (as measured by the total kjeldahl nitrogen [TKN] analysis) appeared to decrease from an average of 337 ppm before treatment to less than detection limits of 13 ppm after treatment. Nitrate was not detected in the posttreatment sample; it was also not detected in most of the pretreatment samples. Total phosphorous increased from an average of 35 to 261 ppm. It is likely that the change in nutrient levels is an artifact of the heterogeneity of the soil and the small number of samples collected rather than microbial activity.

The results of the PLFA analysis are summarized in Figure 8.4. The results of the analysis indicated that the amount of biomass increased following soil mixing. The first samples collected from XA1 and XA2 on September 30 were collected prior to any treatment. The next samples collected from XA2 and XA4 on December 1 contained much higher amounts of biomass. This finding indicates that the indigenous bacterial population was not destroyed by the initial application of steam and air, but rather was stimulated significantly. The data from samples collected at several points after treatment indicate that the amount of bacteria in XA2 decreased with time and returned to very low levels in the span of approximately 10 weeks. The biomass in the biodegradation experiment, however, showed a strong increase for the first six weeks, after which a decline was

TABLE 8.9 Summary of Miscellaneous Measurements for Experimental Area XA4 (Biodegradation — Nutrients Injected 11/20/97)

Soil Temperature		Soil pH		Soil Chloride		Measured Nutrients (mg/kg)			Methanol Concentration in Soil	
Value (°F)	Date Measured	Value (pH Units)	Date Measured	Value (mg/kg)	Date Measured		1/05/98	2/13/98	(mg/kg)	Date Measured
>120	11/6/07	7.5–7.7	12/15/97	78.3[a]	1/5/98	Sulfate	68.7	56.6	<69	1/5/98
116	11/10/97	7.5–7.6	1/5/98	100.7	1/19/98	Total kjeldahl nitrogen (TKN)	<12.9	<13.1	<13	2/13/98
88	11/20/97	7.3–7.5	1/19/98	96.20	2/13/98	Total phosphorous	298	261		2/13/98
76	11/25/97					Nitrate	<0.65	<0.66		2/13/98
74	12/2/97									
70	12/8/97									
57	12/15/97									

Depth to Groundwater Surface		Groundwater pH		Groundwater Oxidation Reduction Potential		Groundwater Dissolved Oxygen Concentration	
Value (ft)	Date Measured	Value (pH Units)	Date Measured	Value (mV)	Date Measured	Value (mg/L)	Date Measured
4.1	12/4/97	6.85	12/5/97	10.2	12/5/97	0.2	12/5/97
+2.0[b]	12/11/97	6.83	1/20/98	19.2	1/20/98	3.7	1/20/98
+1.6	12/12/97	7.70	2/16/98	-40.1	2/16/98	1.1	2/16/98
+1.5	12/16/97						
12.3	12/17/97[c]						
0	1/5/98						
+1.0	1/19/98						
+1.4	2/13/98						

[a] This average chloride value includes an anomalously low value of 14.7 mg/kg from the 0–2 ft interval. Excluding this sample, the average was 99.5 mg/kg.

[b] A plus sign indicates the depth of water above the ground surface.

[c] The well was baled dry on 12/16/97.

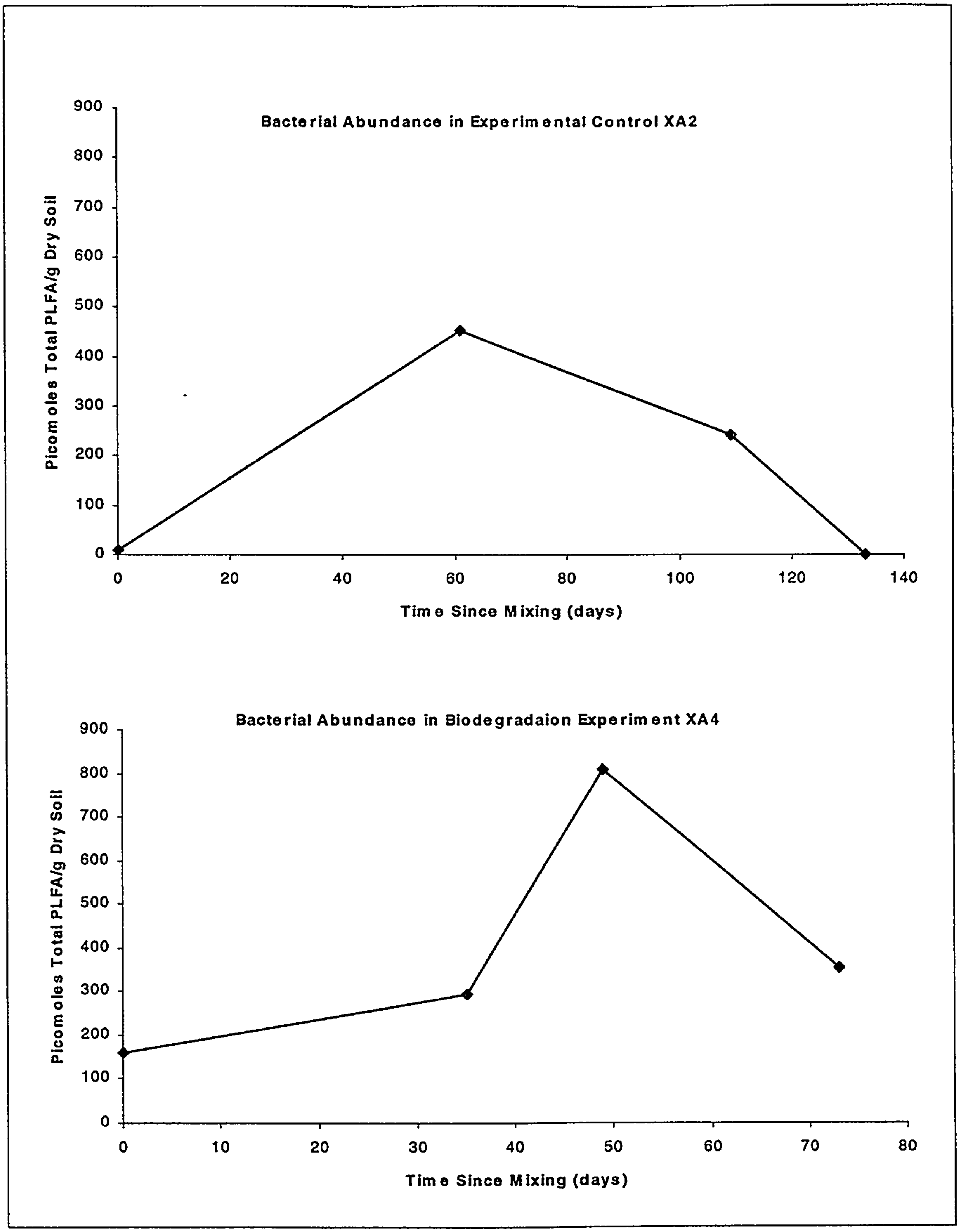


FIGURE 8.4 Results of PLFA Analysis in the Control and Biodegradation Experimental Area XA4

noted. The biomass present in the experimental soil achieved a density of almost twice the highest density present in the control. An analysis of the types of fatty acids detected also indicated that the biodegradation experiment contained a more diverse community of bacteria than the control. Overall, these findings suggest that bacterial growth was stimulated and diversity was enhanced by the mixing and nutrient addition. They also indicate that the bacterial population was changing throughout the study, and that steady-state conditions may not have been achieved.

Table 8.10 contains the groundwater data from this experiment. The concentrations of several volatile constituents, including acetone, 4 methyl-2-pentanone, methylene chloride, and chloroform decreased significantly over a two-month period. Other compounds, such as benzene, trichloroethene, and tetrachloroethene did not decrease significantly. These findings seem to indicate that biodegradation may have been occurring in the groundwater, albeit at so low a rate that the effect on soil concentrations could not be discerned within the 84-day monitoring period.

8.4 IRON-ADDITION EXPERIMENT XA3

In the first iron-addition experiment, the iron particles were mixed into the previously treated soil by pumping a mixture of approximately 50% iron in a water slurry containing a guar gum-thickening agent through the hollow Kelly bars of the soil mixing apparatus while the mixer was moving through the soil. The amount of water contained in the injected slurry was calculated to be less than the maximum amount of water that the soil could absorb, which ensured that the soil would not be fully saturated with water. Sufficient iron powder was added to increase the iron content of the soil by approximately 5%. After injection, the mixing equipment was moved through the soil column several times to ensure thorough mixing of the iron and soil. The resulting mixture of soil and iron was a homogenized, very wet material with the consistency of thick mud.

Following the iron addition, soil samples were collected from several depth intervals to a depth of 6 m (18 ft) bgs. The iron content was measured with a portable x-ray fluorescent analyzer (XRF). The XRF was calibrated by adding known amounts of iron powder to clean soil and by constructing a calibration curve. The XRF readings for the soil samples were then converted to added iron concentrations. This procedure was repeated four times during the experiment. Table 8.11 contains the results of this analysis. It indicates that the iron concentration varied from 3.5 to 9.2%; most concentrations were in the 4 to 5% range. The December 1 samples were collected from each sampling interval and represent the most reliable assessment of iron distribution in the soil. These data are shown in Figure 8.5. This figure shows that most of the values fell within the range of 4 to 5%, which indicates that the mixing of iron with the soil was very effective.

A groundwater monitoring well was placed in a borehole drilled into the treated soil. Groundwater was found to be present in the well within a few days of installation. Water was present

TABLE 8.10 Summary of Groundwater VOC Concentrations in Experimental Area XA4 (Biodegradation)

Constituent (mg/L)	Sample Date 12/19/97	Sample Date 1/20/98	Sample Date 2/16/98
Field VOC Compounds			
Acetone	4.6BD[a]	3.4BD	1.2BD
Benzene	0.066	0.05	0.061
Carbon tetrachloride	0.002J	0.003J	<0.005U
Chloroform	0.57D	0.29D	0.38D
1,1-Dichloroethane	<0.005U	<0.005U	<0.005U
1,2-Dichloroethane	<0.005U	0.002J	0.002J
1,1-Dichloroethene	<0.005U	<0.005U	<0.005U
1,2-Dichloroethene	0.005 (trans) 0.030 (cis)	0.004 (trans) 0.030 (cis)	0.005 (trans) 0.053 (cis)
Isobutanol	<0.2U	<0.2U	<0.2U
4-Methyl 2-pentanone	3.7D	2.6D	1.3D
Methylene chloride	0.13B	0.043B	0.074B
Nitrobenzene	NA[b]	NA	NA
Tetrachloroethene	0.056	0.064	0.057
Toluene	0.008	0.007	0.005
1,1,1-Trichloroethane	<0.005U	<0.005U	<0.005U
Trichloroethene	0.19	0.16	0.18
m/p Xylene	0.004J	0.003J	0.001J
o Xylene	0.004J	0.003J	0.001J
Other Compound[c]			
2-Butanone	0.081	0.027B	<0.02U

[a] Definitions of data qualifiers: B = compound detected in the method blank; D = result from diluted sample; J = estimated concentration; U = compound not detected (the value shown is the analytical detection limit).

[b] NA = not applicable; lab VOC analysis does not measure nitrobenzene.

[c] This compound was detected in the laboratory VOC analyses but was not measured in the field VOC analyses.

TABLE 8.11 Summary of Iron Concentrations in Experimental Area XA3

Sample Number	XRF Reading	Calculated Added Iron Concentrations (%)
Pretreated Soil (background)		
XA3-SB0 (11/1/97) (4–6)	27,400	0.0[a]
XA3-SB01 (11/1/97) (8–10)	24,900	0.0
XA3-SB01 (11/1/97) (12–14)	22,500	0.0
Average XRF background reading	24,933	0.0
Treated Soil		
XA3-SB01 (11/15/97) (0–2)	49,900	5.9
XA3-SB01 (11/15/97) (4–6)	44,400	4.6
XA3-SB01 (11/15/97) (8–10)	42,900	4.2
XA3-SB01 (11/15/97) (10–12)	43,900	4.5
Average		4.8
XA3-SB01 (11/21/97) (4–6)	44,600	4.6
XA3-SB01 (11/21/97) (8–10)	48,600	5.6
XA3-SB01 (11/21/97) (12–14)	49,600	5.8
Average		5.3
XA3-SB01 (12/1/97) (0–2)	45,600	4.9
XA3-SB01 (12/1/97) (2–4)	44,900	4.7
XA3-SB01 (12/1/97) (4–6)	45,300	4.8
XA3-SB01 (12/1/97) (6–8)	43,400	4.4
XA3-SB01 (12/1/97) (8–10)	39,700	3.5
XA3-SB01 (12/1/97) (10–12)	43,100	4.3
XA3-SB01 (12/1/97) (12–14)	43,700	4.4
XA3-SB01 (12/1/97) (14–16)	46,100	5.0
XA3-SB01 (12/1/97) (16–18)	46,900	5.2
Average		4.6
XA3-SB01 (12/8/97) (2–4)	45,700	4.9
XA3-SB01 (12/8/97) (4–6)	45,300	4.8
XA3-SB01 (12/8/97) (8–10)	44,600	4.6
XA3-SB01 (12/8/97) (12–14)	63,900	9.2
Average		5.9

[a] The added iron concentrations of pretreatment samples were assumed to be zero to correct for the effects of naturally occurring iron.

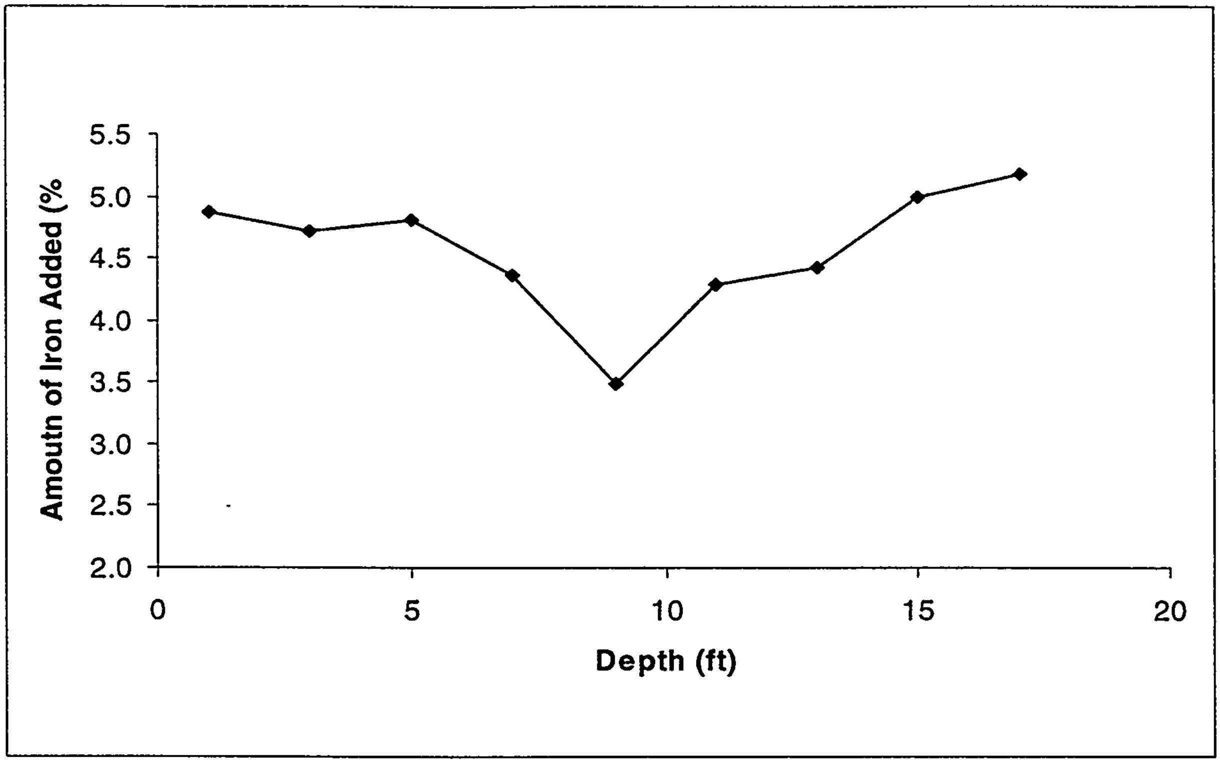


FIGURE 8.5 Amount of Iron Added to Experimental Area XA3

within the well throughout the entire experiment, which indicates that the soil was essentially saturated with water.

Soil cores were collected from this area to determine the effect the iron had on residual VOC concentrations. These cores were analyzed for VOCs by both field and fixed VOC analysis. The results of the average field VOC analysis are shown in Table 8.12. Figure 8.6 graphically depicts the same information for a number of important constituents. Following the SM/TESVE treatment of this area, residual VOC concentrations in the soil were relatively low. As a result, the initial VOC concentrations for this study were all relatively low, with only one contaminant, trichloroethene, present at concentrations above 1 ppm, as compared with several compounds present at concentrations as high as 5 to 7 ppm in the other three main experiments.

Figure 8.6 shows a rapid decrease in residual concentrations of several constituents; most decreases occurred within the first 11 days following iron injection. Several of the compounds of particular interest — 1,2-dichloroethene, chloroform, and trichloroethene — were reduced to the analytical detection limits of the field VOC analysis. The concentrations of several constituents, particularly methylene chloride, benzene, tetrachloroethene, and 4-methyl-2-pentanone, appeared to remain essentially unchanged throughout the experiment. The low initial concentrations of the

TABLE 8.12 Summary of Average Field VOC Measurements in Experimental Area XA3 (Iron Addition No. 1: 11/10/97)

	Pretreatment Samples	Post-SM/TESVE Treatment Samples	Initial Characterization Samples	Performance Monitoring Sample						
Constituent (mg/kg)	(9/30/97)	Day 0 (11/1/97)	Day 1 (11/11/97)	Day 3 (11/13/97)	Day 5 (11/15/97)	Day 11 (11/21/97)	Day 21 (12/1/97)	Day 28 (12/8/97)	Day 36 (12/16/97)	Day 95 (12/13/98)
Acetone	<0.1U[a]	<0.1U	<0.1U	<0.1U	0.13	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U
Benzene	1.39	0.26	0.26	0.28	0.26	0.11	0.17	0.30	0.13	0.21
Carbon tetrachloride	5.10	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U
Chloroform	1.19	0.54	0.14	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U
1,1-Dichloroethane	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U
1,2-Dichloroethane	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U
1,1-Dichloroethene	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U
1,2-Dichloroethene	3.57	0.46	0.27	0.11	0.15	<0.1U	<0.1U	0.10	<0.1U	<0.1U
Isobutanol	4.18	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U
4-Methyl 2-pentanone	0.62	0.37	0.31	0.15	0.24	0.11	0.13	0.20	0.13	0.20
Methylene chloride	1.06	0.55	0.24	0.22	0.33	0.12	0.32	0.38	0.19	0.30
Nitrobenzene	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U
Tetrachloroethene	0.23	<0.1U	0.46	0.85	0.25	0.25	0.40	0.34	0.38	0.26
Toluene	1.04	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U
1,1,1-Trichloroethane	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U
Trichloroethene	7.77	1.47	0.88	0.58	0.38	0.21	0.10	0.11	0.16	0.25
m/p Xylene	0.29	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U
o Xylene	0.27	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U
Total VOC	16.86	3.09	2.12	2.04	1.56	0.44	0.83	1.19	0.56	0.81
Diesel	64.00	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	2.00	1.00
Field screening	44.5	9.9	10.9	7.0	14.3	8.3	22.1	1.8	14.3	6.1
Water content (%)	14.8	30.9	34.4	35.5	34.7	36.4	32.3	32.2	23.5	27.8

[a] Definition of data qualifier: U = compound not detected (the value shown is the analytical detection limit).

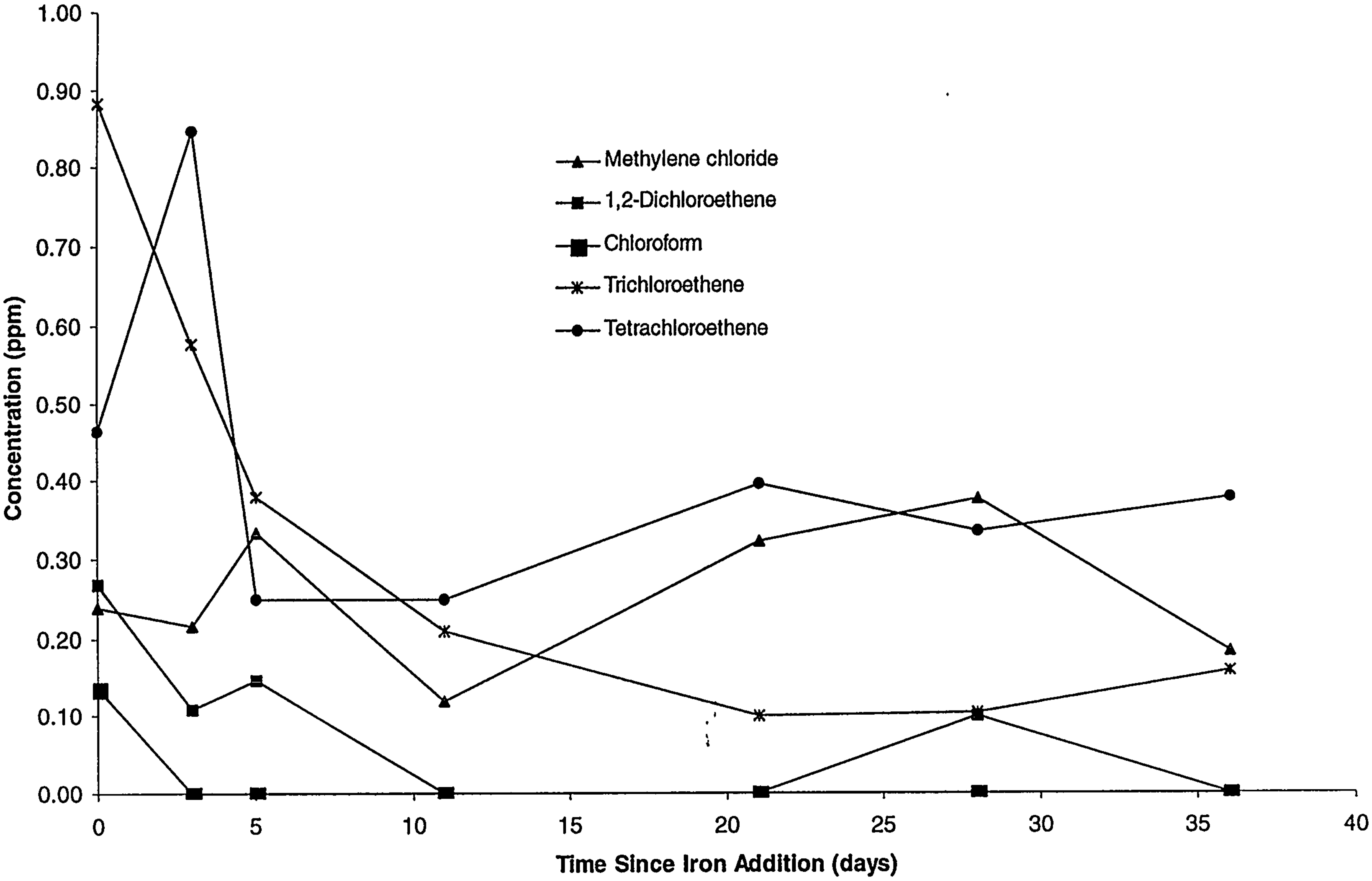


FIGURE 8.6 Average VOC Concentrations in Iron-Addition Experimental Area XA3

contaminants made accurate quantitation of residual concentrations difficult. Field VOC concentrations reported as below the 0.10-mg/kg detection limit are plotted as zero on this and similar figures, whereas their actual values could be somewhere above zero but less than 0.10 mg/kg.

Table 8.13 compares fixed laboratory results with field laboratory results. The results were similar to those discussed earlier; the field VOC results are similar, but overall somewhat higher than the laboratory results. Laboratory results confirmed that chloroform, which was initially present (prior to any treatment) at a concentration of 1.19 mg/kg by the field VOC method, was removed to below the field laboratory's detection limit of 0.10 mg/kg and less than the laboratory's detection limit of 0.007 mg/kg, a reduction of over 99.4%. Similarly, carbon tetrachloride, which was present at 6.34 mg/kg by the field VOC method prior to any treatment, was found to be below the analytical detection limit of 0.10 for the field VOC method and 0.006 mg/kg for the lab VOC method following SM/TESVE and iron addition. Trichloroethene, which was initially present at a concentration of 11.93 mg/kg by the field method and 16.0 mg/kg by the lab method was reported to be less than 0.10 mg/kg in the field analysis and was found to be present at 0.003 mg/kg in the lab analysis following treatment. These data corroborate the very low residual concentrations the iron addition was able to achieve in the test area.

The results of soil sample analysis of chloride ions and other parameters are shown in Table 8.14. Chloride concentrations increased somewhat during the experiment as a result of the dechlorination of the contaminants present. The chloride analysis results indicated an increase in chloride concentrations from 49 to 65 mg/kg. This low increase is not unexpected, given the low concentrations of chlorinated organic compounds present at the start of the experiment. The increase observed in chloride was much lower than the increase observed in subsequent experiments that were performed in soil with much higher initial VOC concentrations.

The soil pH value was also measured at several points in the project. Soil pH values are shown in Table 8.14. The soil pH in the control area was approximately 7.5, whereas in XA3 it was approximately 8.3 during the experiment. This increase in pH is consistent with the types of dechlorination reactions postulated in published literature for iron treatment of VOCs in groundwater.

Two samples of groundwater were removed from the groundwater monitoring well and analyzed for pH, DO, and ORP. One sample was analyzed for VOCs. The data from these analyses are shown in Tables 8.14 and 8.15. The analysis indicated that reducing conditions (i.e., low DO concentrations and negative ORP values) existed in the soil in which iron had been added. This is also consistent with postulated degradation mechanisms.

VOC concentrations in the groundwater were relatively low, compared with groundwater in experimental areas XA1A and XA4. The only contaminants present in concentrations over

TABLE 8.13 Comparison of Field VOC and Laboratory VOC Analytical Results for Experimental Area XA3 (Iron Addition No. 1)

	XA3-SB01 (9/29/97) (4–6)			XA3-SB01 (2/13/98) (8–10)			
Result	Field	Laboratory	Ratio (field/lab)	Field	Laboratory	Ratio (field/lab)	Average Ratio
Field VOC Compounds							
Acetone	<0.1U[a]	2.6BJ	-[b]	<0.1U	0.13B	-	-
Benzene	0.18	0.4J	0.43	0.26	0.064	4.06	2.09
Carbon tetrachloride	6.24	9.0	0.69	<0.1U	<0.006U	-	-
Chloroform	1.19	0.7U	1.61	<0.1U	0.002J	-	1.61
1,2-Dichloroethene	0.32	<0.34U (trans) 0.52 (cis)	-	<0.1U	<0.003U (trans) 0.009 (cis)	-	-
Isobutanol	1.71	<27.0U	-	<0.1U	0.26U	-	-
4-Methyl 2-pentanone	<0.1U	<2.7U	-	0.20	0.1	2.00	2.00
Methylene chloride	<0.1U	1.5B	-	0.35	0.01B	-	-
Tetrachloroethene	0.13	<0.69U	-	0.11	0.023	4.78	4.78
Toluene	0.54	1.1	0.49	<0.1U	0.02	-	-
1,1,1-Trichloroethane	<0.1U	<0.69U	-	<0.1U	<0.006U	-	-
Trichloroethene	11.93	16.0	0.75	<0.1U	0.003J	-	0.75
m/p Xylene[c]	0.17	1.7[c]	-	<0.1U	0.17[c]	-	-
o Xylene[c]	0.21	1.7[c]	-	<0.1U	0.17[c]	-	-
Other Compounds[d]							
Acetonitrile		15.0B			<0.1U3U		
2-Butanone		<0.69U			0.015J		
Carbon disulfide		<0.69U			0.002J		
Ethyl benzene		0.45J			0.003J		

[a] Definitions of data qualifiers: B = compound detected in the method blank; D = result from diluted sample; J = estimated concentration; U = compound not detected (the value shown is the analytical detection limit).

[b] A hyphen indicates that the lab VOC/field VOC ratio was not calculated because the sample was below analytical detection limits, the values were not comparable (such as m/p xylene as compared with total xylene) or, in the case of nitrobenze, lab VOC results were not available.

[c] Laboratory analysis reports xylene results as total xylene rather than as individual species that were measured in the field analysis. The total xylene laboratory result is shown in both rows containing field VOC results.

[d] These compounds were detected in the lab VOC analyses but were not measured in the field VOC analyses.

TABLE 8.14 Summary of Miscellaneous Measurements for Experimental Area XA3 (Control: Iron Injected 11/10/97)

Soil Temperature		Soil pH		Soil Chloride Ions	
Value (°F)	Date Measured	Value (pH Units)	Date Measured	(mg/kg)	Date Measured
>120	11/6/07	8.2-8.4	12/1/97	49	9/29/97
80	11/25/97	7.2-8.0	12/16/97	60[a]	12/4/97
71	12/2/97			65	2/13/98
68	12/8/97				
68	12/11/97				
58	12/18/97				
55	1/5/98				
52	2/2/98				

Depth to Groundwater Surface		Groundwater pH		Groundwater Oxidation/Reduction Potential		Groundwater Dissolved Oxygen Concentration	
(ft)	Date Measured	Value (pH Units)	Date Measured	(mV)	Date Measured	(mg/L)	Date Measured
6.7	12/4/97	8.40	12/5/97	−76.8	12/5/97	0.03	12/5/97
5.4	12/11/97	7.48	1/20/98	−29.6	1/20/98	0.91	12/11/97
5.6	12/12/97						
4.7	12/16/97						
6.6	1/5/98						
5.2	3/4/98						

[a] The chloride concentrations shown are the averages of four discrete samples collected at various depths.

TABLE 8.15 Summary of Groundwater VOC Concentrations in Experimental Area XA3 (Iron Addition No. 1)

Constituent (mg/L)	Sample Date (12/19/97)
Field VOC Compounds	
Acetone	0.55BD[a]
Benzene	0.024
Carbon tetrachloride	<0.005U
Chloroform	0.006
1,1-Dichloroethane	<0.005U
1,2-Dichloroethane	<0.005U
1,1-Dichloroethene	<0.005U
1,2-Dichloroethene	<0.002U (trans) 0.007 (cis)
Isobutanol	<0.200U
4-Methyl 2-pentanone	0.082
Methylene chloride	0.48BD
Tetrachloroethene	0.019
Toluene	0.002J
1,1,1-Trichloroethane	<0.005U
Trichloroethene	0.009
m/p Xylene	<0.005U
o Xylene	<0.005U
Other Compound[b]	
2-Butanone	0.034

[a] Definitions of data qualifiers:
B = compound detected in the method blank; D = result from diluted sample;
J = estimated concentration;
U = compound not detected (the value shown is the analytical detection limit).

[b] This compound was detected in the laboratory VOC analyses but was not measured in the field VOC analyses.

0.1 mg/L were acetone and methylene chloride, which were also reported in the laboratory blank. In addition, the highest concentrations of VOCs were benzene at 0.024 ppm and 4-methyl-2-pentanone, which was present at 0.082 ppm. Neither of these compounds was expected to react with the iron because they are not chlorinated compounds amenable to the abiotic dechlorination reactions with iron. Thus, their relative abundance was expected. The highest concentration of chlorinated organic material was tetrachloroethene at 0.019 ppm. Chlorinated VOC concentrations in the other groundwater samples ranged up to 8.2 ppm in XA1A and 0.57 in XA4. The lower VOC concentrations in groundwater could be an indication of the reactive nature of the iron, as well as an indicator of the lower residual VOC concentrations.

Approximately 48 hours after adding the iron, gas bubbles were noted rising to the surface directly above the mixed area. The gas could be seen rising through a portion of the experimental area where snow melt had collected and created a small puddle. Observations of the area surrounding the puddle indicated that the gas was emanating from numerous locations directly over the iron-augmented soil. Gas flow rate was not measured at this time; however, subsequent measurements of similar gas flow at other locations where iron had been added indicated that the flow of gas was on the order of 0.1 to 0.5 L (0.03 gal)/min/ft^2.

A sample of this gas was captured by placing the inverted funnel device described in Section 4 over one of the gas discharge points. Once the funnel was filled with gas, an evacuated Summa canister was used to collect a sample for analysis. The sampling was repeated several days later. Table 8.16 gives the analysis results of this gas. The gas was determined to be atmospheric air (that may have leaked into the sampling canister during sampling) and hydrogen; lesser amounts of the hydrocarbon gases methane and ethane were present. The second sample contained higher concentrations of hydrogen and other gases and lower concentrations of atmospheric air constituents (i.e., oxygen, nitrogen, and argon), primarily because an improved sample collection methodology reduced the amount of atmospheric air drawn into the sample container. The hydrocarbon gases methane and ethane are endpoints of the complete abiotic dechlorination of the chlorinated organics present in the soil. Thus, their presence is an indicator of the completeness of the dechlorination reaction.

The gas emanations decreased after four to six weeks; however, at the end of the study, more than 100 days after injection of the iron, small amounts of gas could occasionally be seen coming from the study area. Additional discussions regarding gas emanations can be found in Section 8.5.1.

TABLE 8.16 Summary of Gas Analysis in Experimental Area XA3 (Iron Addition No. 1)

	Gas composition (volume %)	
Constituent	11/25/97	12/3/97
Argon	0.675	0.218
Carbon dioxide	0.027	0.064
Carbon monoxide	ND[a]	0.045
Ethane	0.03	0.034
Hydrogen	10	84.2
Methane	0.008	0.04
Nitrogen	72.7	13.2
Oxygen	16.5	1.76
Water	<0.06	<0.3

[a] ND = not detected.

8.5 SUPPLEMENTAL IRON-ADDITION EXPERIMENTS

The success of the iron-addition experiment on reducing residual VOC concentrations prompted the planning and execution of five supplementary iron-addition experiments. These experiments were performed to verify the results of the initial study and to examine the effectiveness of the iron when used in various combinations with the SM/TESVE process.

8.5.1 Experiment XA6: Iron as a Primary Treatment Mechanism

The effectiveness of iron in destroying high concentrations of VOCs in soil was examined in this study. This was investigated to evaluate the potential for using iron as the primary treatment mechanism rather than the SM/TESVE process; the use of iron could result in lower costs. To simulate this treatment approach, the SM/TESVE process was not used prior to iron injection. The soil mixing equipment was used only to inject and mix the iron particles. Iron slurry in an amount sufficient to increase the iron concentration by approximately 3% was mixed with the soil using the soil mixing apparatus. No steam was used during the mixing process; only the water slurry containing iron and guar gum was injected into the soil. Following iron injection, a groundwater monitoring well was installed as discussed previously.

After the iron was injected and mixed, four samples of soil from experimental area XA6 were analyzed for total iron content using the XRF meter on three different occasions. The results are shown in Table 8.17. Calculated iron concentrations ranged from 2.2 to 4.1%, with an average of 3.1%. The vertical distribution of iron was fairly homogeneous; the shallower samples generally contained more iron than the deeper samples. Samples collected over an interval of 40 days did not show any decrease in iron concentration.

The effects of the iron addition were monitored by collecting and analyzing soil and groundwater samples over a 65-day period. Table 8.18 gives the analysis results of soil cores for average field VOC concentrations. Figure 8.7 shows some of these data in graphical form.

Because the soil was not treated by SM/TESEV prior to iron injection, the initial VOC concentrations were several orders of magnitude higher than in experimental area XA3. Following iron addition, the data showed a rapid reduction in certain volatile organics such as chloroform, carbon tetrachloride, and trichloroethene. The field screening VOC concentrations also decreased dramatically.

One chlorinated organic, methylene chloride, did not show a reduction and actually increased and then subsequently decreased over the span of the study. The increase in methylene chloride concentrations could be the result of the generation of methylene chloride as an intermediate in the dechlorination of chloroform and carbon tetrachloride. The literature indicates (Gillham and O'Hannesin 1994; Matheson and Tratnyek 1994) that methylene chloride is not highly amenable to abiotic dechlorination, which would account for the apparent accumulation of methylene chloride at sites where carbon tetrachloride and chloroform were present initially. This argument is complicated by the fact that methylene chloride was also present initially. Thus, its presence is not due exclusively to degradation of other chlorinated species.

As expected, several nonchlorinated volatile organics, including benzene, isobutanol, and 4-methyl-2-pentanone, did not decrease during the experiment. This illustrates the relative ineffectiveness of the iron on nonchlorinated materials.

Several of the soil samples were also analyzed by the conventional laboratory. The results generally corroborate the field VOC results. The laboratory results identified the presence of two other possible intermediates — vinyl chloride and chloroethane. These compounds were present in only one sample collected early in the experiment at concentrations of 0.18 and 0.065 ppm, respectively.

One concern often discussed related to the iron-mediated dechlorination of chlorinated solvents is the accumulation of vinyl chloride in the samples. Vinyl chloride is considered a more

TABLE 8.17 Summary of Iron Concentrations in Experimental Area XA6 (Iron Addition No. 2)

Sample Number	XRF Reading	Calculated Added Iron Concentration (%)
Pretreated Soil (background)		
XA6-SB01 (12/4/97) (0–2)-GS	37,900	0.0[a]
XA6-SB01 (12/4/97) (2–4)-GS	34,600	0.0
XA6-SB01 (12/4/97) (4–6)-GS	24,600	0.0
XA6-SB01 (12/4/97) (4–6)-GS	25,300	0.0
XA6-SB01 (12/4/97) (8–10)-GS	24,300	0.0
XA6-SB01 (12/4/97) (8–10)-GS	23,100	0.0
XA6-SB01 (12/4/97) (12–14)-GS	26,300	0.0
XA6-SB01 (12/4/97) (12–14)-GS	26,200	0.0
Average background XRF reading	27,788	0.0
Treated Soil		
XA6-SB01 (12/10/97) (2–4)-GS	40,000	2.9
XA6-SB01 (12/10/97) (4–6)-GS	40,700	3.0
XA6-SB01 (12/10/97) (8–10)-GS	39,000	2.6
XA6-SB01 (12/10/97) (12–14)-GS	38,000	2.4
Average		2.7
XA6-SB01 (12/15/97) (0–2)-GS	39,300	2.7
XA6-SB01 (12/15/97) (4–6)-GS	39,100	2.7
XA6-SB01 (12/15/97) (8–10)-GS	41,300	3.2
XA6-SB01 (12/15/97) (12–14)-GS	37,100	2.2
Average		2.7
XA6-SB01 (1/19/98) (0–2)-GS	45,300	4.1
XA6-SB01 (1/19/98) (4–6)-GS	45,000	4.1
XA6-SB01 (1/19/98) (4–6)-GS	41,400	3.2
Average		3.8

[a] The added iron concentrations of pretreatment samples were assumed to be zero to correct for the effects of naturally occurring iron.

TABLE 8.18 Summary of Average Field VOC Measurements in Experimental Area XA6 (Iron Addition No. 2: 12/9/97)

Constituent (mg/kg)	Initial Characterization Samples	Performance Monitoring Sample						
	(12/4/97)	Day 1 (12/10/97)	Day 6 (12/15/97)	Day 13 (12/22/97)	Day 27 (1/5/98)	Day 34 (1/12/98)	Day 41 (1/19/98)	Day 65 (2/13/98)
Acetone	1.82	0.78	0.65	0.59	0.52	0.44	0.78	0.66
Benzene	8.19	4.41	3.74	6.62	2.89	3.56	3.65	4.71
Carbon tetrachloride	8.48	1.25	0.23	<0.1U	0.99	<0.1U	0.20	0.15
Chloroform	17.65	2.70	0.14	<0.1U	0.14	0.20	0.23	0.18
1,1-Dichloroethane	<0.1U	<0.1U	<0.1U	<0.1U	0.10	<0.1U	<0.1U	<0.1U
1,2-Dichloroethane	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U
1,1-Dichloroethene	<0.1U[a]	0.15	<0.1U	0.15	<0.1U	<0.1U	<0.1U	<0.1U
1,2-Dichloroethene	<0.1U	0.35	0.18	0.28	0.14	0.34	0.20	<0.1U
Isobutanol	6.42	1.86	1.74	1.70	1.71	1.54	1.88	1.90
4-Methyl 2-pentanone	5.41	0.86	1.11	0.95	0.54	0.79	0.94	0.97
Methylene chloride	1.76	8.92	6.26	19.80	3.30	5.31	7.92	11.37
Nitrobenzene	11.72	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U
Tetrachloroethene	1.24	0.89	1.49	1.14	2.58	0.52	0.55	0.54
Toluene	9.91	0.86	1.31	1.41	2.13	0.91	0.97	1.17
1,1,1-Trichloroethane	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U	<0.1U
Trichloroethene	28.03	28.70	17.19	12.88	5.31	1.53	1.20	0.70
m/p Xylene	0.23	0.26	0.49	0.39	0.58	0.35	0.30	0.36
o Xylene	0.19	0.16	0.32	0.24	0.36	0.20	0.24	0.26
Total VOC	89.09	52.04	34.44	45.93	19.85	15.18	18.62	22.47
Diesel	19.25	4	8	21	24	6	7	8
Field screening	705	495	119	150	30	141	85	14
Water content (%)	18	29.4	23.0	23	31.5	29.7	31	28.7

[a] Definition of data qualifier: U = compound not detected (the value shown is the analytical detection limit).

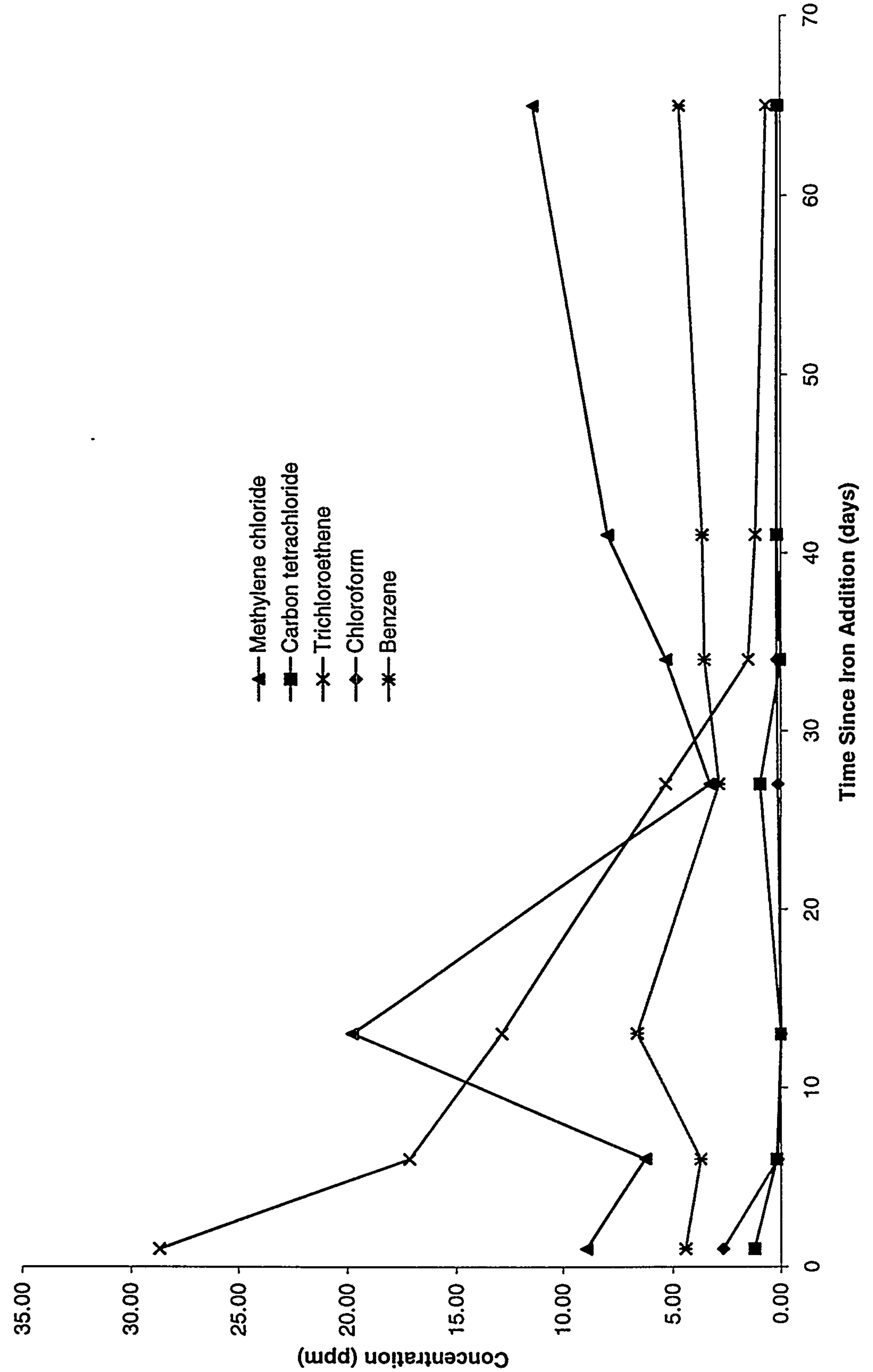


FIGURE 8.7 Average VOC Concentrations in Iron-Addition Experimental Area XA6 (Iron Addition No. 2)

potent hazard than the original products, and, thus, if accumulations had been noted in this study, the effectiveness of the treatment would have been questionable. The lack of detectable vinyl chloride in most of the samples indicates that no such accumulation was occurring.

Soil temperature, chloride, and pH data are shown in Table 8.19. The soil temperature never exceeded 20°C (68°F), which is only 11°C (52°F) above the ambient soil temperature of 10–13°C (50–55°F). The small increase in temperature was probably the result of the friction created by the soil mixing equipment during injection and mixing of the iron.

Chloride concentrations increased with time from pretreatment levels of approximately 100 ppm to a maximum of 366 ppm after 41 days of treatment. A calculation of the amount of chlorine initially present associated with the various chlorinated solvents indicated that approximately 50 ppm of chloride would be liberated if all of the chlorinated solvent was completely dechlorinated. The fact that the chloride concentration increased by 260 ppm could mean that other chlorine-containing materials not detected in the field or laboratory VOC analysis were present and degraded by the iron, or that a greater quantity of chlorinated solvents was destroyed than that measured in the soil.

Initially, soil pH values increased slightly but later returned to previous levels.

Groundwater depth, pH, ORP, and DO are shown in Table 8.19; sample data from the well in experimental area XA6 are shown in Table 8.20. Several days after soil was treated, the water level in the well was found to be approximately 0.6 m (2 ft) above the ground surface, much like what was found in experimental area XA4. Groundwater was actually overflowing from the well casing. Gas bubbles also were noted to be rising to the surface within the well casing. It appears that hydrogen gas generation near the well screen pressurized the groundwater sufficiently to raise the water level within the casing.

The DO data indicate that only very small amounts of DO were present. A low but positive ORP value was recorded. The groundwater DO and ORP values were measured in water baled from the wells in which there was opportunity for oxygen to contact the water, which would have altered the DO and ORP values. Thus, the reported values should not be considered definitive.

Several VOCs were detected in the groundwater collected on December 19, 1998, 10 days after the iron injection. The highest concentration was methylene chloride at 17 ppm. Methylene chloride was also found in relatively high concentrations in treated soil samples. Possible reasons for the presence of methylene chloride in the iron-treated soil were discussed above. The same rationale applies to the water samples; however, in the case of the groundwater sample, methylene chloride was also found in the blank sample, which makes the quantitation of methylene chloride somewhat uncertain. The other compounds found at high concentrations were acetone (which was

TABLE 8.19 Summary of Miscellaneous Measurements for Experimental Area XA6 (Iron Addition No. 2 — Iron Injected 12/9/97)

Soil Temperature		Soil pH		Soil Chloride Ions[a]	
Value (°F)	Date Measured	Value (pH Units)	Date Measured	Value (mg/kg)	Date Measured
68	12/12/97	7.2–7.3	12/10/97	107	12/4/97
68	12/16/97	7.1–7.5	1/19/98	357	1/5/98
67	12/18/97			366	1/19/98
64	12/22/97			328	2/13/98
60	1/5/98				

Depth to Groundwater Surface		Groundwater pH		Groundwater Oxidation/Reduction Potential		Groundwater Dissolved Oxygen	
Value (ft)	Date Measured	Value (pH Units)	Date Measured	Value (mV)	Date Measured	Value (mg/L)	Date Measured
+ 2.9 (casing overflowing)	12/16/97	7.15	2/19/98	2.6	2/19/98	0.72	2/19/98
5.6	1/5/98						
4.2	2/16/98						

[a] The chloride concentrations shown are the averages of four discrete samples collected at various depths.

also found in the blank), benzene, and 4-methyl 2-pentanone. As mentioned previously, these are all nonchlorinated species that were not expected to be destroyed by the iron; thus, their relative abundance in groundwater was expected. Trichloroethene, carbon tetrachloride, and chloroform, which were the most abundant compounds in the soil prior to treatment, were present only at very low or nondetectable levels in the groundwater samples. The relatively low concentrations in groundwater collected only 10 days after injecting the iron, as contrasted with their abundance in soil prior to treatment and their abundance in groundwater from experimental areas not treated with iron, demonstrates the effectiveness of the iron in reducing residual concentrations of chlorinated organic compounds in groundwater as well as soil.

As mentioned previously, gas emanations were observed 48 hours after injection of the iron. The emanations decreased greatly after approximately three weeks; however, some gas emanations were noted as late as March 3, 1998, almost four months after treatment. Two gas samples were collected from this area by using the methodology discussed in Section 4. One sample was collected

TABLE 8.20 Summary of Groundwater VOC Concentrations in Experimental Area XA6 (Iron Addition No. 2)

Constituent (mg/L)	Sample Date (12/19/97)
Field VOC Compounds	
Acetone	2.20BD[a]
Benzene	1.50D
Carbon tetrachloride	<0.005U
Chloroform	0.15
1,1-Dichloroethane	0.008
1,2-Dichloroethane	0.04
1,1-Dichloroethene	<0.005U
1,2-Dichloroethene	<0.002 (trans) 0.130 (cis)
Isobutanol	<0.2U
4-Methyl 2-pentanone	1.20DJ
Methylene chloride	17.00BD
Tetrachloroethene	0.045
Toluene	0.073
1,1,1-Trichloroethane	<0.005U
Trichloroethene	0.49DJ
Xylene (total)	0.022
Other Compound[b]	
1,1,2 Trichloroethane	0.002J

[a] Definitions of data qualifiers: B = compounds detected in the method blank; D = result from diluted sample; J = estimated concentration; U = compound not detected (the value shown is the analytical detection limit).

[b] This compound was detected in the laboratory VOC analyses but was not measured in the field VOC analysis.

from the well casing and the other from a gas discharge point in the soil approximately 0.6 m (2 ft) from the well casing. Table 8.21 gives the results of analysis of these samples. As with the previous samples, the gas was determined to be essentially pure hydrogen with lesser amounts of hydrocarbon gases. The most significant finding of the gas composition analysis was the presence of methane (0.387%), ethane (0.876%), and propane (0.03%); these three compounds are likely terminal degradation products from the dechlorination reaction.

One of the gas samples was also analyzed for trace organics. The results of this analysis are included in Table 8.21. Significant concentrations of the same chlorinated VOCs found in the soil were present in the gas as well, particularly methylene chloride and trichloroethene. This gas sample was collected on December 18, 1998, nine days into the experiment. At this point in time, the trichloroethene was still over 15 mg/kg in the soil and methylene chloride was almost 20 mg/kg in the soil, which accounts for their high concentrations in the off-gas. In addition to methylene chloride, two other possible breakdown products, 1,2-dichloroethene and 1,1-dichloroethane, were found in the gas but were not found in soil prior to treatment.

The generation of by-product gas from the iron-mediated hydrolysis of water resulted in a small but measurable flux of gas from the soil into the atmosphere. Because this gas also contained VOCs, there was also a flux of VOCs from the soil into the atmosphere. To determine the magnitude of this flux, the gas flow rate was measured several times and at several locations, and the mass of VOCs that could have been emitted from the study area was calculated. Table 8.22 shows the results of these calculations and the flux as a percentage of the VOCs originally present in the soil for selected compounds. The amount of VOCs removed from the soil by gas generation ranged from 0.15 to 21% of the total amount initially present. Methylene chloride emissions were estimated to be greater than the amount originally present, which supports the hypothesis that methylene chloride was being generated by the dechlorination of chloroform and carbon tetrachloride.

8.5.2 Experiment XA7: Iron Treatment with Limited Steam Addition

This experiment was very similar to XA6, except that approximately one-half the amount of iron was injected (1.5% iron as compared with 3% in XA6). As with XA6, the soil was not previously treated by the SM/TESVE process. However, a limited amount of steam was injected at the same time the iron slurry was added. The steam was added only in an amount sufficient to aid the soil mixing operation. Mixing of soil in XA6 was very slow and difficult because of the lack of steam and the moisture associated with the steam condensation. To improve mixing, steam was added. A side benefit of the steam was that it heated the soil, which increased the reaction rate. No hot air was used. The rate of steam injection was such that the steam condensed in the soil immediately after injection. Thus, no off-gas generation or removal of organics through air stripping

TABLE 8.21 Off-Gas Composition and Trace Organic Constituents for Experimental Area XA6 (Iron Addition No. 2)

Constituent (mg/kg)	Gas Composition (volume %)	
	12/17/97	12/18/97
Argon	0.229	0.071
Carbon dioxide	0.07	0.142
Carbon monoxide	<0.009	<0.015
Ethane	0.464	0.876
Hydrogen	71.3	91.4
Methane	0.286	0.387
Nitrogen	21.8	5.62
Oxygen	5.37	1.43
Propane	0.031	<0.03
Water	<0.3	<0.13

Trace Organics	Gas Concentration (ppmv)
Benzene	56.1E[a]
1-Butanol	40.5E
Carbon tetrachloride	0.43
Chloroform	1.64
Cyclohexane	28.6E
1,1 Dichloroethane	1.01
cis-1,2-Dichloroethene	4.71E
Ethyl benzene	0.83
Methylene chloride	134.4E
Tetrachloroethene	8.16E
Toluene	14.7E
Trichloroethene	128.1E
1,2,4 Trimethylbenzene	0.2
m/p Xylene	2.81
o Xylene	0.79

[a] Definition of data qualifier: E = concentration exceeded the calibration range of the instrument.

TABLE 8.22 Summary of Gas Flow Rates and VOC Flux for Experimental Area XA6 (Iron Addition No. 2)

Constituent (mg/kg)	Gas Concentration (ppmv)	Molecular Weight	Mass Discharged per Day[a] (g)	Mass Discharged in Three Weeks (g)	Concentration Originally Present (mg/kg)	Mass Originally Present[b] (g)	% Released
Benzene	56.1	78.11	1.42	29.72	8.19	288.4053	10.31
1-Butanol	40.5	74.14	0.97	20.37	6.42	225.8667	9.02
Carbon tetrachloride	0.43	153.82	0.02	0.45	8.48	298.584	0.15
Chloroform	1.64	119.38	0.06	1.33	17.65	621.192	0.21
cis-1,2-Dichloroethene	4.71	96.14	0.15	3.07	<0.10U[c]	3.52	87.25
1,1-Dichloroethane	1.01	96.94	0.03	0.66	<0.10U	3.52	18.87
Methylene chloride	134.4	84.93	3.69	77.42	1.76	61.776	125.32
Tetrachloroethene	8.16	165.83	0.44	9.18	1.24	43.736	20.99
Toluene	14.7	92.14	0.44	9.19	9.91	348.832	2.63
Trichloroethene	128.1	131.39	5.44	114.16	28.03	986.656	11.57
m/p Xylene	2.81	106.17	0.10	2.02	0.23	7.92	25.55
o Xylene	0.79	106.17	0.03	0.57	0.19	6.512	8.74

[a] The gas flow rate used in this calculation was 7,800 L/day per test area.

[b] Mass of soil in test column 26 $yd^3 \times 27\ ft^3/yd^3 \times 110\ lb/ft^3 \times 454$ g/lb = 3.52E7 g.

[c] Definition of data qualifier: U = compound not detected (the value shown is the analytical detection limit).

occurred. Therefore, the only difference between experiments XA6 and XA7 was the amount of iron and the increased soil temperature.

Soil samples from XA7 were analyzed on three occasions for total iron content with the XRF meter. Calculated iron concentrations ranged from 0.6 to 2.3%, with an average of 1.3%. The distribution of iron in this experiment was not as consistent as was found in XA3 and XA6. The shallow samples 0–1.8 m (0–6 ft) contained iron concentrations two to three times as high as the deeper samples 2.4–4.3 m (8–14 ft). Samples collected over an interval of 40 days did not show any decrease in iron concentrations.

Gas emanations were observed in this experiment; however, the rate of gas generation appeared to be much lower than in XA6, most likely because of the lower iron concentration. No gas sample was collected from this area.

The effect of the iron on VOC concentrations was monitored for 64 days. Table 8.23 gives the results of performance monitoring of this system for VOCs, averaged across the depth of the experimental area. Figure 8.8 shows how the concentrations of the most abundant VOC contaminants changed over time. The results of this experiment were very similar to XA6, except that the reduction rate of VOCs was somewhat higher than in XA6. The increased degradation rate was presumably because of the higher soil temperature. The soil temperature at the start of the experiment was 41°C (106°F) in XA7, compared with approximately 20°C (68°F) in XA6. The rapid destruction rate also indicates that even at less than 2% iron addition, the reaction proceeded rapidly.

Split samples for laboratory VOC analysis were also collected and compared with the field VOC results. The results of the comparison were similar to those discussed for XA6.

Table 8.24 gives the data for miscellaneous parameters. The soil temperature remained elevated for approximately one month after mixing. As with XA6, chloride concentrations increased; in this case, by approximately 185 ppm. The soil pH did not change appreciably.

A groundwater monitoring well was installed in this area as well. The depth to groundwater decreased throughout the experiment; it was 1 m (3.4 ft) bgs by the end of the study. One sample was recovered from the well. The ORP and DO were measured, and both parameters indicated that reducing conditions existed below the ground.

The results of VOC analysis of this groundwater sample are shown in Table 8.25. The results were very similar to XA6, in that relatively high concentrations of methylene chloride were found. Also, the concentrations of the other chlorinated solvents such as chloroform, carbon

TABLE 8.23 Summary of Average Field VOC Measurements in Experimental Area XA7 (Iron Addition No. 3: Iron Injected 12/10/97)

	Initial Characterization Samples	Performance Monitoring Sample						
Constituent (mg/kg)	(12/4/97)	Day 1 (12/11/97)	Day 5 (12/15/97)	Day 12 (12/22/97)	Day 26 (1/5/98)	Day 33 (1/12/98)	Day 41 (1/20/98)	Day 64 (2/13/98)
Acetone	2.56	0.75	0.57	0.58	0.51	0.45	0.41	0.36
Benzene	4.47	2.76	0.98	3.17	1.45	2.36	1.62	1.64
Carbon tetrachloride	17.36	0.11	0.20	<0.10U[a]	<0.10U	<0.10U	<0.10U	<0.10U
Chloroform	23.80	1.58	1.29	0.50	0.26	0.25	0.21	0.22
1,1-Dichloroethane	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
1,2-Dichloroethane	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
1,1- Dichloroethene	<0.10U	0.13	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
1,2-Dichloroethene	1.28	0.45	0.12	0.25	0.22	0.19	0.16	0.21
Isobutanol	0.47	0.23	0.30	0.23	0.27	0.25	0.25	0.16
4-Methyl 2-pentanone	1.63	0.60	0.69	0.59	0.63	0.99	0.51	0.41
Methylene chloride	5.35	8.70	1.37	11.80	3.46	5.48	5.50	3.98
Nitrobenzene	0.32	<0.10U	<0.10U	<0.10U	<0.10U	0.10	<0.10U	<0.10U
Tetrachloroethene	0.87	0.75	0.33	0.73	0.40	0.68	0.36	0.24
Toluene	1.80	1.21	0.56	1.30	0.67	1.45	0.89	0.86
1,1,1-Trichloroethane	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
Trichloroethene	38.49	20.13	3.36	4.21	1.01	1.14	0.62	0.59
m/p Xylene	0.30	0.32	0.21	0.35	0.21	0.46	0.28	0.26
o Xylene	0.27	0.21	0.18	0.23	0.17	0.40	0.24	0.18
Total VOC	91.76	37.83	8.80	23.55	8.75	13.12	10.61	8.54
Diesel	24	7	6	9	6	11	9	7
Field screening	1,275	311	207	114	30	81	11	10
Water content (%)	15.7	29.5	22.7	23	28.5	27.8	28.2	26.0

[a] Definition of data qualifier: U = compound not detected (the value shown is the analytical detection limit).

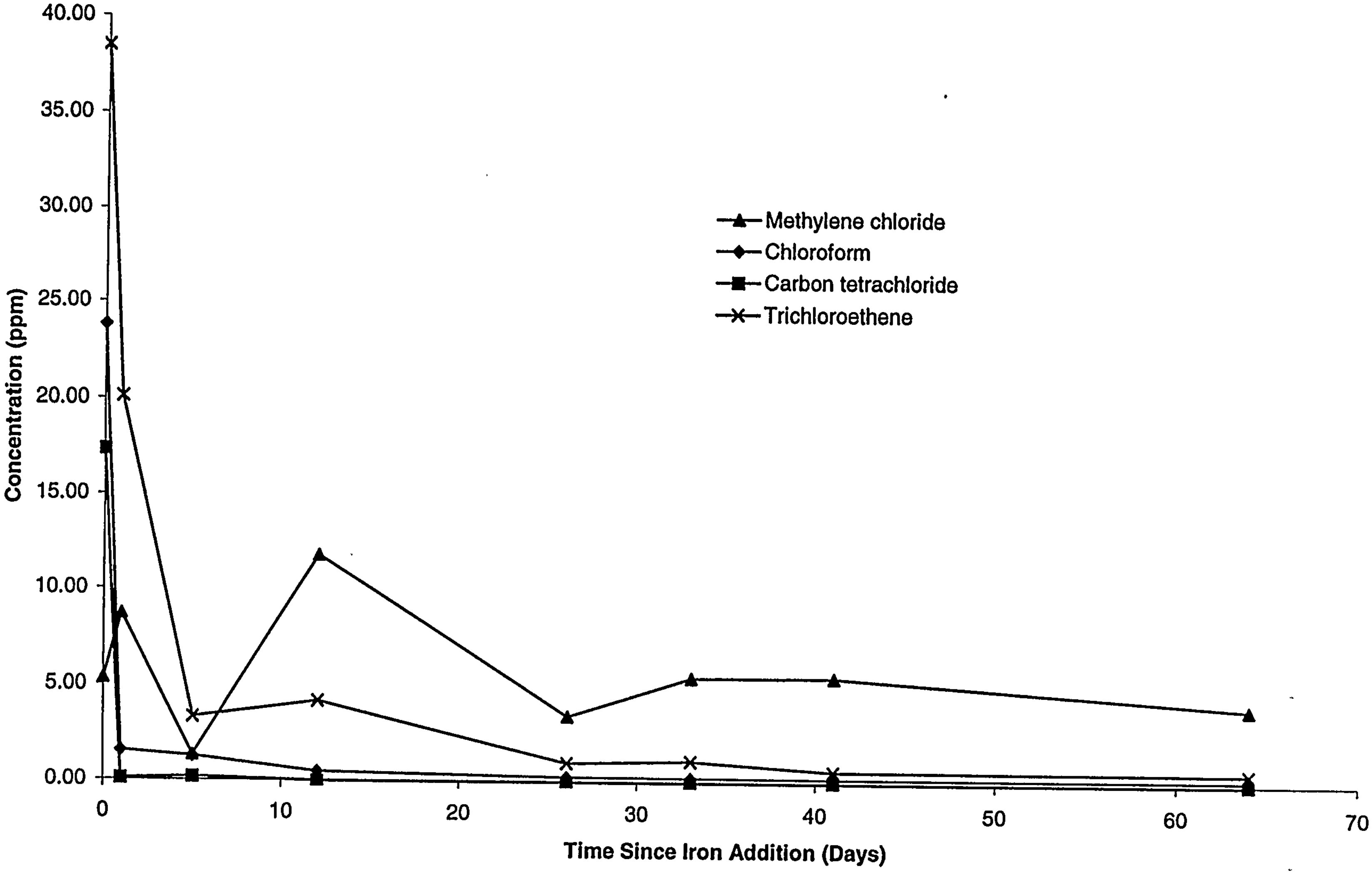


FIGURE 8.8 Average VOC Concentrations in Experimental Area XA7

TABLE 8.24 Summary of Miscellaneous Measurements for Experimental Area XA7 (Iron Addition No. 2)

Soil Temperature		Soil pH		Soil Chloride Ions[a]	
Value (°F)	Date Measured	Value (pH Units)	Date Measured	Value (mg/kg)	Date Measured
104	12/11/97	7.4–7.5	12/11/97	94.6	12/4/97
99	12/12/97	7.4–7.8	12/15/97	247	1/5/98
71	12/18/97			282	1/19/98
68	12/22/97			216	2/13/98
58	1/5/98				
50	2/2/98				

Depth to Groundwater Surface		Groundwater pH		Groundwater Oxidation/Reduction Potential		Groundwater Dissolved Oxygen	
Value (ft)	Date Measured	Value (pH Units)	Date Measured	Value (mV)	Date Measured	Value (mg/L)	Date Measured
6.7	12/12/97	7.54	2/19/98	-0.2	2/19/98	0.5	2/19/98
4.5	1/5/98						
3.4	2/16/98						

[a] The chloride concentrations shown are the averages of four discrete samples collected at various depths.

tetrachloride, and trichloroethene, which were present in high concentrations in the soil, were present only in relatively low concentrations in groundwater.

8.5.3 Experiments XA8 and XA9: Iron Injection Integrated with SM/TESVE

The discussion of these two experiments was combined because they were essentially identical. While injecting the iron for experiment XA8, an underground bolder was encountered that stopped further progress at this location. The rig was moved over several feet and a second attempt was made, this time successful. This second attempt was called experiment XA9.

TABLE 8.25 Summary of Groundwater VOC Concentrations in Experimental Area XA7 (Iron Addition No. 3)

Constituent (mg/L)	Sample Date 2/19/98
Field VOC Compounds	
Acetone	2.90BD[a]
Benzene	0.540D
Carbon tetrachloride	<0.005U
Chloroform	0.170
1,1-Dichloroethane	0.004J
1,2-Dichloroethane	0.015
1,1-Dichloroethene	<0.005U
1,2-Dichloroethene	<0.002 (trans) 0.058 (cis)
Isobutanol	<0.20U
4-Methyl 2- pentanone	0.590DJ
Methylene chloride	11.00BD
Tetrachloroethene	0.130
Toluene	0.052
1,1,1-Trichloroethane	<0.005U
Trichloroethene	0.240DJ
Xylene (total)	0.013
Other Compounds[b]	
Chloromethane	0.060
Ethyl benzene	0.003J
1,1,2 Trichloroethane	0.001J

[a] Definitions of data qualifiers: B = compound detected in the method blank; D = result from diluted sample; J = estimated concentration; U = compound not detected (the value shown is the analytical detection limit).

[b] These compounds were detected in the laboratory VOC analyses but were not measured in the field VOC analyses.

In these two experiments, the iron slurry was injected simultaneously with the SM/TESVE process, while the steam and air were being injected. The goal of the experiments was to determine whether a second soil mixing step, which prior to this experiment had been used to inject and mix the iron particles, could be eliminated by injecting the iron during the initial SM/TESVE step. The iron content of these experiments was approximately 2%.

Soil samples from these areas were collected for 38 days following iron injection. VOC concentrations were measured by using field VOC screening and field VOC techniques. At several points during the evaluation period, samples were collected for VOC analysis in the fixed laboratory to verify the field laboratory's results and to determine whether intermediates or stable end products that were not being quantified by the field VOC method were being formed.

Two samples of gas emanations were collected from this area. These samples were analyzed for trace organic compounds only.

Tables 8.26 and 8.27 give the average VOC concentrations from the field VOC method for these two experiments. At this location, the main contaminant of concern was tetrachloroethene, which was initially present at 116 ppm in XA8 and 97 ppm in XA9. The other VOCs detected were trichloroethene and 1,2-dichloroethene, which are breakdown products of tetrachloroethene. Both areas showed a dramatic drop in VOC concentrations before the first sample was collected, five days after treatment. Tetrachloroethene concentrations were reduced by over 99% in five days. The other contaminants were generally reduced to below detection limits. Because of the integration of the iron addition with the SM/TESVE process, it is impossible to tell which mechanism was responsible for the high degree of removal, the vapor extraction or the iron treatment.

No methylene chloride was detected during this experiment. This observation supports the hypothesis that the methylene chloride observed in XA3, XA6, and XA7 was due to the degradation of carbon tetrachloride and chloroform, because neither of these materials was present in XA8 or XA9.

Table 8.28 compares field and lab VOC results for two samples from XA9, taken 30 days after treatment. These samples confirm the destruction of the VOCs originally present. Tetrachloroethene was found at 0.004 and 0.008 mg/kg in the lab VOC analysis results for the two samples, compared with an initial concentration of 96.6 mg/kg (99.99% removal). All other VOCs initially present were at or below analytical detection limits of 0.006 ppm. No evidence of breakdown products was observed.

No other soil analyses were performed, and no groundwater samples were collected from these test areas.

TABLE 8.26 Summary of Average Field VOC Measurements in Experimental Area XA8 (Iron Addition No. 4: 12/12/97)

Constituent (mg/kg)	Initial Characterization Samples (12/11/97)	Performance Monitoring Sample Results[a] Day 5 (12/17/97)	Day 10 (12/22/97)	Day 25 (1/6/98)	Day 31 (1/13/98)	Day 38 (1/20/98)
Acetone	<0.10U[b]	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
Benzene	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
Carbon tetrachloride	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
Chloroform	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
1,1-Dichloroethane	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
1,2-Dichloroethane	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
1,1-Dichloroethene	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
1,2-Dichloroethene	1.27	<0.10U	<0.10U	<0.10U	<0.10U	0.25
Isobutanol	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
4-Methyl 2-pentanone	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
Methylene chloride	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
Nitrobenzene	0.10	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
Tetrachloroethene	115.68	0.22	0.95	0.97	1.25	1.40
Toluene	0.73	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
1,1,1-Trichloroethane	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
Trichloroethene	3.74	<0.10U	0.19	<0.10U	<0.10U	<0.10U
m/p Xylene	0.20	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
o Xylene	0.23	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
Total VOC	121.34	0.22	1.01	0.97	1.25	1.48
Field screening	432	12	12	13	10	7
Water content (%)	16.8	19.8	16	20.8	26.2	22.6

[a] The values reported are the mathematical averages of samples collected from depth intervals of 0–2, 4–6, and 8–10 ft bgs.

[b] Definition of data qualifier: U = compound not detected (the value shown is the analytical detection limit).

TABLE 8.27 Summary of Average Field VOC Measurements in Experimental Area XA9 (Iron Addition No. 5)

Constituent (mg/kg)	Initial Characterization Samples	Performance Monitoring Sample Results[a]				
	(12/11/97)	Day 5 (12/17/97)	Day 10 (12/22/97)	Day 25 (1/6/98)	Day 30 (1/13/98)	Day 38 (1/20/98)
Acetone	<0.10U[b]	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
Benzene	0.24	<0.10U	<0.10U	0.10	<0.10U	<0.10U
Carbon tetrachloride	<0.10U	<0.10U	<0.10U	0.22	<0.10U	<0.10U
Chloroform	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
1,1-Dichloroethane	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
1,2-Dichloroethane	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
1,1-Dichloroethene	0.10	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
1,2-Dichloroethene	2.72	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
Isobutanol	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
4-Methyl 2-pentanone	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
Methylene chloride	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
Nitrobenzene	0.10	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
Tetrachloroethene	96.62	0.27	0.55	1.35	0.12	0.75
Toluene	0.55	<0.10U	<0.10U	0.17	<0.10U	<0.10U
1,1,1-Trichloroethane	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
Trichloroethene	4.74	0.08	0.31	0.49	<0.10U	0.40
m/p Xylene	0.20	<0.10U	<0.10U	<0.10U	<0.10U	<0.10U
o Xylene	0.23	<0.10U	<0.10U	0.10	<0.10U	<0.10U
Total VOC	104.49	0.28	0.65	1.47	0.06	0.88
Field screening	243	15	14	17	10	7
Water content (%)	16.5	22.9	22	24.4	28.5	26.9

[a] The values reported are the mathematical averages of samples collected from depth intervals of 0–2, 4–6, 8–10, 12–14, 16–18, and 20–22 ft bgs.

[b] Definition of data qualifier: U = compound not detected (the value shown is the analytical detection limit).

TABLE 8.28 Comparison of Field VOC and Laboratory VOC Analytical Results in Experimental Area XA9 (Iron Addition No. 5)

	XA9-SB1 (1/12/98) (4–6)			XA9-SB1 (1/12/98) (8–10)		
Constituent (mg/kg)	Field	Laboratory	Ratio (field/lab)	Field	Laboratory	Ratio (field/lab)
Field VOC Compounds						
Acetone	<0.1	0.06B[a]	-[b]	<0.1	0.10B	-
Benzene	<0.1	<0.006U	-	<0.1	<0.006U	-
Carbon tetrachloride	<0.1	<0.006U	-	<0.1	<0.006U	-
Chloroform	<0.1	<0.006U	-	<0.1	<0.006U	-
1,1-Dichloroethane	<0.1	<0.006U	-	<0.1	<0.006U	-
1,2-Dichloroethane	<0.1	<0.006U	-	<0.1	<0.006U	-
1,1-Dichloroethene	<0.1	<0.006U	-	<0.1	<0.006U	-
1,2-Dichloroethene	<0.1	<0.003U	-	<0.1	<0.003U	-
Isobutanol	<0.1	<0.26U	-	<0.1	<0.26U	-
4-Methyl 2-pentanone	<0.1	<0.026U	-	<0.1	<0.026U	-
Methylene chloride	<0.1	0.00BJ	-	<0.1	0.00BJ	-
Nitrobenzene	<0.1	NA[c]	-	<0.1	NA	-
Tetrachloroethene	<0.1	0.004J	-	0.11	0.008	13.75
Toluene	<0.1	<0.006U	-	<0.1	0.006J	-
1,1,1-Trichloroethane	<0.1	<0.006U	-	<0.1	<0.006U	-
Trichloroethene	<0.1	<0.006U	-	<0.1	<0.006U	-
m/p Xylene	<0.1	<0.006U[d]	-	<0.1	<0.006U	-
o Xylene	<0.1	<0.006U[d]	-	<0.1	<0.006U	-
Other Compound[e]						
2-Butanone		0.013 J			0.021 J	

[a] Definitions of data qualifiers: B = compound detected in the method blank; J = estimated concentration; U = compound not detected (the value shown is the analytical detection limit).

[b] A hyphen indicates that the field VOC/lab VOC ratio could not be calculated because one or both analyses were below detection limits.

[c] NA = not applicable; lab VOC analysis does not measure nitrobenzene.

[d] Laboratory analysis reports xylene results as total xylene rather than as individual species that were measured in the field analysis. The total xylene laboratory result is shown in both rows containing field VOC results.

[e] This compound was detected in the lab VOC analyses but was not measured in the field VOC analyses.

8.5.4 Iron-Addition Experiment XA10: Validation of Final Integrated Treatment Method

Experiment XA10 was a final short-term experiment used to validate the treatment approach that was ultimately used to treat the 317 French Drain site. The approach developed was based on the results of the earlier experiments, particularly XA7, XA8, and XA9, which proved to be the most effective. These experiments demonstrated that iron addition was highly effective at reducing residual VOC concentrations with iron concentrations of less than 2%. On the basis of these findings, the full-scale treatment approach was modified to include the injection of nominal 1.5% iron during the SM/TESVE treatment process. This approach was subsequently used during remediation of approximately 6,116 m^3 (8,000 yd^3) of contaminated soil. During this treatment effort, a test area was selected and pretreatment and two posttreatment samples were collected; one was collected 3 days and the other 17 days after treatment. Table 8.29 gives the results of the field VOC analysis; Figure 8.9 is a graphical representation of these data. Table 8.30 summarizes the results of the laboratory VOC analysis and compares them with corresponding field VOC results.

The VOC reduction was similar to previous studies; chloroform and carbon tetrachloride were completely destroyed (from initial concentrations of 5.85 and 9.34 mg/kg to below the detection limits of 0.10 mg/kg), and trichloroethene was significantly reduced from 34.4 to 2.28 mg/kg. An increase in methylene chloride from 0.52 to 10.9 mg/kg occurred, followed by a decrease to 3.48 mg/kg. The decrease indicates that methylene chloride is likely to be amenable to iron reduction, albeit at a lower rate than other VOCs.

Table 8.31 summarizes the miscellaneous soil analyses performed. Chloride concentrations were observed to increase from 83 to 226 ppm (an increase of 143 ppm). This increase confirms the dechlorination of the chlorinated organics, which resulted in increasing chloride ions in the soil. The soil samples were analyzed for the presence of petroleum products. After treatment, no petroleum was detected above the detection limit of 30 ppm. Initial concentrations of petroleum products were 678 ppm. This reduction in petroleum was most likely the result of the SM/TESVE process; it was probably not related to the iron addition. It does, however, indicate the effectiveness of the SM/TESVE process at removing nonchlorinated organics from soil.

Gas emanations from XA10 were collected and analyzed for composition and trace organic constituents. The results of this analysis are given in Table 8.32. The composition was similar to previous samples; the majority of the samples were hydrogen gas and atmospheric air. In addition, significant amounts of methane and ethane were found. Unlike the other gas samples, significant quantities of carbon monoxide (CO_2) and butane were found.

The analysis of trace organics shown in Table 8.32 revealed the presence of the expected organics — benzene, chloroform, carbon tetrachloride, methylene chloride, trichloroethene, ethyl benzene, toluene, xylene, and other materials. The relatively high concentrations of benzene, toluene,

TABLE 8.29 Summary of Field VOC Measurements in Experimental Area XA10 (Iron Addition No. 6: 4/3/98)

	Field VOC Data		
	Pretreatment Samples	Performance Monitoring Sample	
Constituent (mg/kg)	(3/4/98)	Day 3 (4/06/98)	Day 17 (4/20/98)
Acetone	0.48	0.83	0.46
Benzene	1.14	3.55	2.19
Carbon tetrachloride	9.34	0.83	<0.10U[a]
Chloroform	5.85	4.99	<0.10U
1,1-Dichloroethane	<0.10U	<0.10U	<0.10U
1,2-Dichloroethane	<0.10U	<0.10U	<0.10U
1,1-Dichloroethene	<0.10U	<0.10U	<0.10U
1,2-Dichloroethene	<0.10U	0.23	0.18
Isobutanol	1.27	<0.10U	0.28
4-Methyl 2-pentanone	1.20	0.87	0.81
Methylene chloride	0.52	10.89	3.48
Nitrobenzene	<0.10U	<0.10U	<0.10U
Tetrachloroethene	0.71	0.89	0.15
Toluene	2.48	1.16	0.49
1,1,1-Trichloroethane	<0.10U	<0.10U	<0.10U
Trichloroethene	34.40	13.72	2.28
m/p Xylene	0.35	1.03	0.40
o Xylene	1.44	0.55	0.19
Total VOC	55.71	39.37	8.89
Field screening	619	79.8	-[b]
Water content (%)	8.0	26.6	25.3

[a] Definition of data qualifier: U = compound not detected (the value shown is the analytical detection limit).

[b] A hyphen indicates no data available.

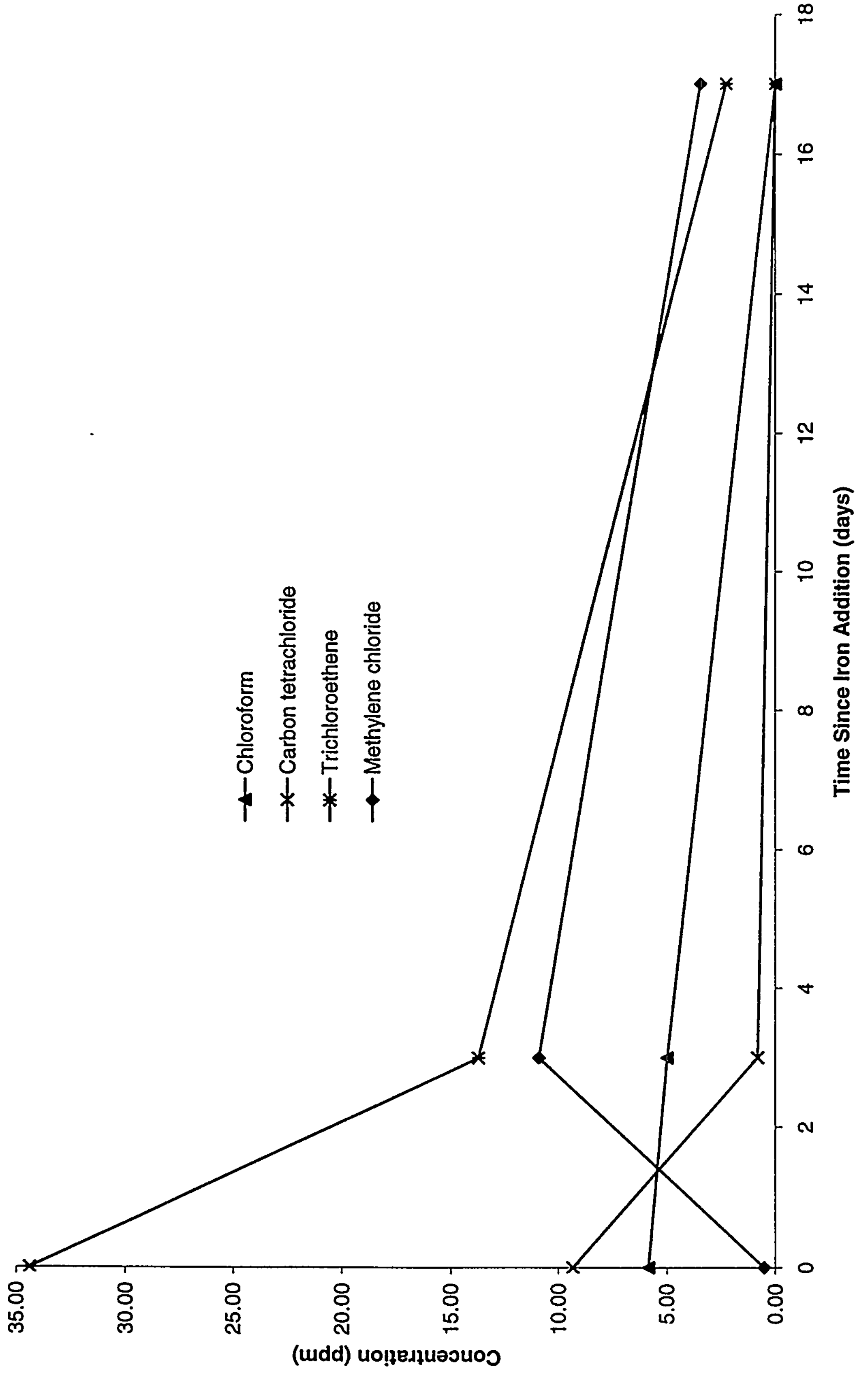


FIGURE 8.9 Average VOC Concentrations in Experimental Area XA10

TABLE 8.30 Comparison of Field VOC and Laboratory VOC Analytical Results for Experimental Area XA10 (Iron Addition No. 6)

Constituent (mg/kg)	XA10-SB01 (3/4/98) (8–10)			XA10-SB01 (4/6/98) (8–10)			XA10-SB01 (4/20/98) (8–10)		
	Field	Laboratory	Ratio (field/lab)	Field	Laboratory	Ratio (field/lab)	Field	Laboratory	Ratio (field/lab)
Field VOC Compounds									
Acetone	0.26	<0.110U[a]	-[b]	0.58	3.7B	-	0.55	5.2B	0.11
Benzene	0.93	2.5DJ	0.37	5.68	0.78	7.28	2.59	0.22J	11.77
Carbon tetrachloride	10.15	97.0D	0.10	1.50	<0.78U	-	<0.10U	<0.78U	-
Chloroform	8.16	2.4DJ	3.40	6.10	0.64J	9.53	<0.10U	<0.78U	-
1,2-Dichloroethane	<0.10U	0.047	-	<0.10U	<0.78U	-	<0.10U	<0.78U	-
1,2-Dichloroethene	<0.10U	<0.014 (trans) 0.012 (cis)	-	0.37	<0.39U	-	<0.10U	<0.39U	-
Isobutanol	1.19	<1.1U	-	0.48	<31.0U	-	0.34	<31.0U	-
4-Methyl 2-pentanone	0.70	0.51	1.37	0.86	<3.1U		0.64	3.1U	0.21
Methylene chloride	0.19	0.072B	2.64	15.84	2.6B	6.09	2.78	1.1B	2.53
Tetrachloroethene	1.02	0.18	5.67	0.52	0.30J	1.73	<0.10U	<0.78U	-
Toluene	4.15	1.1	3.77	0.96	0.51J	1.88	0.46	0.16J	2.88
Trichloroethene	66.03	38.0D	1.74	19.96	3.0	6.65	0.49	<0.78U	-
m/p Xylene[c]	0.53	2.6	0.20	0.47	1.3	-	0.54	1.1	-
o Xylene[c]	1.59	2.6		0.22	1.3	-	0.24	1.1	-
Other Compounds[d]									
Ethyl benzene		0.28			0.18J			<0.78U	
Chloromethane		0.059			<1.5U			<1.6U	

[a] Definitions of data qualifiers: B = compound detected in the method blank; D = result from diluted sample; J = estimated concentration; U = compound not detected (the value shown is the analytical detection limit).

[b] A hyphen indicates that the field VOC/lab VOC ratio could not be calculated because one or both analyses were below detection limits.

[c] Laboratory analysis reports xylene results as total xylene rather than individual species that were measured in the field analysis. The total xylene laboratory result is shown in both rows containing field VOC results.

[d] These compounds were detected in the laboratory VOC analyses, but were not measured in the field VOC analyses.

TABLE 8.31 Summary of Miscellaneous Measurements for Experimental Area XA10 (Control)

Soil Chloride Measurement[a]		Soil Hydrocarbons		
Value (mg/kg)	Date Measured	Type	Concentration (mg/kg)	Sample Collection Date
83	3/4/98	Diesel	<25	3/4/98
246	4/6/98	Waste oil	670	
226	4/20/98	Gasoline	7.5	
		Diesel	<30	4/6/98
		Waste oil	<30	
		Gasoline	NA[b]	
		Diesel	<31	4/20/98
		Waste oil	<31	
		Gasoline	NA	

[a] The chloride concentrations shown are the average of four discrete samples collected from depth intervals of 0–2, 4–6, 8–10, and 12–14 ft bgs.

[b] NA = not applicable; analysis did not detect gasoline components.

and xylene (BTX), as well as numerous straight and branched chain hydrocarbons in the off-gas, compared with other gas samples, results from the presence of petroleum products in the soil, which were measured at 678 ppm before treatment. An estimation of the mass of materials removed from the soil in off-gas compared to the total mass initially present, similar to that derived for XA6, is given in Table 8.33. This estimation indicates that from 23 to 49.4% of the VOCs originally present could have been released to the air in the off-gas. Three compounds — benzene, methylene chloride, and m/p xylene — were emitted in greater amounts than those estimated to be present initially. This either indicates production of these materials as end products (e.g., methylene chloride) or possibly an underestimation of the amount initially present.

8.6 OTHER INVESTIGATIONS RELATED TO IRON ADDITION

In addition to the studies discussed above, two supporting investigations were performed. Both studies were carried out in response to the observation that in several investigations (particularly XA7 and XA8), after a rapid drop in VOC concentrations during the first 10 to 15 days, the rate of destruction declined greatly or the reduction stopped all together. While the residual

TABLE 8.32 Off-Gas Composition and Trace Organic Constituent Concentrations for Experimental Area XA10 (Iron Addition No. 6)

	Gas Composition (volume %)		Trace Organics Concentration (ppmv)[b]
Constituent	Sample Date 4/10/98	Constituent[a]	Sample Date 4/10/98
Argon	0.124	Benzene	128.0 E
Butane	0.019	Carbon tetrachloride	7.1 E
Carbon dioxide	0.911	Chloroform	7.6 E
Carbon monoxide	0.466	Cyclohexane	15.4 E
Ethane	0.173	1,1 Dichloroethene	0.47
Hydrogen	89.1	cis-1,2-Dichloroethene	2.59
Methane	0.13	Ethyl benzene	5.42
Nitrogen	8.66	Methylene chloride	63.0 E
Nitrogen oxides	0.008	Tetrachloroethene	10.9 E
Oxygen	0.214	Toluene	19.7 E
Water	<0.25	Trichloroethene	36.9 E
		1,2,3 Trimethylbenzene	1.6
		1,2,4 Trimethylbenzene	2.93
		m/p Xylene	27.0 E
		o Xylene	4.66

[a] In addition to the compounds shown, 20 tentatively identified compounds were detected in concentrations less than 10 ppmv. These compounds were various straight and branched hydrocarbons.

[b] Definition of data qualifier: E = concentration exceeded the calibration range of the instrument.

concentrations were much lower than the initial concentrations, the final concentrations were still relatively high (in some cases >1 ppm). The experience of other researchers with iron treatment of groundwater indicates that the reaction should continue to completion and leave essentially none of the VOCs amenable to iron reduction in the soil. While this degree of treatment was observed in some cases during soil treatment, it did not appear to be occurring in all cases. Two theories were proposed. The first was that the iron had been oxidized by the reaction with the contaminants and soil moisture, thus reducing the mass of zero-valent iron (being oxidized to ferrous or ferric iron) to the point where it was no longer effective. The second hypothesis was that the surface of the iron particles was becoming coated with some type of material that inhibited free movement of contaminants dissolved in soil moisture to and away from the iron. Inhibiting such movement would result in the decrease in reactivity noted.

TABLE 8.33 Summary of VOC Emissions in Off-Gas from Experimental Area XA10

Constituent	Gas Concentration (ppmv)	Molecular Weight	Mass Discharged per Day[a] (g)	Mass Discharged in Three Weeks (g)	Concentration Originally Present (ppm)	Mass Originally Present[b] (g)	Portion of Constituent Released (%)
Benzene	128.0	78.11	3.23	67.81	1.14	40.13	168.98
Carbon tetrachloride	7.1	153.82	0.35	7.42	9.34	328.59	2.26
Chloroform	7.6	119.38	0.29	6.19	5.85	205.74	3.01
1,1-Dichloroethene	0.47	96.14	0.01	0.31	ND[c]	-[d]	-
cis-1,2-Dichloroethene	2.59	96.14	0.08	1.69	ND	-	-
Cyclohexane	15.4	84.18	0.42	8.79	ND	-	-
Ethyl benzene	5.42	106.18	0.19	3.90	ND	-	-
Methylene chloride	63.0	84.93	1.73	36.29	0.52	18.13	200.18
Tetrachloroethene	10.9	165.83	0.58	12.26	0.71	24.82	49.40
Toluene	19.7	92.14	0.59	12.31	2.48	87.30	14.10
Trichloroethene	36.9	131.39	1.57	32.88	34.40	1210.70	2.72
1,2,3-Trimethylbenzene	1.6	120.12	0.06	1.33	ND	-	-
1,2,4-Trimethylbenzene	2.93	120.12	0.11	2.39	ND	-	-
m/p Xylene	27.0	106.17	0.93	19.44	0.35	12.44	156.32
o Xylene	4.66	106.17	0.16	3.36	1.44	50.69	6.62

[a] The gas flow rate from the test area was estimated to be 7,764 L/day on the basis of measurements at seven locations.

[b] Mass of soil in the test column was 26 $yd^3 \times 27\ ft^3/yd^3 \times 110\ lb/ft^3 \times 454\ g/lb = 3.52 \times 10^{-7}$ g.

[c] ND = this compound was not detected in the initial soil samples.

[d] A hyphen indicates that these compounds were not detected in the soil samples; thus, the mass originally present and the portion of the constituent released could not be calculated.

The first hypothesis was tested by quantitatively recovering metallic iron particles from the treated soil by magnetic separation. A known mass of a soil sample from a treated area, collected at several points in time after the treatment had occurred, was added to water and mixed until a wet slurry of soil, iron, and water was formed. The slurry was passed over a magnet held onto the outside of a glass or plastic container. Iron particles adhered to the inside of the container directly above the magnet while nonmetallic material passed over. The iron particles were gently flushed with clean water to remove sand and soil particles trapped along with the iron particles. This magnetic separation step was repeated about five times; the metallic iron was carefully recovered after each separation step. The total mass of recovered iron was dried in an oven at 100°C (212°F) and weighed. The percentage of iron was then calculated. The process was validated by performing the extraction on clean soil to which a known amount of iron powder was added. Recovery of this iron from the soil was nearly 100% (101.8% in one test and 97.3% in a second). The extraction was performed on soil from one of the iron-treated areas (designated as 10N-14W) at three different times — 1, 8, and 14 days following treatment. The results are shown in Table 8.34. Metallic iron was present in all samples at amounts ranging from 1.2 to 1.8% (the target iron concentration was 1.5%). No apparent trend was evident in iron concentrations, which indicated that the iron was not consumed during the process. Because of the manual nature of the extraction process, the values should be considered only semiquantitative.

The second hypothesis was tested by conducting microscopic examinations of iron particles recovered from the treated soil and comparing the appearance of the iron surface with new iron. The iron was recovered from treated soil by using the method described above, except for minimizing the amount of agitation used to release the iron from the soil matrix to prevent the loss of any coating that may have developed on the iron. The examination of iron that had been in the soil for several months revealed the presence of a yellow-to-orange deposit that coated many of the iron particles. Many of the iron particles appeared to have formed small clusters that were coated with this material rather than being uniformly distributed throughout the soil matrix. In some samples, as much as 50 to 80% of the iron appeared to be enclosed in clusters coated with the material. Several of the clusters were broken open and were found to contain clean, shiny iron particles. Unused iron and iron recovered from newly treated soil did not contain such clusters of coated particles. The chemical nature of these coatings was not determined; however, it most likely consisted of a mixture of ferrous or ferric hydroxides, sulfates, or chlorides. The amount of surface deposition appears to be inconsistent between areas tested; some areas appeared to have little or no visible deposits, while others were almost completely covered. It is unknown what conditions in the soil were responsible for this formation or how much of this soft, gelatinous material was lost during the extraction process. Figure 8.10 contains four photomicrographs of the iron particles.

The presence of such a significant amount of surface coating of the iron may have been responsible for reducing the iron's effectiveness in destroying the chlorinated materials. The process relies heavily on the ability of groundwater to move freely between the soil, where the VOCs have

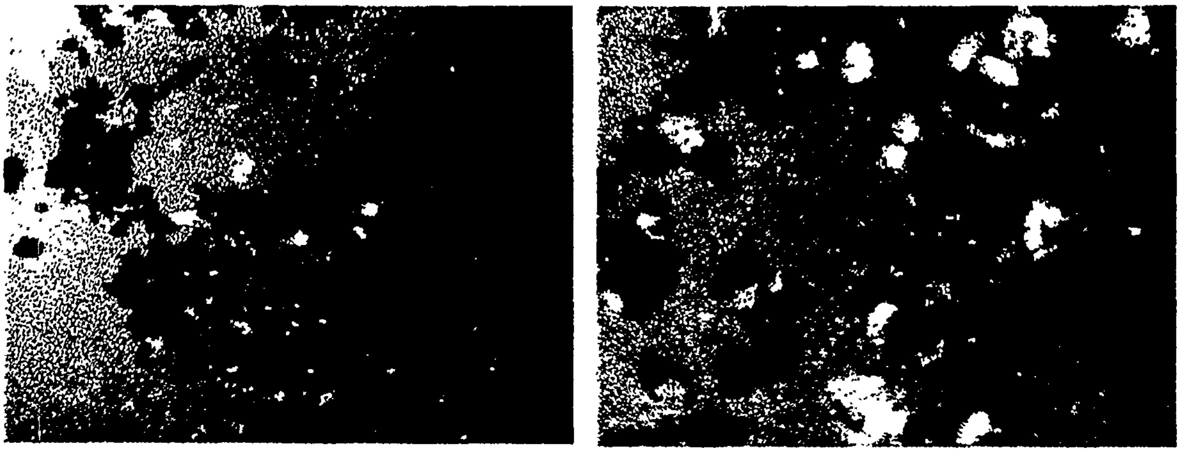
TABLE 8.34 Summary of Iron Recovery Experiments

	Method Verification Trial 1	Method Verification Trial 2	Sample Location and Date			
Parameter Evaluated	Dry Sand	Clean Clay Soil	10N-14W 4/28/98	10N-14W 5/5/98	10N-14E 6/6/98 DUP[a]	10N-14W 5/11/98
Time since treatment (days)	-[b]	-	1	8	8	14
Weight % iron (dry basis)	10.2	-	1.8	1.2	1.3	1.5
Weight % iron (wet basis)	-	4.9	1.3	0.9	1.0	1.2
Iron recovery (%)	101.8	97.3	NA	NA	NA	NA

[a] DUP = duplicate sample.

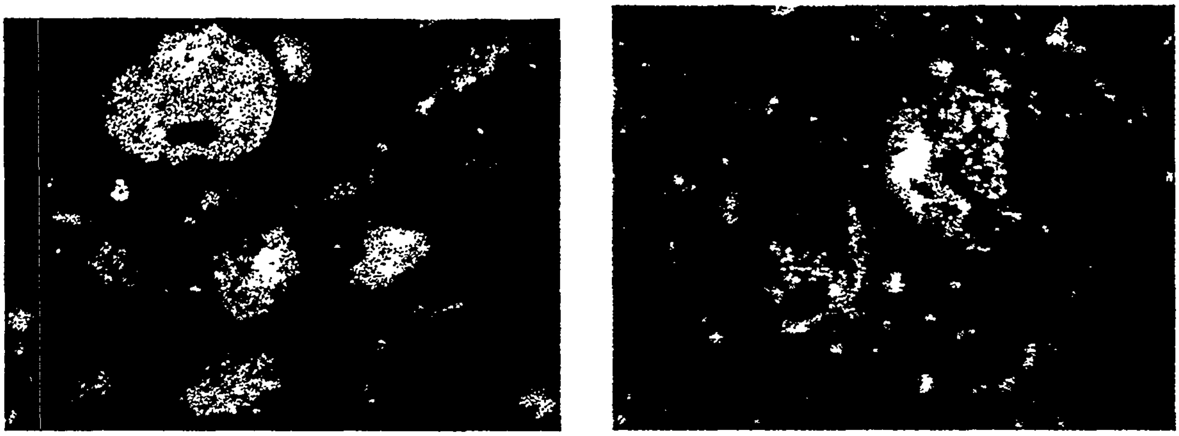
[b] A hyphen indicates that these parameters are not applicable to the verification samples.

been absorbed, and the surface of the iron, where the reaction occurs. Anything that inhibits this movement, such as a coating of iron hydroxide, greatly reduces the effectiveness of the iron. It is possible that because iron is still present within the coated areas, the dechlorination reaction will continue, though at a much reduced rate. Long-term monitoring of the treated area should indicate whether the reaction continues.



Iron particles recovered from soil immediately after injection.

Iron particles recovered from soil approximately two months after injection.



Closeup of iron particle clusters coated with unknown material.

Closeup of iron particle cluster that had been broken open showing clean iron particles inside.

FIGURE 8.10 Photomicrographs of Iron Particles

9 SUMMARY

9.1 CONTROL

As anticipated, the VOC concentrations in the control area did not exhibit a noticeable trend during the experiment. The lack of a clear trend in VOC concentrations demonstrated that once the initial removal accomplished by the SM/TESVE process was achieved, no further reductions in VOC concentrations occurred.

9.2 SOIL VENTILATION EXPERIMENT

The VOC concentrations in the soil ventilation experiment did not decrease significantly during this experiment. The apparent inability of this system to reduce VOC concentrations is not surprising, given the fact that the soil was saturated with groundwater starting at several feet below the surface. The presence of groundwater filled the available pore space in the soil, thus preventing the flux of air needed to carry away the volatile contaminants.

That the water level did not decrease throughout the experiment despite the removal of accumulated water in the exhaust well on a regular basis and intentional removal of water from the inlet well, indicates that the groundwater may have been replenished by infiltration of rainwater at the surface or by subsurface migrations from nearby areas. It is also likely that the soil was so impermeable that the water in the soil could not migrate fast enough to either well to effectively dewater the soil in this manner. Whatever the reason, it is clear that the soil conditions, combined with the water added by the steam, rain, and snow melt, were such that the soil ventilation system could not function effectively.

That the experiment was not effective at this site may be related to the type of SM/TESVE process used. Of the three vendors that bid on this project, two use hot air only, with no steam. The contractor chosen uses steam. If either of the other vendors had been chosen, the investigation results may have been very different. Without the added water introduced by steam injection, and with the drying effect of the hot air injection, the soil may have stayed dry enough to allow the soil ventilation process to work more effectively than it did. Indeed, in similar projects (DOE 1996) using hot air without steam, followed by soil ventilation, this type of polishing treatment was effective.

A second factor preventing the soil ventilation system from working effectively was the soil type. If the soil had been more permeable, the excess water would have drained away and would have allowed more air to move through the pore spaces. With the high clay content in the 317 Area, this did not occur.

9.3 AUGMENTED BIODEGRADATION EXPERIMENT

The results of VOC measurements of this system indicate that no chlorinated or nonchlorinated organics absorbed onto the soil were destroyed. This was confirmed by the lack of an increase in chloride concentrations. Groundwater data indicate that some biodegradation may have occurred; however, it was not occurring fast enough to reduce the soil concentrations by the end of the study.

Biological assays of the soil by the PLFA test indicated that in the early part of the study, a bacterial population was present at levels that appeared to be higher than the control and increasing with time, and that the population was more diverse. However, within the time frame of this investigation, the bacterial population was apparently not able to metabolize large enough quantities of the contaminants to register a decreasing trend in VOC concentrations in the soil. It is possible that the length of the performance monitoring period for this study may have been too short to determine whether this is a viable technology. Time is required for soil conditions to stabilize and bacterial populations to grow sufficiently and to become acclimated to the contaminants present. Without the benefit of long-term biodegradation study results, the time necessary for these changes to occur is unknown. Therefore, the failure of this experiment to yield measurable decreases in VOC concentrations in the soil may be the result of insufficient predeployment testing and insufficient evaluation time, rather than a weakness in the process itself.

The soil mixing process is an ideal means of injecting the required nutrients, cometabolites, bacteria, and additives into low permeability soils. The potential for cost savings from using this approach is significant. Additional research is warranted to determine the potential for this type of integrated technology.

9.4 IRON-ADDITION EXPERIMENTS

In all the iron-addition experiments, most of the chlorinated compound concentrations (trichloroethane, chloroform, carbon tetrachloride, and 1,2-dichloroethene) showed rapid decline within the first few days after iron injection. The chloroform and carbon tetrachloride concentrations decreased to below the analytical detection limits (0.1 ppm) within several days of iron injection. The 1,2-dichloroethene disappeared within approximately 10 days of iron injection. The trichloroethane decreased more than 85% within 10 to 20 days. Tetrachloroethane, when present at high concentrations, showed rapid reduction within a few days; however, at low initial concentrations, little destruction was noted. This observation was complicated by the fact that in the only tests that contained high concentrations of tetrachloroethene (XA8 and XA9), the iron addition was integrated with the SM/TESVE process. Thus, the relative importance of iron reduction versus soil mixing in removing the tetrachloroethane is not known.

Of the various combinations of iron and SM/TESVE treatment, the most effective treatment for the 317 Area site was achieved with simultaneous injection of iron during the SM/TESVE process. This combination effectively reduced nonchlorinated organics because of the SM/TESVE process and effectively removed recalcitrant chlorinated organics through iron-mediated reductive dechlorination. The combination resulted in lower residual VOC concentrations than either approach used individually.

After approximately 15 to 20 days, there was no more discernable reduction in VOC concentrations in most of the iron experiments. The residual concentrations of chlorinated compounds at this point were low, often less than 1.0 ppm; in many cases, however, this amount of residual contamination would still exceed remediation objectives. The reason for the reduction in contamination effectiveness appears to be related to a buildup of a precipitate on the outside of the iron particles and not to consumption (oxidation) of the iron itself. The long-term reduction in the residual concentration is possible because zero-valent iron is still present in the soil; to determine whether this is occurring, however, would require further study.

Nonchlorinated organics (benzene, toluene, and 4-methyl 2-pentanone) did not demonstrate a trend in concentrations but remained essentially stable throughout the monitoring period. When the iron addition was integrated with the SM/TESVE process, these compounds were significantly reduced immediately after mixing, as were petroleum products. This was confirmed by the drastic decrease in petroleum concentrations following the SM/TESVE process. However, following mixing, the concentrations of nonchlorinated compounds were generally stable. This was as expected, because iron is known to be effective only with chlorine-containing materials, as the result of the primary mode of reaction being an abiotic dechlorination reaction.

The increase in chloride concentrations as well as the detection of degradation products (methane, ethane, propane, and butane) in the off-gas confirm that dechlorination was the principle means of destroying these compounds.

Measurement of pH indicated an increase in pH during the first few weeks of the experiment; from initial pH values of 7.3 to 7.6 to a high of 8.3. This period corresponds to the period of the highest gas emanation rate. Soil samples collected later in the monitoring period indicated that the pH had returned to the initial values. The increased pH values, as well as the increase in chloride ion concentrations, are consistent with the postulated degradation mechanism for iron treatment, which involves a reductive dechlorination reaction that consumes hydrogen ions and results in a surplus of hydroxyl ions that raise the pH.

$$\begin{gathered} Fe^0 \rightleftharpoons Fe^{2+} + 2e^- \\ RCl + 2e^- + H^+ \rightleftharpoons RH + Cl^- , \end{gathered} \qquad (1)$$

where R is an organic base compound, such as ethene.

Gas composition measurements, which determined that hydrogen was the primary constituent of the off-gas, with lesser amounts of hydrocarbon gases, were also consistent with the postulated degradation mechanism for iron treatment. A side reaction to the reductive dechlorination is the anaerobic oxidation of the iron, which hydrolyzes water molecules. The hydrogen forms nascent hydrogen atoms that quickly combine to form hydrogen gas. The oxygen is combined with the iron to form iron hydroxide.

$$2H_2O + Fe^0 \rightleftharpoons Fe^{2+} + 2OH^- + H_2 \qquad (2)$$

The monitoring of the off-gas for trace organics revealed the presence of up to several hundred ppmv of the same materials found in the soil. The off-gas, as it made its way to the surface, carried with it significant concentrations of these compounds. Because the rate of gas generation from this system was very low and subsided within a few weeks of iron addition, the mass of materials carried from the soil by the off-gas was low; from less than 1 to 20% of the mass originally present. However, the presence of these materials in the off-gas is an important consideration should a mass balance be attempted on this type of system. Because of the numerous sources of experimental error associated with this type of field deployment, no attempt was made to perform a mass balance on carbon or chlorine. Experiments in the controlled environment of a laboratory would be required to gather data of such quality that a mass balance would be meaningful.

10 CONCLUSIONS

Given the soil conditions naturally present in the 317 Area (high clay content with resultant low permeability) and the conditions created in the soil by the type of SM/TESVE process utilized in this project (steam injection that resulted in nearly saturated soil conditions), the only viable soil polishing treatment system of the three evaluated was the iron addition. The addition of 1 to 3% iron dramatically reduced residual VOC concentrations, compared with no polishing or polishing using the soil ventilation or the augmented biodegradation processes. The optimum method of delivering the iron was to inject it into the soil at the same time as the SM/TESVE process was being conducted, thus eliminating a costly second mixing step in the process. The combination of heat and moisture from the steam addition appears to have greatly enhanced the VOC reduction capabilities of this process.

The data collected during this study indicate that the reduction in VOC concentrations was accomplished by dechlorination of the chlorinated solvents, which resulted in increased chloride ion concentrations. A much smaller amount of removal occurred because of volatilization of the organics into the gas emanations generated by the anaerobic oxidation of the iron particles.

The effectiveness of the iron addition appears to have varied significantly, depending on the compound being treated. The most amenable chlorinated compounds were chloroform, carbon tetrachloride, 1,2-dichloroethene, trichloroethene, and tetrachloroethene (at high concentrations). Methylene chloride was found to be generated as a relatively stable end product of the dechlorination of chloroform and carbon tetrachloride. However, there were indications that it too would have eventually been removed to very low levels.

The conclusion that iron addition is a viable soil polishing treatment system is likely to be very site specific. The effectiveness of the iron appears to depend on the presence of sufficient soil moisture to essentially saturate the soil. In addition, soil conditions must be such that the soil moisture stays in intimate contact with both the soil and the iron for extended periods of time (weeks to months). The low permeability soil of the 317 Area provided these conditions. Other sites, with higher permeability soil or in more arid locations, may not be able to support such high moisture levels for the length of time necessary to see residual concentrations decrease to acceptable levels.

The iron addition did not prove to be effective in reducing the concentrations of nonchlorinated volatile organic species. However, concentrations of hydrocarbons identified as diesel fuel did decrease significantly in all test areas, most likely because of the initial SM/TESVE treatment, at test areas where it was used.

The relative ineffectiveness of the iron on the nonchlorinated volatile organic species indicates that the most effective remedial approach to removing as much contamination from the soil as possible in the 317 Area is the integration of iron addition and the SM/TESVE process. The soil mixing and steam and air stripping will remove the bulk of the nonchlorinated organics, as well as chlorinated organics, while the iron will continue to reduce the concentration of the chlorinated species left behind by the SM/TESVE process.

11 RECOMMENDATIONS

This study determined that the injection of zero-valent iron is an effective enhancement to the SM/TESEV process for removing VOCs from the soil in the 317 Area. However, the conclusions derived from this study are likely to be highly site specific. A better understanding of the effectiveness of this process under different conditions is warranted. The iron-addition process needs to be studied in a controlled environment so that the various factors contributing to its success or failure can be better understood. In addition, a better understanding of all mechanisms responsible for reducing VOC concentrations is needed. Because of the complexity of performing treatability studies in the field, laboratory-scale studies to identify treatment mechanisms and confirm the fate of the compounds are recommended. Only through such studies can the applicability of this technology to other sites with different soil conditions and different contaminants be assessed.

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