



SITE Technology Capsule

ZENON Environmental, Inc. Cross-Flow Pervaporation System

Abstract

The U.S. Environmental Protection Agency (EPA) has focused on policy, technical, and informational issues related to exploring and applying new technologies to Superfund site remediation. One EPA initiative to accelerate the development, demonstration, and use of innovative technologies for site remediation is the Superfund Innovative Technology Evaluation (SITE) Program.

EPA SITE technology capsules summarize the latest information available on selected innovative treatment and site remediation technologies. The capsules assist EPA remedial project managers, EPA on-scene coordinators, contractors, and other remedial managers in the evaluation of site-specific chemical and physical characteristics to determine a technology's applicability for site remediation.

This capsule contains information on the cross-flow pervaporation technology developed by ZENON Environmental, Inc. (ZENON). The technology is designed to remove volatile organic compounds (VOC) from aqueous media. In early 1995, a full-scale ZENON system was evaluated at a former disposal area on Naval Air Station North Island (NASNI) in Coronado, California. Groundwater at the site is contaminated with trichloroethene (TCE) and other organic compounds. Results of the demonstration are summarized in the

Performance Data section of this capsule. Results from a 1993 pilot-scale SITE demonstration of the technology in Burlington, Ontario, Canada, are also summarized in the Performance Data section.

Introduction

The ZENON pervaporation technology is a membrane-based process that removes VOCs from aqueous matrices. The ZENON cross-flow pervaporation technology uses an organophilic membrane made of nonporous silicone rubber, which is permeable to organic compounds but highly resistant to degradation. The composition of the membrane causes organics in solution to adsorb to it; the organics then diffuse through the membrane by a vacuum and condense into a highly concentrated liquid called permeate. The permeate separates into aqueous and organic phases. The organic phase can either be disposed of or sent off site for further processing to recover the organics. The aqueous phase is sent back to the pervaporation unit for retreatment.

The ZENON technology effectively removes organic contamination from groundwater and other aqueous waste streams. The technology is not practical for reducing VOC concentrations to most regulatory limits, notably drinking water standards. It is best suited for reducing high concentrations of VOCs to levels that can be reduced further and more economically by conventional treatment technologies, such as carbon

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adsorption. According to the developer, once the ZENON technology is installed and equilibrated, it requires minimal support from on-site personnel.

The full-scale SITE demonstration of the ZENON technology took place at a former disposal area referred to as Site 9, on NASNI in Coronado, California. The demonstration was performed as a cooperative effort by EPA, the U.S. Navy, ZENON, and Canadian environmental agencies. Site 9 groundwater is contaminated with VOCs, primarily TCE. The purpose of the demonstration was to (1) evaluate the technology's removal efficiency for TCE concentrations in groundwater, and (2) determine if TCE concentrations could be reduced to the federal maximum contaminant level (MCL) for TCE of 5 micrograms per liter ($\mu\text{g/L}$).

The demonstration results showed that the ZENON system removed TCE from groundwater by an average of 97.3 percent. Sixteen of 18 comparisons of treated water samples to untreated samples showed average TCE removal efficiencies of 99.3 percent. However, the average TCE concentration in the treated water was approximately 1,380 $\mu\text{g/L}$, which did not meet the federal MCL.

The ZENON cross-flow pervaporation technology was also evaluated based on the nine criteria used for decision making in the Superfund feasibility study (FS) process. Table 1 presents the results of the evaluation.

Technology Description

The ZENON pervaporation technology involves modules containing dense polymeric membranes. Each membrane consists of a nonporous organophilic polymer, similar to silicone rubber, formed into capillary fibers measuring less than 1 millimeter in diameter. Silicone rubber exhibits high selectivity toward organic compounds and is highly resistant to degradation. The capillary fibers are aligned in parallel on a plane and spaced slightly apart. This arrangement of capillary fibers forms one membrane layer.

Separate membrane layers are aligned in series, as shown in Figure 1, with the interior of the capillary fibers exposed to a vacuum (about 1 pound per square inch absolute). The number of membranes used in a particular system depends on expected flow rates, contaminant concentrations in the untreated water, and target concentrations for contaminants in the treated water. Process temperatures may be elevated to improve treatment; however, temperatures are kept at or below 165 °F (75 °C).

The organophilic composition of the membrane causes organics to adsorb into the capillary fibers. The organics migrate to the interior of the capillary fibers and are then extracted from the membrane by the vacuum.

Figure 2 displays a schematic diagram of the ZENON cross-flow pervaporation system in a typical field application. Contaminated water is pumped from an equalization tank through a 200-micron prefilter to remove debris and silt particles, and then into a heat exchanger that raises the water temperature to about 165 °F (75 °C). The heated contaminated water then flows into the pervaporation module. Organics and small amounts of water are extracted from the contaminated water, and treated water exits the pervaporation module and is discharged from the system.

The extracted organics and small amount of water is called permeate. As the permeate exits the membranes, it is drawn into a condenser by the vacuum, where the organics and any water vapor are condensed. Because emissions are vented from the system downstream of the condenser, organics are kept in solution, thus minimizing air releases.

The condensed permeate contains highly concentrated organic compounds and has a significantly reduced volume compared to the untreated water. Because of this high concentration, the liquid permeate generally separates into aqueous and organic phases, rendering the organic fraction potentially recoverable. The organic phase permeate is pumped from the condenser to storage, while aqueous phase permeate can either be returned to the pervaporation module for further treatment or removed for disposal.

Technology Applicability

The ZENON cross-flow pervaporation technology removes VOCs from aqueous matrices, such as groundwater, wastewaters, and leachate. The technology can treat a variety of concentrations; however, it is best suited for reducing high concentrations of VOCs to levels that can be reduced further and more economically by conventional treatment technologies, such as carbon adsorption. The technology can also remove a number of semivolatiles organic compounds (SVOC) and petroleum hydrocarbons. Both the pilot-scale and full-scale demonstrations have evaluated the ZENON technology's treatment of contaminated groundwater.

Table 1: Evaluation Criteria for the ZENON Technology

CRITERION	ZENON TECHNOLOGY PERFORMANCE
1 Overall Protection of Human Health and the Environment	Provides short- and long-term protection by reducing contaminants in water. Can be part of a pump-and-treat system to prevent further groundwater contamination and off-site migration. Worker protection is required when handling concentrated permeate.
2 Compliance with Federal ARARs'	Requires compliance with National Pollutant Discharge Elimination System (NPDES) and Safe Drinking Water Act (SDWA) limitations for discharge. Storage of concentrated permeate requires compliance with Resource Conservation and Recovery Act (RCRA) hazardous waste storage requirements. Emission controls are needed to ensure compliance with air quality standards.
3 Long-Term Effectiveness and Performance	Effectively removes groundwater contaminants. Involves disposal of some residuals (wastewater and permeate).
4 Reduction of Toxicity, Mobility, or Volume Through Treatment	Reduces the toxicity of groundwater by the removal of contaminants.
5 Short-Term Effectiveness	Contaminants are removed upon completion of treatment. Presents potential short-term risks to workers from moving and handling of concentrated permeate.
6 Implementability	Easy to implement and transport. Requires minimal site preparation and utilities, and minimal operational support.
7 Cost ^b	ZENON estimates treatment costs from \$2.00 to \$4.00 per 1000 gallons of contaminated water.
8 Community Acceptance	The small risk to the community and permanent removal of contaminants make public acceptance of this technology likely.
9 State Acceptance	If remediation is conducted as part of RCRA corrective actions, state regulatory agencies may require permits.

Notes:

a Applicable or relevant and appropriate requirements

b Actual cost of a remediation technology is highly specific and dependent on the original and target cleanup levels, contaminant concentrations, groundwater characteristics, and volume of water.

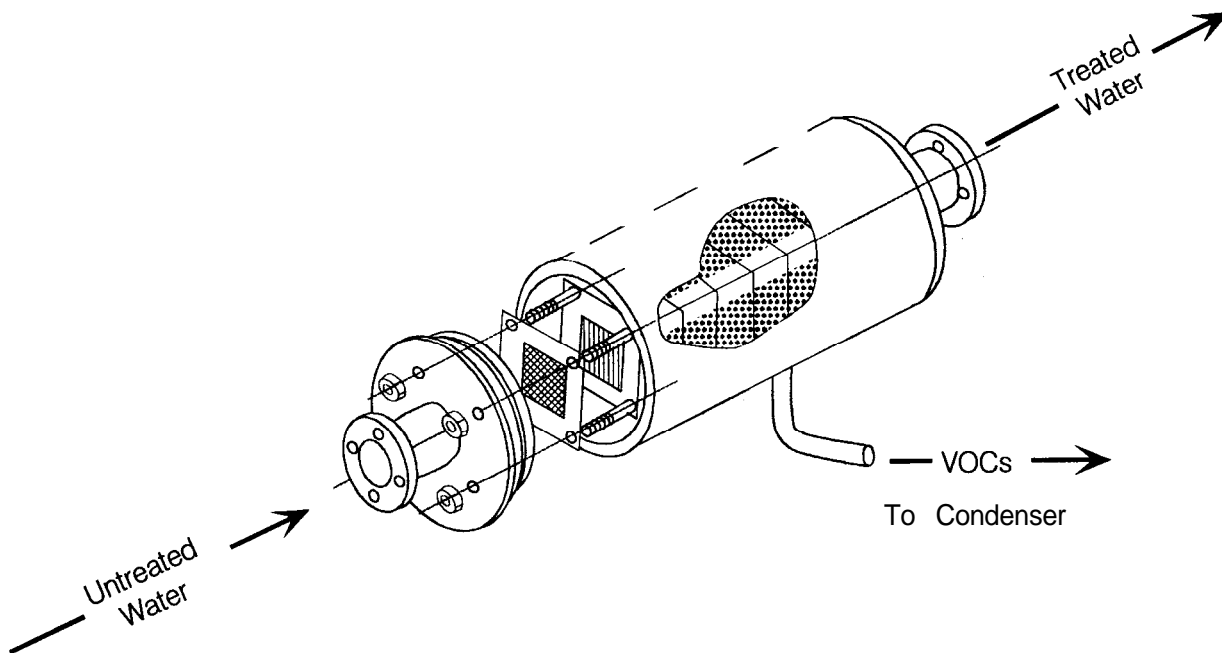


Figure 1: ZENON Cross-flow Pervaporation Module

A full-scale ZENON pervaporation system is easily transportable and can fit in a small semi-trailer. It is a stand-alone technology but can be used in series with other conventional technologies such as soil washing, carbon adsorption, or flocculation with solids removal. Contaminated aqueous media can be pumped directly to the pervaporation module; however, it is recommended that water be equalized in a bulk tank before entering the system. Depending on local pretreatment standards, treated water exiting the ZENON system may be discharged to a publicly owned treatment works (POTW). To comply with NPDES or SDWA limitations, further treatment with a separate technology is usually required.

Pervaporation provides an alternative approach to treating organic-contaminated water at sites where conventional air stripping or carbon adsorption are currently used. Unlike air stripping, pervaporation releases low amounts of VOCs to the outside air. Also, the pervaporation membranes do not require replacement and disposal, unlike activated carbon. Because contaminants pass through the membrane, it can be used for an extensive period of time (years) before degradation requires replacement.

Technology Limitations

As noted previously, the prefilter prevents solids from reaching the pervaporation module and inhibiting the movement of organics through the membrane. Solids can clog the prefilter, requiring it to be cleaned frequently. Influent with a high alkalinity or high amounts of calcium or iron can cause scaling of the system. In these cases, anti-scalents can be added to the untreated water as a preventive measure.

The ZENON technology does not remove inorganic contamination and can only remove a limited number of SVOCs and petroleum hydrocarbons. Dissolved heavy metals in groundwater have not adversely affected the treatment ability of the technology.

VOCs with water solubilities of less than 2 percent are generally suited for removal by pervaporation. Highly soluble organics, such as alcohols, are not effectively removed by a single-stage pervaporation process. Also, low-boiling VOCs, such as vinyl chloride, tend to remain in the vapor phase after moving through the condenser.

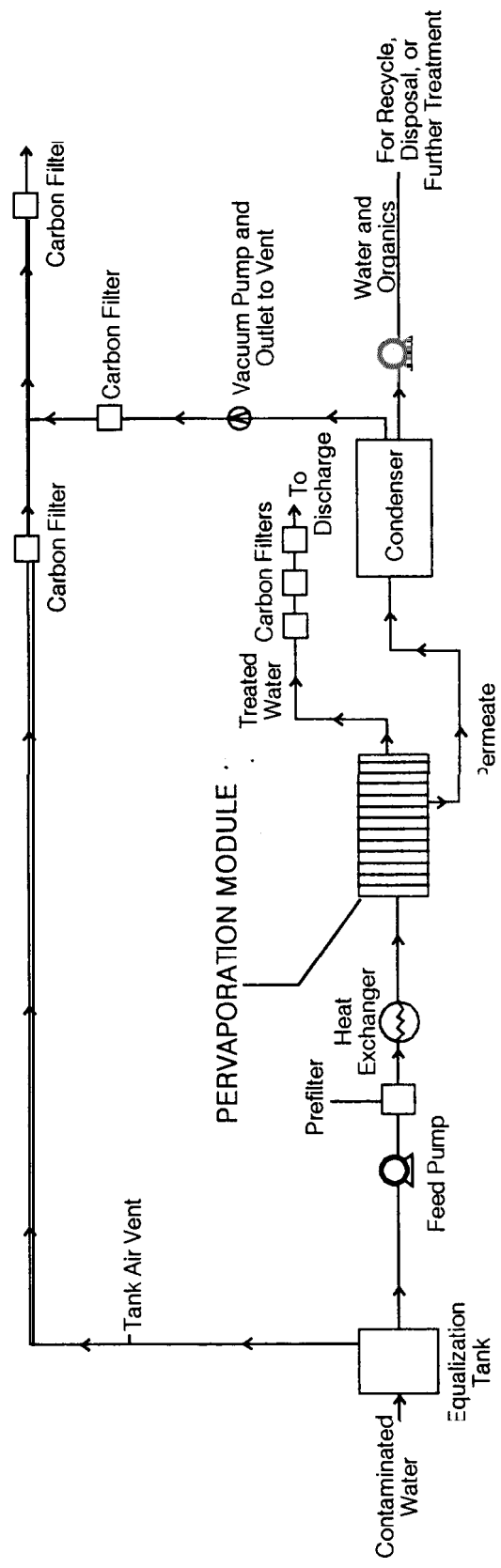


Figure 2: ZENON Cross-Flow Pervaporation System

For elevated concentrations of most low-boiling VOCs, a carbon filter placed on the vacuum vent ensures that contaminants are not released to the outside air.

The system has proven effective in reducing VOC concentrations in groundwater to near MCLs. However, lowering concentrations to below MCLs may require multiple passes through the pervaporation module, which can prove impractical when compared to other technologies, such as carbon adsorption. Water containing high concentrations of contaminants, including light nonaqueous phase liquids (LNAPL) and dense nonaqueous phase liquids (DNAPL), also require multiple passes through the module. To decrease the number of passes, LNAPLs and DNAPLs should be removed from water before it enters the system.

Water quality standards normally will not allow water exiting the ZENON system to be discharged directly into surface water bodies. Depending on local standards, treated water may be acceptable for discharge to a local POTW. During the demonstration at NASNI, treated water required additional treatment through a series of two 1,000-pound carbon filters for polishing. VOC concentrations were then monitored with an on-site gas chromatograph (GC), and the water was discharged to the sanitary sewer.

The ZENON system tested at NASNI could achieve a maximum flow rate of 11 gallons per minute (gpm), which is the largest capacity of the technology to date. Sites requiring treatment at higher flow rates will require multiple systems or additional pervaporation modules.

Process Residuals

The ZENON system generates two waste streams: treated water and concentrated permeate. As noted above, treated water may require further treatment to meet local or site-specific discharge requirements.

Permeate usually separates into an organic and an aqueous phase. The organic phase permeate is pumped from the condenser to storage, while aqueous phase permeate can either be returned to the pervaporation module for further treatment or removed for disposal. During the NASNI demonstration, the system treated about 65,000 gallons of contaminated groundwater producing about four 55-gallon drums of permeate. The aqueous permeate was pumped from the drums through the 1,000-pound carbon filters and discharged to the sanitary sewer. The organic permeate was transferred to one 55-gallon drum which was sent to a treatment facility for incineration.

Depending on the application and local regulations, personal protective equipment, along with field laboratory waste, may require disposal at a licensed disposal facility.

Site Requirements

Because a full-scale ZENON cross-flow pervaporation system is shipped to sites in a semi-trailer, access roads at treatment sites are necessary. The ZENON system is mounted in a steel enclosure measuring about 12 by 7 by 7 feet. The enclosure is slightly elevated from the ground, allowing it to be moved with a large forklift or a small crane. The enclosure must be placed on a hard surface, preferably an asphalt or concrete pad, although packed soil will support it.

The ZENON system requires utility hook-ups for electricity and water. A full-scale ZENON system capable of 11 gpm requires 460-volt, 3-phase, 15-ampere service. During shakedown, clean water is necessary to verify that all components are operating correctly before contaminated water enters the system. Clean water is also needed for decontaminating process equipment and for health and safety. Permeate must be stored in drums or bulk tanks, which under RCRA regulations, requires secondary containment and possibly permits. A receptacle for treated water, such as bulk tanks or sewer lines, is also necessary. A small office trailer and a telephone are recommended for moderate- to long-term operations.

Performance Data

The ZENON cross-flow pervaporation technology has been demonstrated under the SITE Program at the pilot-scale and full-scale levels. The objectives of both demonstrations were to determine the technology's ability to remove VOCs from contaminated groundwater and to determine the percent removal for each contaminant of concern. Results for each demonstration are summarized in the following sections.

Pilot-Scale Demonstration

The pilot-scale demonstration of the ZENON technology was performed in October 1993, at a small site just south of Burlington, Ontario, containing groundwater contaminated with petroleum hydrocarbons. Benzene, ethylbenzene, toluene, and total xylenes (BTEX) were the critical contaminants. Demonstration objectives were achieved by collecting untreated and treated water eight times over an 8-hour period, while the system operated

at a flow rate of 0.2 gpm. The system was equipped with a small carbon filter to minimize releases of VOCs from the vacuum vent of the system to the surrounding air. A photoionization detector was used to monitor the air released from the vacuum vent.

Analytical results indicated that BTEX concentrations were significantly reduced in treated groundwater samples compared to untreated samples (see Table 2). Removal efficiencies averaged 98 percent. No VOC releases from the vacuum vent after carbon filtration were detected during the pilot-scale demonstration.

Full-Scale Demonstration

The full-scale demonstration of the ZENON technology was performed during February 1995, at a former waste disposal area at NASNI, referred to as Site 9. Site 9 was used for over 40 years as a disposal area for a wide range of wastes; however, organics are the primary groundwater contaminants. TCE was selected as the contaminant of concern for the demonstration because of its identification, through groundwater sampling, as the primary contaminant at Site 9, at varying concentrations among monitoring wells.

During the initial stages of the demonstration, groundwater was pumped from a series of existing monitoring wells at the site to two 21,000-gallon steel bulk tanks for equalization. Rust particles from the interior of the tanks caused the prefilter to easily clog, requiring frequent cleanings. The particles also caused fouling and scaling problems with the pervaporation module, reducing its treatment efficiency. Eventually, groundwater was pumped directly from the monitoring wells to the system; however, because of high calcium bicarbonate concentrations in the groundwater, scaling of the pervaporation module continued. After attempts with a variety of chemicals, ZENON settled with an anti-scalent similar to zinc phosphate, which proved fairly effective.

TCE influent concentrations were varied by altering the flow rates into the system from the selected wells. Demonstration objectives were achieved by collecting samples of untreated and treated groundwater over five 8-hour sampling runs; air samples were collected directly from the vacuum vent of the system before and after a carbon filter. Flow rates of the system ranged from 2 to 11 gpm; influent TCE concentrations ranged from 33 to 240 milligrams per liter (mg/L). After the third run, sampling was delayed to allow cleaning of the

pervaporation module. Sampling ended after 4 hours into the fifth run because of a corroded stainless steel tube on the pervaporation module.

Table 3 presents analytical results for groundwater. Removal efficiencies for TCE averaged about 97.3 percent. The highest levels of contaminant removal were achieved when the system operated at a flow rate of about 5.5 gpm with an influent concentration of about 230 mg/L of TCE. Removal efficiencies were lowest when the system operated at about 2 gpm with an influent concentration of about 40 mg/L of TCE. Although the system significantly reduced TCE concentrations in the groundwater to an average of 1.37 mg/L (1,370 ug/L), the federal MCL of 5 $\mu\text{g/L}$ was not achieved.

VOC releases from the vacuum vent of the system ranged from 2,500 milligrams per cubic meter (mg/m^3) to 21,000 mg/m^3 . The data indicate that VOC releases from the vent increased with higher VOC influent concentrations; varying flow rates appeared to have little effect on air releases. Analytical results for air released from the vacuum vent of the system are shown in Table 4. Samples were also taken from the vent after air was allowed to pass through a 55-gallon carbon filter. Analytical results indicate that the carbon was 99.9 percent effective in removing the VOCs.

Technology Status

The SITE demonstration at NASNI represents the first full-scale use of the ZENON cross-flow pervaporation technology. As noted, the full-scale system is portable and requires minimal site preparation. Multiple pervaporation modules can be added to the system to accommodate a variety of sites. The technology is best suited for reducing high concentrations of VOCs to levels that can be reduced further and more economically by conventional treatment technologies. The technology provides an alternative approach to treating organic-contaminated water at sites where conventional treatment technologies are used, such as air stripping or carbon adsorption.

Disclaimer

The data presented in this technology capsule have passed internal laboratory quality assurance checks but have not been reviewed by EPA Risk Reduction Engineering Laboratory Quality Assurance personnel.

Table 2: BTEX Concentrations in water

Sample Number	Benzene			Ethylbenzene			Toluene			Total Xylenes		
	Untreated Concentration (µg/L)	Treated Concentration (µg/L)	Percent Removal	Untreated Concentration (µg/L)	Treated Concentration (µg/L)	Percent Removal	Untreated Concentration (µg/L)	Treated Concentration (µg/L)	Percent Removal	Untreated Concentration (µg/L)	Treated Concentration (µg/L)	Percent Removal
1	700	11	98%	150	2	99%	490	6	99%	820	13	98%
1D	720	6	99%	150	1	99%	500	4	99%	840	8	99%
2	340	11	97%	110	3	97%	260	7	97%	570	14	98%
3	360	11	97%	110	2	98%	280	6	98%	630	12	98%
4	360	7	98%	110	2	98%	270	4	99%	650	9	99%
5	700	9	99%	130	2	99%	450	5	99%	800	11	99%
6	370	8	98%	120	2	98%	290	5	98%	670	11	98%
7	370	10	97%	130	2	99%	290	6	98%	700	12	98%
8	650	8	99%	120	2	98%	400	5	99%	700	11	98%
Average	509	9	98%	113	2	98%	358	5	98%	709	11	98%

Note:

D Duplicate sample

Table 3: TCE Concentrations in water

Run Number	Flow Rate (gallons per minute)	Grab Number	Untreated Concentration (mg/L)	Treated Concentration (mg/L)	Percent Removal
1^a	2.10-2.15	1	40	0.17	99.5%
		2	43	1.0	97.7%
		3	33	3.8	88.5%
		4	42	11	73.8%
Average			40	3.9	89.9%
2	5.16 - 5.21	1	41	ND ^b	>99.9%
		2	44	0.09	99.8%
		3	48	0.16	99.7%
		4	48	0.19	99.6%
Average			42	0.11	99.8%
3	9	1	33	0.32	99.0%
		2	35	0.27	99.2%
		3	38	0.22	99.4%
		4	37	0.24	99.4%
Average			36	0.26	99.3%
4	5.46	1	220	0.45	99.8%
		2	220	0.40	99.8%
		3	240	0.51	99.8%
		4	240	0.46	99.8%
Average			230	0.46	99.8%
5^c	11.18-11.23	1	130	2.7	97.9%
		2	120	2.7	97.8%
Average			125	2.7	97.9%
Total Average Percent Removal					97.3%

Notes:

- ^a A sampling run is defined as one 8-hour period at a given flow rate.
- ^b Not detected.
- ^c Sampling run was abbreviated due to system failure.

Table 4: TCE Concentrations in Air

Run Number	Average Groundwater TCE Concentration (mg/L)	Flow Rate (gpm)	Grab Number	Untreated Concentration (mg/m ³)	Treated Concentration (mg/m ³)	Percent Removal
1 ^a	40	2.10 - 2.15	1	6,100	0.02	99.9%
			2	5,500	0.05	99.9%
2	42	5.16 - 5.21	1	3,700	0.02	99.9%
			2	2,500	ND ^c	>99.9%
3	36		1	7,300	ND	>99.9%
			2	7,200	ND	>99.3%
4	230	546	1	18,000	0.17	99.9%
			2	20,000	0.01	99.9%
5 ^d	125	11.18 - 11.23	1.	21,000	0.71	99.9%
Average	95			10,100	0.11	99.9%

Notes:

- ^a A sampling run is defined as one a-hour period for a given flow rate.
- ^b Concentration after vented air passed through a carbon filter.
- ^c Not detected
- ^d Sampling run was abbreviated due to system failure.

Sources of Further Information

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