



## Project Summary

# Soil Vapor Extraction Column Experiments on Gasoline Contaminated Soil

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Soil vapor extraction (SVE) is a technique that is used to remove volatile organic compounds from unsaturated soils. Air is pumped through and from the contaminated zone to remove vapor phase constituents. In this work, laboratory soil column experiments were conducted using a sandy soil residually saturated with gasoline to evaluate the performance of SVE under controlled conditions. Both vapor extraction and aqueous leaching of the soil columns were conducted. The progress of the vapor extraction event was continuously monitored by an in-line total hydrocarbon analyzer (THA). Performance of vapor extraction was evaluated by a series of soil chemical analyses including total petroleum hydrocarbons, headspace measurements, and extraction techniques with quantification by GC/FID and GC/MS. Contaminant levels in aqueous percolate were compared before and after SVE. After 60 pore volumes of water flow through a column, the percolate from the contaminated soil still contained at least 100 mg/L of total hydrocarbons. Vapor extraction of contaminated soil reduced total hydrocarbons by 99.96%, and subsequent aqueous leaching resulted in percolate concentrations of 3.7 mg/L initially and 0.6 mg/L after 60 pore volumes of water flow.

*This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Introduction

SVE is an innovative technology used to remove volatile compounds from unsaturated soils. The basic principles of SVE technology are straightforward. By inducing air flow from and through the subsurface vadose zone, vapor phase contaminants are flushed from the soil pores. Extraction wells are the usual route by which contaminants are recovered from the subsurface.

The process consists of the following steps. Contaminant laden air is withdrawn through extraction wells under a vacuum created by an above-ground blower or vacuum pump. The air flow is controlled by ball or butterfly valves and is monitored by vacuum gauges. The extracted vapor stream passes through an air/water separator to remove moisture and protect the blower. After the blower, the air stream passes through a heat exchanger to control the relative humidity and improve the efficiency of the subsequent vapor treatment operation. Injection wells are optional as a means to enhance air flow. A cap or surface seal placed over the treatment area to control the vapor flow path is also an optional component of the system. The seal, which could be as simple as plastic sheeting, serves to induce the air to flow in a horizontal manner as opposed to a vertical flow pathway that may result from air being drawn from the surface only near the extraction well.

Vapor extraction is most effective in removing compounds that exhibit significant volatility at ambient temperatures in soil (i.e., vapor pressure greater than 0.5 mm of mercury at 20°C and a dimensionless



Henry's Law constant greater than 0.01). This includes most gasoline constituents and solvents. Additionally, the mobility of the compound due to its affinity for the soil organic matter and small pore spaces affects the success of the treatment. Compounds strongly sorbed to the soil matrix tend to be more difficult to extract.

Although SVE has been used with great success at numerous sites, the behavior of the contaminants remaining in the soil has not been completely assessed. The efficacy of SVE as a remedial technology for extraction of gasoline contaminated soils was investigated using laboratory scale soil column experiments. One dimensional air flow rates were controlled within a small soil sample with distinct boundaries. Other parameters controlled included moisture content, chemical contaminants, and soil characteristics.

The experimental program had three main objectives:

- Determine the limitations on gasoline removal from soil using vapor extraction under controlled, optimized laboratory conditions.
- Evaluate the aqueous mobility of the constituents in contaminated soil and those that remain in the soil following SVE.
- Assess the appropriateness of available analytical techniques to measure soil contaminant levels.

## Experimental Methods

Stainless steel soil columns were 29.8 cm (1 ft) in length with a 10.8 cm (4.25 in.) internal diameter. A rigid, porous Teflon disk sat at the bottom of the column and supported the soil sample; a second porous disk rested on top of the soil. Stainless steel endplates were bolted to either end of the columns, and Viton<sup>®</sup> gaskets were used to create an air- and water-tight seal. The columns terminated at each end in needle valves, which could be closed to isolate the system. The internal volume of each column was 2.5 L.

The columns were weighed to the nearest gram following each manipulation. Four identical columns were packed with Connecticut sand; 97% of those particles were between 0.1 mm and 5 mm in diameter, with an average diameter of 0.5 mm. The sand was predominantly quartz (35%) and feldspar (35%) and had a surface area of 1.9 m<sup>2</sup>/g. As the soil was added to the columns in 2.5 cm lifts, the columns were vibrated to achieve maximum compaction. The process of soil addition and shaking were repeated until the columns were full

\* Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

(approximately 4.7 kg of soil). The in-place bulk density was 1.9 g/cm<sup>3</sup>, and the porosity was 30% as determined by mass difference (columns empty, packed with soil, and saturated with water).

The packed columns were saturated with water containing 100 mg KCN/L to prevent microbial activity, drained to field capacity moisture content, saturated with gasoline, and allowed to drain to residual saturation. At various stages of the experiment, a column was opened, the soil was poured into a stainless steel bowl, transferred to sample vials and jars, and analyzed by the battery of techniques listed in Table 1. One column was sacrificed for soil analysis after residual saturation with gasoline.

For headspace analysis, 1 g of soil was spiked with 500 ppm of  $\alpha,\alpha,\alpha$ -trifluorotoluene in a 10 mL Teflon-lined, septum-sealed vial and was heated in a water bath at 90°C for 20 min. This treatment was assumed to displace all volatile compounds in the sample into the headspace. A 200- $\mu$ L sample of the headspace was injected directly into a GC/FID to obtain a value for headspace volatiles.

Chromatographic peaks eluting between 2-methylpentane and 1,2,4-trimethylbenzene, defined as the gasoline range organic (GRO) compounds, were summed. The area of the internal standard was subtracted from this total area. The subsequent sample peak area was directly correlated to a five point calibration curve utilizing the peak area summation of a 10-compound mixture containing 2-methylpentane; 2,2,4-trimethylpentane; heptane; benzene; toluene; ethylbenzene; m-xylene; p-xylene; o-xylene; and 1,2,4-trimethylbenzene. Varying measured

amounts of this mixture were added to clean soil, and 1 g portions were analyzed as above to create the calibration curve for soil GRO concentration.

The final two columns were vapor extracted simultaneously at a flow rate of 2.1 L/min (4.5 scfh). Air, supplied by compressed air cylinders, passed through an activated carbon column to remove hydrocarbons, and then through a flask of water via a diffuser stone. The humidified air split into two equal streams and flowed first through flow meters, then the soil columns. The column exhaust air flowed to a sequential sampler. The vapors from one column, then the other, were sent every minute to a THA for continuous monitoring of total hydrocarbon levels.

After 6.5 days of vapor extraction, one column was sacrificed for soil analysis; the other received 60 pore volumes of rainwater flow as above. The soil from this final column was analyzed at the conclusion of the experiment.

## Results and Discussion

Measurements are recorded for a soil column residually saturated with gasoline, a column following aqueous leaching, and a vapor extracted column. Multiple values for any measurement are replicate sample analyses.

The gasoline retained in each column was measured directly by mass difference. The mass of each column at field capacity moisture content was subtracted from the mass of the same column residually saturated with gasoline. Any additional water that was lost during the drainage of the excess gasoline was collected in a graduated cylinder and was also subtracted to yield the final value. Initial gasoline concentrations ranged from 12,700 to 15,300

Table 1. Soil Analytical Techniques

Measurement	USEPA SW-846 Method No. or Ref.	Procedure
Total volatile solids	160.4	Heat to 103°C then 550°C
Total petroleum hydrocarbons	9071/418.1	Freon extraction, IR
Gasoline range organics	Enseco-RMAL, 1990	Methanol extraction, GC/FID or GC/MS, integration of peaks
Headspace	Method described below	GC/FID
Semi-volatile organic compounds	8270	Methylene chloride extraction, GC/MS
Volatile organic compounds	8260	Methanol extraction, GC/MS

mg/kg. These values were greater than the results of each of the analytical methods employed. The discrepancy can be attributed to volatilization losses during the transfer of soil samples from the columns to vials and jars for storage before analysis as well as to losses incurred during the performance of the analytical methods themselves.

Aqueous leaching of a soil column residually saturated with gasoline resulted in the mobilization of some of the retained GRO during 60 pore volumes (about 43.2 L) of water flow. In the percolating water during the leaching experiment, the peak concentration of GRO was 3,000 mg/L at the onset of leaching. The concentrations continually dropped, and after about 5 pore volumes, they began to level off; however by the end of the run, they were still as high as 170 mg/L.

Integration of the GRO concentrations during the aqueous leaching experiment yielded a total of 9.8 g of GRO removed. The original mass of gasoline in the column was 79 g, so that about 12% of the contaminants were mobilized in the percolating water. Although benzene dropped below the detection limit of 1.25 mg/L by 60 pore volumes, the levels of toluene, ethylbenzene, and xylene remained steady at 70, 5, and 30 mg/L, respectively.

Vapor extraction was conducted continuously for 6.5 days, with only brief breaks in the flow to make adjustments to the system. Vapor extraction of two contaminated columns brought the soil GRO

levels down as low as 0.5 mg/kg, a removal of 99.96% of the original GRO.

During the initial 7 min of vapor extraction, exhaust gas hydrocarbon concentrations exceeded the instrument's THA maximum limit of detection of 100,000 ppm (v/v). After this period, hydrocarbon levels steadily declined with brief periods of increased concentration spikes following pauses in the flow. The vapor concentrations exiting the two columns were similar at first during the rapid decline and in the final stages as the concentrations leveled off. Hydrocarbon values, however, differed by as much as 50% during the middle stages of the extraction process. These differences can be explained by different hydrocarbon starting concentrations, since the column giving rise to the higher levels had retained 88 g of gasoline before SVE, whereas the other began with only 66 g. Final vapor hydrocarbon levels were between 20 and 40 ppm (v/v).

Integration of the vapor extraction data yielded a total hydrocarbon mass removal that was greater than the initial gasoline mass by about 70%. This is understandable since the THA was operated under circumstances that were best suited for generation of qualitative data only. The THA was calibrated only once and for one concentration range at the start of gas flow, whereas several concentration ranges were used during the course of the experiment. Furthermore, the calibration mixture contained only butanes and pentanes; these were not completely repre-

sentative of the complex gasoline mixture. The longer chain hydrocarbons and aromatic compounds also found in gasoline exhibit greater THA response factors than the calibration gas compounds. Concentrations fell from a maximum of 3.7 mg/L at 2 pore volumes to a plateau of 0.6 mg/L after 60 pore volumes.

## Conclusions

The gasoline contaminated sandy soil was susceptible to aqueous leaching of the hydrocarbon components. After 60 pore volumes of water flow, however, the majority of product remained in the soil and significant concentrations of BTEX were still found in the percolating water.

SVE was effective in removing gasoline from the soil, with a reduction in the GRO of 3.5 orders of magnitude. After this period, the vapor extracted soil still contained low levels of water-mobile contaminants. GRO was the most reproducible of the analytical techniques tested, and headspace analysis by GC/FID recorded the highest concentrations.

Soil column experiments provided a well controlled, effective measurement of the soil processes occurring in the aqueous leaching and vapor extraction of gasoline contaminated soil.

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*The complete report, entitled "Soil Vapor Extraction Column Experiments on Gasoline Contaminated Soil," (Order No. PB92-226430/AS; Cost: \$19.00, subject to change) will be available only from:*

*National Technical Information Service*

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