ornl

OAK RIDGE
NATIONAL
LABORATORY

MARTIN MARIETTA

ORNL/TM-13156

Chemically Enhanced Mixed Region Vapor Stripping of TCE-Contaminated Saturated Peat and Silty Clay Soils

Olivia R. West
Paula A. Cameron
Andrew J. Lucero
Laurence J. Koran, Jr.

Environmental Sciences Division

Publication No. 4503

MANAGED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615) 576-8401, FTS 626-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ORNL/TM-13156

Enrivonmental Sciences Division

CHEMICALLY ENHANCED MIXED REGION VAPOR STRIPPING OF TCE-CONTAMINATED SATURATED PEAT AND SILTY CLAY SOILS

A Treatability Study for the In Situ Remediation of the NASA Michoud Rinsewater Impoundment

Olivia R. West, Paula A. Cameron
Environmental Sciences Division

Andrew J. Lucero, Laurence J. Koran, Jr.
Chemical Technology Division

Environmental Sciences Division
Publication No. 4503

Date Published: January, 1996

Prepared for
Martin A. Rowland
Facilities Site Remediation
Lockheed Martin Manned Space Systems
Michoud Assembly Facility
New Orleans, Louisiana 70219

Prepared by
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6036
managed by
LOCKHEED MARTIN ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR-21400

MASTER

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

EXECUTIVE SUMMARY

Chemically enhanced mixed region vapor stripping (MRVS) is an innovative approach for extending the applicability of MRVS to saturated, low-permeability soils contaminated with volatile organic compounds (VOCs). In this process, calcium oxide (CaO) is mixed with saturated soil immediately prior to vapor stripping. The hydration reaction of calcium oxide [$CaO + H_2O \rightarrow Ca(OH_2)$] removes free moisture from the soil matrix, resulting in an increase of air-filled soil porosity and an improvement in soil friability (i.e., the ability of the soil to break up into soil clumps or aggregates). Both the increased air-filled porosity and reduced soil aggregate sizes increase VOC removal efficiency of MRVS. Heat released during the exothermic hydration reaction can also increase the temperature of the soil, thereby improving VOC removal by increasing the fugacity of the contaminants.

The objective of this study was to evaluate MRVS, chemically enhanced with calcium oxide conditioning, for the in situ remediation of contaminated soils underlying an inactive hazardous waste facility located at the National Aeronautics Space Administration (NASA) Michoud Assembly Facility in New Orleans, Louisiana. This facility, known as the NASA Michoud Rinsewater Impoundment, is underlain by low permeability soils with moisture contents as high as 200-500% dry weight and with natural organic contents on the order of 20%. These soil conditions have made remediation of this site by conventional in situ methods infeasible. Laboratory simulations of chemically enhanced MRVS were conducted on relatively undisturbed 4-in-diam, 6-in-long soil cores collected from the site. Residual levels of the predominant VOCs [trichloroethylene (TCE) and cis-1,2-dichloroethylene (cis-1,2-DCE)] measured as a function of treatment time showed that TCE and cis-1,2-DCE removals were extremely rapid in the first 60 min after the cores were amended with a sufficient amount of CaO. On average, ~95% of initial TCE levels were removed within the first 60 minutes of vapor stripping from cores having initial concentrations of ~3 to 3000 mg/kg. Removal rates were significantly lower when vapor stripping was continued beyond 60 minutes. A TCE removal curve (percent TCE removed as a function of treatment time) was developed by averaging the removal curves obtained from the MRVS tests. Based on this curve, it is estimated that ~30 and ~300 minutes of treatment is needed to remove 90%

and 99% of initial TCE contamination. For example, starting with an initial concentration of 3000 mg/kg, it would only require 30 minutes of MRVS to achieve a target residual of 300 mg/kg. The same amount of time would be needed to go from 300 to 30 mg/kg of contamination. However, a significantly longer time (300 minutes) would be required to achieve a residual level of 30 mg/kg if the initial contaminant level were 3000 mg/kg. This substantial increase in treatment time when remediation goals for TCE increase beyond 95% is a reflection of the bi-phasic removal patterns observed in the MRVS tests (i.e., rapid followed by slower TCE removal beyond 60 minutes of treatment). Rapid removals were accompanied by increased soil temperatures ranging from 40°C to 75°C. The more gradual removals observed beyond 60 min of treatment may be a result of temperatures returning to ambient levels, as well as increased sorption on drier soils.

The amount of CaO required to achieve high removal rates is dependent on the initial moisture content of the soil; a 400-500 kg/m^3 CaO loading is expected to be sufficient for the Michoud soils, which have moisture contents ranging from 26 to 534% dry weight. High CaO loading is needed to dehydrate the soil sufficiently and to achieve temperature increases necessary for rapid TCE removal. Some concerns exist regarding the volumetric expansion of the soil when this much CaO is added in situ. However, this may because of the unconsolidated nature and low density of the contaminated soil under the Rinsewater Impoundment. This concern can be best addressed through a field test.

Costs for chemically enhanced MRVS were estimated for remediation goals specified either as a percentage removal of TCE, or as target residual TCE concentration. Remediation costs are expected to be on the order of ~\$100/ton to achieve a 95% removal goal using an 8-in-diam soil mixer for a treatment depth of 15 ft. For target residual levels of 5, 50, and 100 mg/kg, remediation of the Michoud Rinsewater Impoundment is estimated to cost \$2.6M, \$800K, and \$400K, respectively. These were calculated by subdividing the site into subregions, and estimating treatment times for these subregions according to initial contaminant levels. The latter were taken from contour maps drawn from existing site characterization data. Better estimates can be obtained from vendors that can do soil mixing and calcium oxide additions, using the removal curve generated by the mixing experiments.

Two other technologies were identified as having the potential for remediating the highly saturated, low-permeability soils underlying the Rinsewater Impoundment. These technologies, electroosmosis and 2-Phase extraction, are fairly new and have not been applied to a wide variety of sites. Specific performance and cost data for remediating the Rinsewater Impoundment with these methods can only be obtained if laboratory and/or field tests were conducted.

To resolve the issue of contamination underlying the Michoud Rinsewater Impoundment, we recommend that (1) soil-mixing vendors be contacted to obtain better estimates for chemically enhanced MRVS on the basis of the removal data obtained from this work, (2) chemically enhanced MRVS be field tested, and (3) vendors that can provide electroosmosis and 2-Phase extraction be contacted for possible field tests.

1. INTRODUCTION

1.1 BACKGROUND

Mixed region vapor stripping (MRVS) is an in situ technology for removing volatile organic compounds (VOCs) from low-permeability soils. Its effectiveness in unsaturated silty clays has been demonstrated in laboratory tests, field demonstrations, and at the full-scale cleanup of soil underlying the X-231B land treatment facility at the Portsmouth Gaseous Diffusion Plant [*1-4*]. On the basis of its successful application at the X-231B site, MRVS was considered as a potential in situ technology for cleaning up trichloroethylene (TCE)-contaminated soil underlying an inactive rinsewater impoundment at the National Aeronautics and Space Administration (NASA) Michoud Assembly Facility. Similar to the soils at the X-231B site, the soil underlying the Michoud Rinsewater Impoundment has extremely low permeabilities (10^{-7} to 10^{-8} cm/sec, [*5*]), which precluded the applicability of conventional soil vacuum extraction. However, in contrast to X-231B soil, which was unsaturated and consolidated, the NASA contaminated soils underlying the Michoud Rinsewater Impoundment are unconsolidated and have moisture contents as high as ~500% dry weight (~84% wet weight) [*5*] (see Sect. 3).

A set of scoping laboratory tests revealed that MRVS alone could not remove TCE contamination from the Michoud soils within a reasonable time frame [*6*]. During these tests, the mixed soil turned into a viscous soil paste instead of aggregating into small-diameter soil clumps. A previously developed model for VOC removal during MRVS showed that process efficiency improves when the mixed soil consists of small-diameter soils aggregates with high air-filled porosities (Fig. 1), [*1*]. The extremely high moisture content of the Michoud soil contributed to both the paste-like mixed soil morphology and low air-filled porosities. Hence, high moisture contents were believed to be the primary reason behind the slow MRVS removal efficiencies reported by Lucero, et al. [*6*]. Calcium oxide conditioning was conceived during these tests as a means for reducing the moisture content of the soil. The hydration reaction of calcium oxide [$CaO + H_2O \rightarrow Ca(OH_2)$] removes free moisture from the soil matrix, resulting in increased air-filled soil porosities and improved soil friability (i.e., the ability of the soil to break up into soil clumps or aggregates). Heat released during the exothermic hydration reaction can also increase the temperature of the soil, thereby improving VOC removal by increasing the fugacity of the contaminants. Chemically enhanced MRVS through calcium oxide conditioning showed promising results on a few soil cores during previous work [*6*]; however, a more comprehensive study of the process could not be conducted because of a lack of resources at the time.

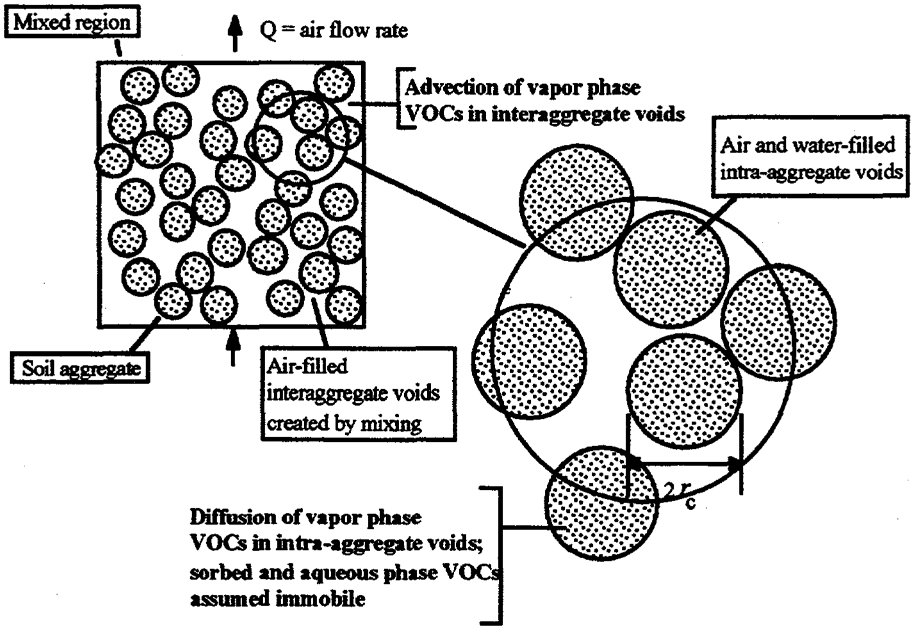


Fig. 1. Schematic illustrating a model for transport of volatile organic compounds in mixed soils.
Source: West, O. R., R. L. Siegrist, J. S. Gierke, S. W. Schmunk, A. J. Lucero, H. L. Jennings. "In Situ Mixed Region Vapor Stripping in Low Permeability Media: 1. Process Features and Laboratory Experiments." *Environ. Sci. Technol.* **29**, 2191-2197 (1995).

1.2 OBJECTIVES AND SCOPE

The objective of this study was to conduct further testing of MRVS, chemically enhanced with calcium oxide conditioning, on field-contaminated soils collected from beneath the NASA Michoud Rinsewater Impoundment. In this study, residual soil VOC levels as a function of vapor stripping time were measured to quantify VOC removal rates. Physical and chemical soil parameters expected to affect MRVS efficiency were measured (e.g., moisture content before and after calcium oxide conditioning, soil temperature during mixing, total organic content). The effects of varying the calcium oxide loadings (i.e., mass of calcium oxide per unit volume of soil) as well as varying the vapor stripping flow rates on VOC removal were also evaluated. The results of this study will be used to determine whether acceptable removals can be achieved within reasonable treatment times, remediation costs being directly proportional to the latter.

The purpose of this report is to document the experimental results of this study, as well as to address issues that were raised after completion of the previous Michoud treatability work [*6,7*]. The experimental approach (Sect. 2) and results of chemically enhanced MRVS tests (Sect. 3) are described in detail, including a discussion of treatment mechanisms and how these are affected by the physical and chemical properties of the mixed soil (also in Sect. 3). The transferability of the laboratory test results to a full-scale application, as well as a projection of expected costs for achieving various remediation goals at the Michoud Rinsewater Impoundment, is presented (Sect. 4). The technical feasibility of chemically enhanced MRVS is compared to alternative technologies that have potential application at the site (Sect. 4). This document concludes with recommendations on how to resolve the issue of existing contamination at the Michoud Rinsewater Impoundment (Sect. 5).

2. EXPERIMENTAL APPROACH

Field-contaminated soil cores were taken from three boreholes within the northern area of the NASA Michoud Rinsewater Impoundment (see Fig. 2 for boring locations). The cores were collected in 4-in.-diam, 6-in.-long stainless steel sleeves which were sealed immediately with Teflon-lined silicone sheets and aluminum plates clamped to each end of the sleeves. Previous testing at Oak Ridge National Laboratory (ORNL) has shown that this method of sealing can make sleeves air tight, thereby minimizing VOC losses from the soil during core shipment and storage. The cores were sent to ORNL in coolers filled with dry ice. The cores were stored at 4°C until testing.

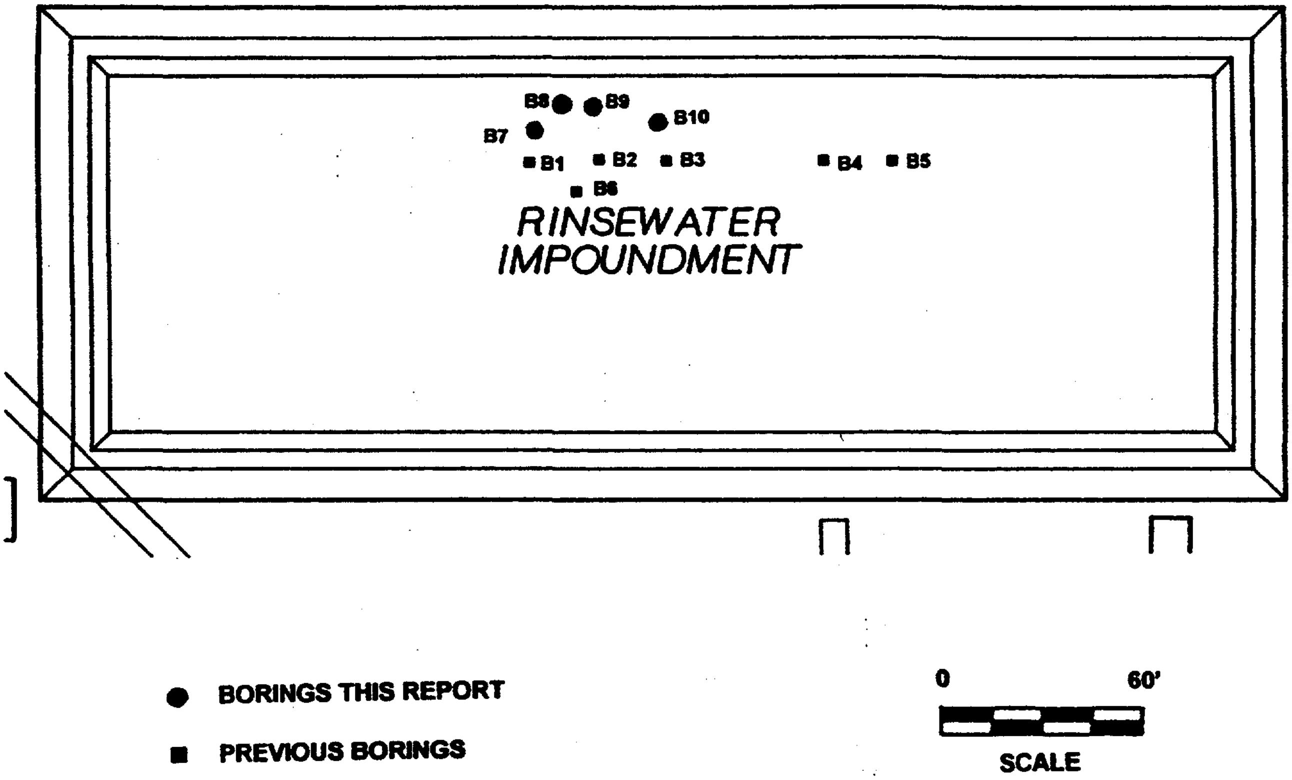


Fig. 2. Locations of boreholes from which soil cores were collected for this and previous treatability studies (B1 through B6 for previous study; B7 through B10 for this study; no cores were recovered from B7).

Chemically enhanced MRVS was conducted in the laboratory on the field-contaminated soil cores using the experimental apparatus schematically shown in Fig. 3.

The apparatus consists of a soil mixer, which was used to blend calcium oxide into the soil cores, and a fretted funnel, to which the mixed soils were transferred and subsequently vapor stripped. Previously, soil mixing and vapor stripping were performed simultaneously with the soil mixer shown in Fig. 2 [*1,6*]. In these earlier experiments, air was delivered to the soil by flowing it through the soil mixer's swivel joint, then through its hollow shaft, and finally through a number of orifices along the mixing blades. Because of difficulties encountered with air leakage at the soil mixer's swivel joint, vapor stripping in the experiments described here was conducted in a fretted funnel. Better quantification of air flow through the mixed soil was achieved with this revised approach.

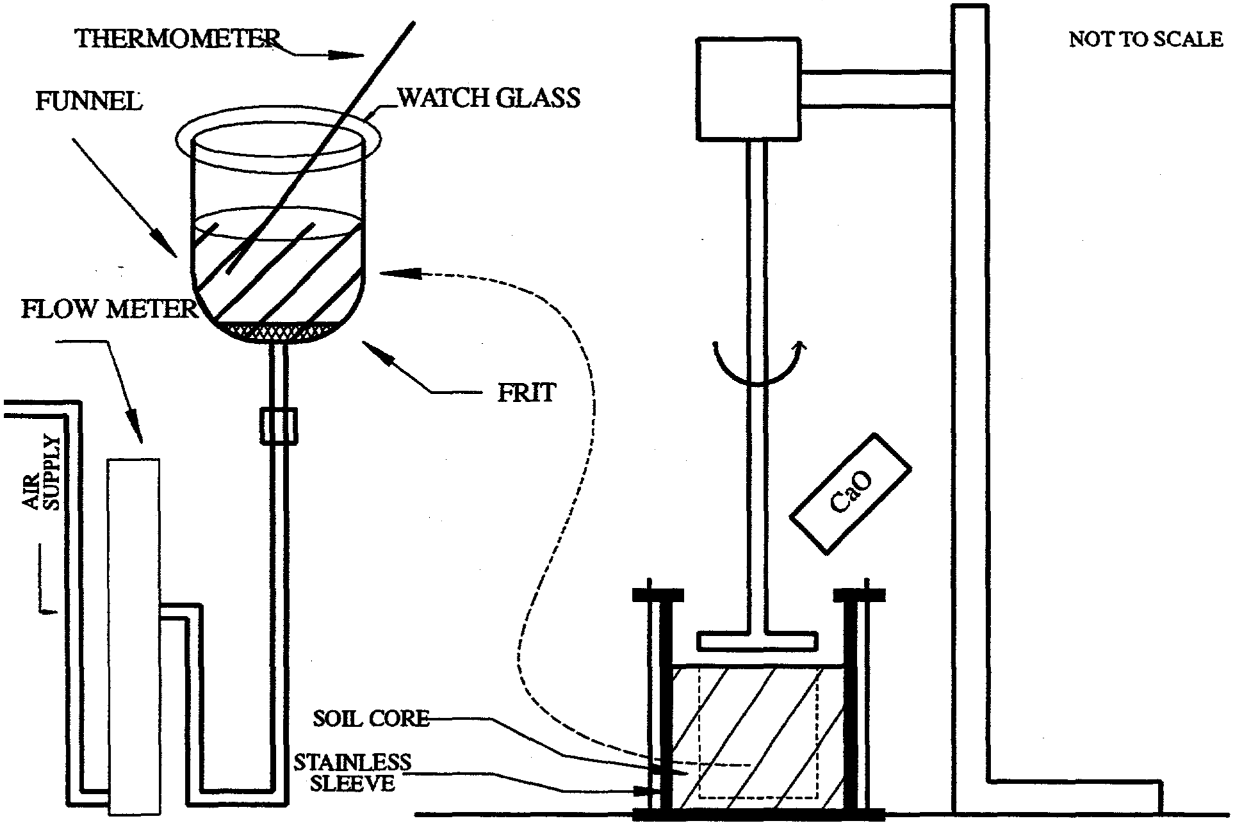


Fig. 3. Schematic of laboratory apparatus for simulating chemically enhanced mixed region vapor-stripping.

To keep track of soil VOC concentrations throughout the duration of core treatment, 2- to 3-g soil samples for VOC analysis were collected before mixing, after the mixed soil was transferred to the fretted funnel (time 0 min for vapor stripping), and at specific time intervals during the stripping process. For the first 11 of the 16 cores treated, vapor stripping was conducted for 360 min with VOC samples collected at 15, 30, 60, 120, 180, 240, and 360 min of treatment. Duplicate samples were collected before mixing and after 240 and 360 minutes of vapor stripping. Triplicate samples were collected at time 0 of vapor stripping, and single samples were collected for the rest of the time intervals. After it was determined that significant removals did not occur beyond 3 hours of vapor stripping, the remaining 5 of the 16 cores treated were vapor stripped for 180 min. Duplicate samples were taken at 0, 15, 30, 60, 120, and 180 min of vapor stripping. VOC levels in the soil were measured by 24-h extractions of the soil samples with 10 mL of high-purity hexane and subsequent analysis of 1-µL aliquots of the hexane extracts on a Hewlett Packard Model 5890 gas chromatograph/electron capture detector (GC/ECD). The GC/ECD was calibrated for TCE and cis-1,2-DCE; these were the two compounds that were predominantly found during the previous MRVS tests [*6*]. Instrument response was found to be linear for TCE concentrations in the hexane extracts ranging from 100 ppb to 50,000 ppb; this approximately corresponds to soil concentrations ranging from 500 µg/kg to 10,000 µg/kg. Whenever the concentrations in the hexane extracts exceeded 50,000 ppb, analyses were repeated with 1:100 dilutions.

Prior to mixing a soil core, soil physical parameters which were expected to affect MRVS removal efficiency [*1*] were measured. These parameters were wet bulk density, moisture content, total organic content, and grain size distribution (percent silt, percent clay). Wet bulk density was estimated from the mass of the soil core divided by the volume of the sleeve. Moisture content was quantified from the change in mass of 20- to 30-g soil samples after oven-drying for several days at 60°C or 100°C. Total organic content (TOC) was measured with a Rosemount-Dohrmann DC-190 TOC analyzer equipped with a Model 183 TOC Boat Sampler. Soil samples were pretreated with hydrochloric acid to remove inorganic carbon before TOC analysis. Particle size analysis for selected soil cores was performed following ASTM methods.

Soil temperature was measured immediately after the soil was mixed and transferred to the fretted funnel. In the last 7 cores treated, soil temperature was monitored throughout the vapor stripping process. After vapor stripping, the soil aggregate size distribution was measured in the treated soil through dry sieve analysis. Moisture content samples were also collected and analyzed to determine the degree to which calcium oxide conditioning and vapor stripping reduced soil moisture.

3. RESULTS AND DISCUSSION

3.1 SOIL CORE CHARACTERISTICS

The soil cores tested were all taken at depths ranging from 5.5 to 12 ft below ground surface (see Table 1 for a summary of physical and contaminant properties). Bulk densities were highly variable, with very low values found in the shallower B9 cores, and slightly higher values at B8 and B10. Except for cores B10,11.5-12.0 and B9,8.0-8.5[1], zero compressive strengths were registered on a pocket penetrometer for the cores. Of the three borings, cores from B9 had the highest visible organic content consisting of partially decomposed plant material. Measured TOC values were consistent with this visual observation (see Table 1). Moisture contents were high for all the cores but tended to decrease with depth. The extremely high moisture contents in the B9 cores are probably caused by the presence of partially decomposed organic matter in these cores. Air-filled porosities were estimated from the wet bulk density, moisture content, and an assumed typical soil grain density of 2.6 g/cc. Estimated air-filled porosities were fairly low for all cores, indicating that these soils were close to or at saturation. TCE and cis-1,2-DCE levels were quite variable. The cores from B8 had no detectable levels of TCE or cis-1,2-DCE. Cores collected from B9 (~15 ft from B8) had higher concentrations of VOCs, although levels changed more than an order of magnitude within 12 in. in this borehole (114 mg/kg TCE in B9,8.5-9.0 compared with 9 mg/kg TCE in B9,9.0-9.5). Cores from B10 were all very highly contaminated; core B10,9.5-10.0 had the highest TCE concentrations (3072 mg/kg).

3.2 TREATMENT CONDITIONS

Table 2 shows calcium oxide (CaO) loadings, air flow rates, and mixing times used on the treated cores. CaO loadings are reported in terms of absolute mass added to the cores (column 2), and in terms of mass of CaO added per unit volume of soil treated (column 3). The latter unit is more useful for estimating and specifying CaO loadings in field applications. Air flow rates were set either at 300 mL/min or 600 mL/min (column 4, corresponding to normalized flow rates of 1 and 2 min^{-1} (column 5). These values are

---

[1] Core B9,8.0-8.5 and B9,11.0-11.5 may have been mislabelled in the field. If the cores were switched, then the moisture content and VOC concentration in B9 would follow the same decreasing trend with depth observed in the cores from B10. The stiffer consistency of B9,8.0-8.5 is also more consistent with the consistency of B10,11.5-12.

comparable to the normalized flow rates used during the MRVS demonstration at the X-231B Unit [*2*].

Table 1. Physical and contaminant characteristics of soil cores collected from the Michoud Rinsewater Impoundment for this study

Core	Wet Bulk Density (g/cc)	Moisture content (dry weight %)	Air-filled porosity[a]	Silt (%)	Clay (%)	Total organic content (%)	TCE[b] (mg/kg)	cis-1,2-DCE[c] (mg/kg)
B8 6.5-7.0	1.12	290	6			14.42	nd	nd
B8 8-8.5	1.30	102	10			2.95	nd	nd
B8 8.5-9	1.34	97	8			1.48	nd	nd
B9 8-8.5	1.51	26	23				144	21
B9 8.5-9.0	1.17	487	saturated	6	78	21.65	114	128
B9 9.0-9.5	1.32	103	8			2.34	9	74
B9 9.5-10	1.47	69	7			1.04	3	47
B9 11.0-11.5	1.27	312	saturated				398	138
B10 5.5-6.0	1.00	532	10				945	287
B10 6.0-6.5	1.04	183	19				1302	718
B10 6.5-7.0	1.14	154	14				775	221
B10 9.5-10	1.20	177	7	21	75	4.52	3072	328
B10 10-10.5	1.39	88	6			1.12	407	159
B10 10.5-11	1.44	71	8			0.80	220	230
B10 11-11.5	1.43	105	0			1.58	269	180
B10 11.5-12	1.58	50	7	61	29	0.56	172	86

[a] Values are estimates.

[b] TCE = Trichloroethylene

[c] cis-1,2-DCE = cis-1,2-Dichloroethylene

Core B8,6.5-7.0 was the first core treated in this study. The amount of CaO used for this core (30 g or 100 kg/m^3) was clearly inadequate, since the soil remained pasty and did not aggregate even after the CaO was mixed into the core. For the rest of the cores, CaO amounts were increased if the soil remained slurry-like and pasty after the predetermined amount of CaO was added. For the next core treated (B9,8.5-9.0), CaO was added until the soil appeared dry and aggregated (with small aggregate diameters) after mixing. This core required 91.5 g (305 kg/m^3) of CaO to achieve the desired physical effects on the mixed soil. In the next three cores tested (B8,8.0-8.5; B8,8.5-9.0; B9,9.0-9.5), 100 g of CaO (333 kg/m^3) was used. This amount was then reduced to ~65-g (217 kg/m^3) for B9,9.5-10.0 and B10,10.0-10.5 through B10,11.5-12. Because these cores were not as water-filled as the previous cores, 65 g of CaO was adequate to achieve the desired aggregated soil texture. A 65-g CaO loading was attempted for B10,9.5-10; however, the soil remained very soft and slurry-like, so additional CaO was added until the soil appeared to drier and aggregated. A total of 242 g of CaO (807 kg/m^3) was applied to B10,9.5-10. Cores B10,5.5-6.0 and B10,6.0-6.5 had moisture contents higher than B10,9.5-10; these cores were treated with 250 g of CaO (833 kg/m^3). Only 200 g of CaO (667 kg/m^3) were required to achieve the aggregated soil texture in cores B10,6.5-7.0 and B9,11.0-11.5.

Table 2. Treatment conditions for laboratory simulations of chemically enhanced mixed region vapor stripping

Core	Mass of calcium oxide added (g)	Mass of CaO per unit soil volume[a] (kg/m^3)	Air flow rate (mL/min)	Air flow rate per unit soil volume[a] (min^{-1})	Mixing time (min)
B8 6.5-7.0	30	100	300	1.00	
B8 8-8.5	100	333	300	1.00	
B8 8.5-9	100	333	300	1.00	
B9 8.0-8.5	100	333	600	2.00	10
B9 8.5-9.0	91.5	305	300	1.00	8
B9 9.0-9.5	100	333	300	1.00	12
B9 9.5-10	65	217	300	1.00	5
B9 11.0-11.5	200	667	600	2.00	10
B10 5.5-6.0	250	833	600	2.00	10
B10 6.0-6.5	250	833	600	2.00	10
B10 6.5-7.0	200	667	600	2.00	10
B10 9.5-10	242	807	300	1.00	20
B10 10-10.5	60	200	300	1.00	8
B10 10.5-11	65	217	600	2.00	3
B10 11-11.5	65	217	300	1.00	9
B10 11.5-12	65	217	600	2.00	5

[a] Estimated from an average treated soil volume of 300 cc.

The first 11 of the 16 cores treated were mixed until the CaO appeared to be well-blended into the soil. Mixing time for these cores varied (column 6, Table 2) because some of the cores required additional applications of CaO. The last five cores treated were all mixed for 10 min before vapor stripping.

Air flow rates were selected to correspond with values for air flow rate per unit soil volume that are reasonable for field applications. Air flow rates during the MRVS field demonstration at the X-231B Unit ranged from 1000 cfm to 1400 cfm [*2*]. Soil mixers were 10 ft in diameter and were used to treat soils to a depth of 15 ft. These process parameters correspond to values of air flow rate per unit soil volume ranging from 0.85 to 1.2 min^{-1}. Higher VOC removals are not necessarily achieved by increasing air flow rates since VOC transport rate may be limited by diffusion through the soil aggregates [*1*]. Varying air flow rates were used in this study to determine whether VOC removals for Michoud soils could be diffusion-limited.

3.3 VOC REMOVAL RATES AND EFFECTS OF TREATMENT ON SOIL PHYSICAL CHARACTERISTICS

Tables 3 and 4 contain average values for TCE and cis-1,2-DCE levels, respectively, in the treated cores before mixing, immediately prior to, and after 60 and 360 minutes of vapor stripping (180-minutes for some cores). The following discussion focuses on TCE removal since cis-1,2-DCE removals were substantially more rapid than TCE.[2] Significant decreases in contamination even before vapor stripping were noted for all the B9 cores and for core B10,9.5-10.0 (compare "pre-mix" and "t=0 minutes" VOC levels in Table 3). These removals may have been brought about by large increases in temperature when the CaO was initially mixed with the soil (see Table 5 and Appendix B). Soil from B10,9.5-10, which was amended with 242 g of CaO, was at 66°C when vapor stripping began. This high temperature coupled with 20-minutes of mixing may have brought about the 3 orders of magnitude decrease in contamination. Slight or no changes in VOC content immediately after mixing were noted for cores B10,10.0-10.5 through B10,11.5-12.0. Temperatures did not increase beyond 35°C in these cores, possibly due to the fact that only 65 g of CaO was added to these cores.

---

[2] Appendix A contains TCE vs treatment time data for all cores treated.

Table 3. Trichloroethylene concentrations during laboratory simulations of chemically enhanced mixed region vapor stripping

Core	Trichloroethylene (mg/kg)				
	Pre-mix[a]	t = 0 min[b]	t = 60 min[c]	t = 180 min[d]	t = 360 min[e]
B8 6.5-7.0	nd[f]	nd	nd		nd
B8 8-8.5	nd	nd	nd		nd
B8 8.5-9	nd	nd	nd		nd
B9 8.0-8.5[g]	143.83	29.42	4.67	3.13	
B9 8.5-9.0	113.61	24.05	10.63		1.30
B9 9.0-9.5	8.75	0.52	0.17		0.10
B9 9.5-10	3.23	0.82	0.10		0.06
B9 11.0-11.5[g]	398.13	25.92	1.20	12.78	
B10 5.5-6.0[g]	945.48	118.65	11.07	17.16	
B10 6.0-6.5[g]	1302.27	654.88	55.28	18.40	
B10 6.5-7.0[g]	775.18	507.51	90.24	14.27	
B10 9.5-10	3071.82	60.89	4.71		10.79
B10 10-10.5	407.24	253.94	87.40		2.81
B10 10.5-11	228.83	156.54	6.00		2.01
B10 11-11.5	397.19	368.40	285.85		44.27
B10 11.5-12	216.51	110.25	12.91		5.49

[a] Pre-mix concentration; average of 2 samples.

[b] Concentration at start of vapor stripping; average of 2 or 3 samples.

[c] Concentration after 60 min of vapor stripping; 1 sample or average of 2 samples.

[d] Concentration after 180 min of vapor stripping; average of 2 samples.

[e] Concentration after 360 min of vapor stripping; average of 2 samples.

[f] nd = not detected; detection limit ≈ 1 µg/kg.

[g] Test stopped after 180 min of vapor stripping.

Table 4. Cis-1,2-dichloroethylene concentrations during laboratory simulations of chemically enhanced mixed region vapor stripping

Core	cis-1,2-Dichloroethylene (mg/kg)				
	Pre-mix[a]	t = 0 min[b]	t = 60 min[c]	t = 180 min[d]	t = 360 min[e]
B8 6.5-7.0	nd[f]	nd	nd		nd
B8 8-8.5	nd	nd	nd		nd
B8 8.5-9	nd	nd	nd		nd
B9 8.0-8.5 [g]	20.81	nd	nd	nd	
B9 8.5-9.0	128.47	11.34	2.27		0.29
B9 9.0-9.5	74.22	2.25	0.11		nd
B9 9.5-10	46.51	7.73	nd		nd
B9 11.0-11.5 [g]	137.91	2.47	nd	nd	
B10 5.5-6.0 [g]	286.79	nd	nd	nd	
B10 6.0-6.5 [g]	718.09	36.96	nd	nd	
B10 6.5-7.0 [g]	220.53	47.78	1.69	nd	
B10 9.5-10	328.01	3.94	nd		nd
B10 10-10.5	158.84	185.42	13.67		nd
B10 10.5-11	229.72	184.17	0.15		nd
B10 11-11.5	189.75	155.87	20.95		1.53
B10 11.5-12	180.94	91.88	0.26		0.75

[a] Pre-mix concentration; average of 2 samples.

[b] Concentration at start of vapor stripping; average of 2 or 3 samples.

[c] Concentration after 60 min of vapor stripping; 1 sample or average of 2 samples.

[d] Concentration after 180 min of vapor stripping; average of 2 samples.

[e] Concentration after 360 min of vapor stripping; average of 2 samples.

[f] nd = not detected; detection limit ≈ 1 μg/kg.

[g] Test stopped after 180 min of vapor stripping.

One of the issues raised after the treatability studies reported by Lucero et al. [*6*] was whether VOC removal efficiencies were dependent on initial levels of TCE in the soil. This was not found to be true in the tests conducted for this study, as shown in Fig. 4 where TCE removal efficiency is plotted against the pre-mix soil TCE concentration. In this figure, TCE removal efficiency for each core was calculated as follows:

$$\%\text{Removal}_{60\,/\,pre-mix} = \left(1 - \frac{C_{ave,t=60}}{C_{ave,pre-mix}}\right) \times 100 \; ,$$

where $C_{ave,pre\text{-}mix}$ and $C_{ave,t=60}$ are the average TCE concentrations before mixing and after 60 min of vapor stripping, respectively. In general, removals on the order of 90% were achieved for most of the cores, with initial contaminant levels ranging from 3071 mg/kg down to 3.75 mg/kg. Low removals of 28% and 78% were noted for B10,10.0-10.5 and B10,11.0-11.5. These were the same two cores for which VOC content did not change significantly immediately after being mixed with CaO. As mentioned previously, this may be caused by the inadequate amount of CaO (65 g) that was added to these cores. Of the five cores treated with 65 g of CaO, these two had the highest moisture contents (see Fig. 5). Even though the soil appeared aggregated, the amount of CaO may not have been adequate to reduce the moisture in these cores. Slow removals in cores B10,10.0-10.5 and B10,11.0-11.5 are also consistent with their aggregate sizes which tended to be larger than those of the rest of the B10 cores (see Table 5 and Fig. 6). Temperatures that did not exceed 35°C may also have contributed to the low removals in these cores.

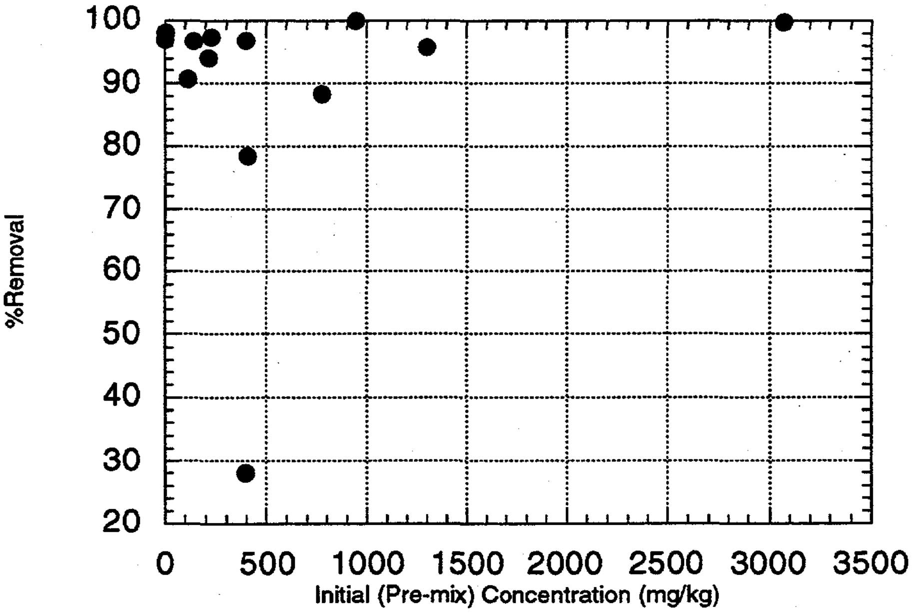


Fig. 4. Percent of trichloroethylene removed after mixing with CaO and 60 minutes of vapor stripping vs initial (pre-mix) trichloroethylene soil concentration.

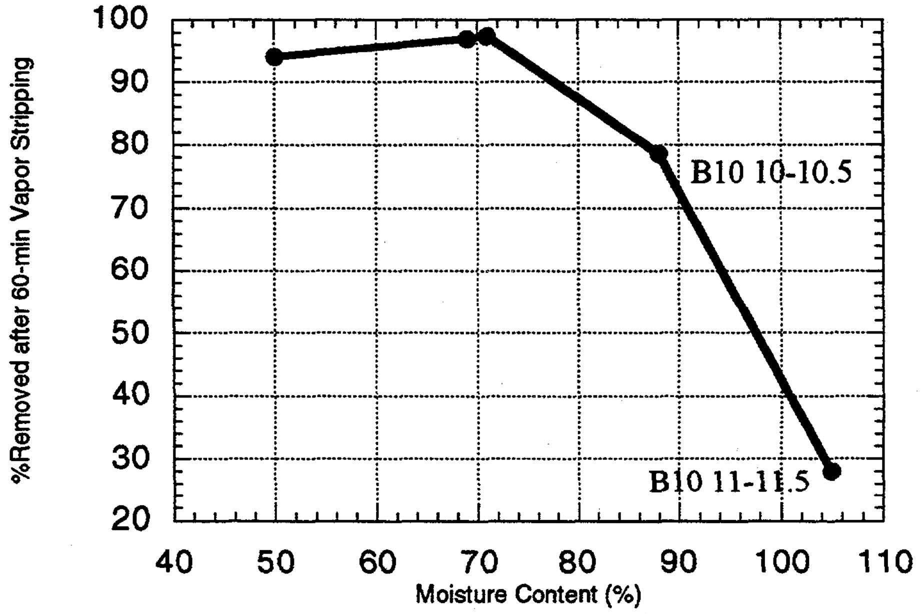


Fig. 5. Percent of trichloroethylene removed after mixing with CaO and 60 min of vapor stripping vs initial moisture content by dry weight, for cores treated with 65 g of CaO.

For most of the cores treated, VOC removals were fairly rapid within the first 30 to 60 min of vapor stripping, but were significantly lower thereafter (refer to Appendix A). This trend is illustrated in Fig. 7, where residual TCE levels in core B10,11.5-12 are plotted on a log-scale vs vapor stripping time. In this figure, the dashed line represents a piece-wise first-order kinetic curve [i.e., *(residual TCE)/(initial TCE) = exp(-kt)* where *k* is a rate constant and *t* is vapor stripping time], in which one rate constant is assumed to govern removal within the first 30 min of vapor stripping, and a second rate constant governs removal after 30 min. Removals in cores B10,10.0-10.5 and B11,11.0-11.5 were more gradual over 360 min of vapor stripping (see Fig. 8). The effects of the vapor stripping flow rate were evaluated by comparing removal rate constants among cores treated with the same CaO loadings (see Table 6). If VOC removal were diffusion-limited, then removal rates are not expected to increase with increasing flow rate. No such trends were observed in the cores that were treated with 100 g or 250 g of CaO (see Table 6). There appeared to be an increase of removal with higher flow rates in the cores treated with 65 g of CaO. However, it was noted previously that the low removals in cores B10,10.0-10.5 and B10,11-11.5 (which were vapor stripped at 300 mL/min) may have been due to an inadequate amount of CaO added to these cores. The latter could have been the main influence over the apparent trends with flow rate, given that no such trends were observed in the cores treated with 100 g and 250 g of CaO.

Table 5. Physical soil characteristics during and after laboratory simulations of chemically-enhanced mixed region vapor stripping.

Core	Post-treatment Moisture Content (%)	Reduction in Moisture Content (%)	Temperature[a] (°C)	Post-treatment pH[b]	Sieve diameter at 50% passing (mm)
B8 8.0-8.5	148	142		12.8	clumpy
B8 8-8.5	67	35			2.6
B8 8.5-9	52	45			1.9
B9 8.0-8.5	17	8	57		
B9 8.5-9.0	82	405	72	13.3	3.7
B9 9.0-9.5	53	50	41	10.3	2.3
B9 9.5-10	48	21	42	10.2	4.7
B9 11.0-11.5	57	254	53		
B10 5.5-6.0	66	466	58		
B10 6.0-6.5	61	123	75		
B10 6.5-7.0	52	102	60		
B10 9.5-10	52	125	66	12.4	3.0
B10 10-10.5	68	20	33	11.4	4.2
B10 10.5-11	48	23	37	11.4	1.9
B10 11-11.5	67	38	29	12.1	6.3
B10 11.5-12	40	10	36	12.3	3.3

[a] Ambient temperature ~18°C. Initial core temperatures ~12 - 18°C.

[b] Pre-treatment pH of soil ranged from 5.9 to 8.1.

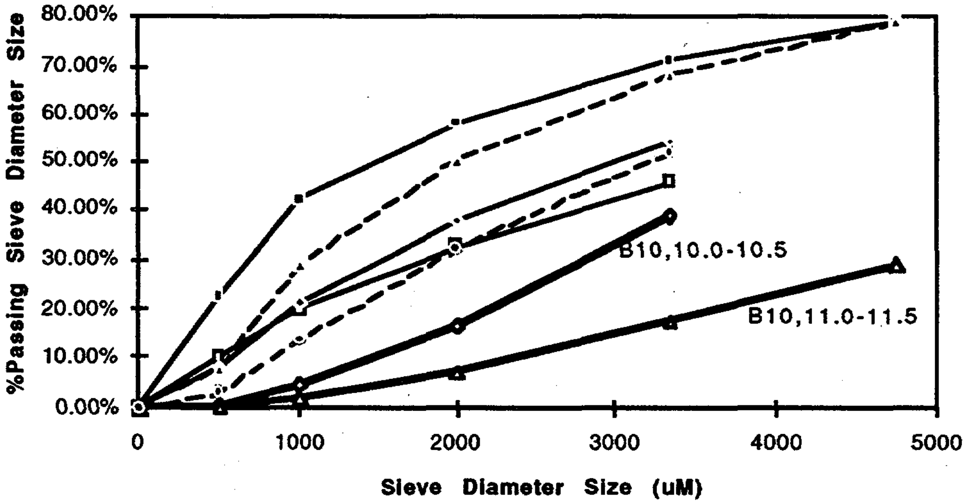


Fig. 6. Aggregate size distribution in mixed cores from B10. Cores B10,10.0-10.5 and B10,11.0-11.5 have larger aggregate sizes.

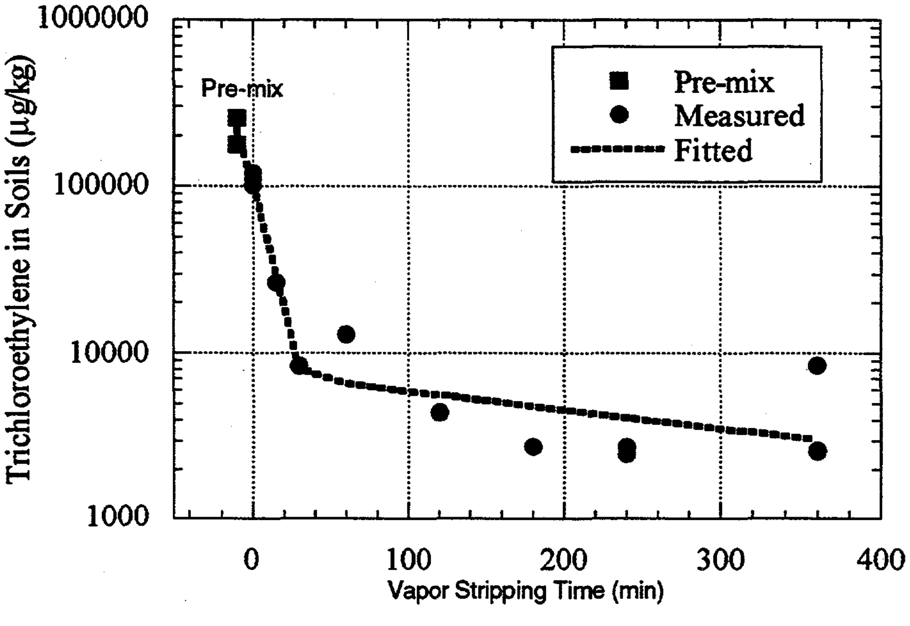


Fig. 7. Example of a piece-wise residual trichloroethylene vs treatment time curve. Data shown taken from core B10,11.5-12. Line represents first-order kinetic curves fit through the data, with one rate constant governing removal from 0 to 30 minutes, and a second rate constant governing removal from 30 to 360 minutes.

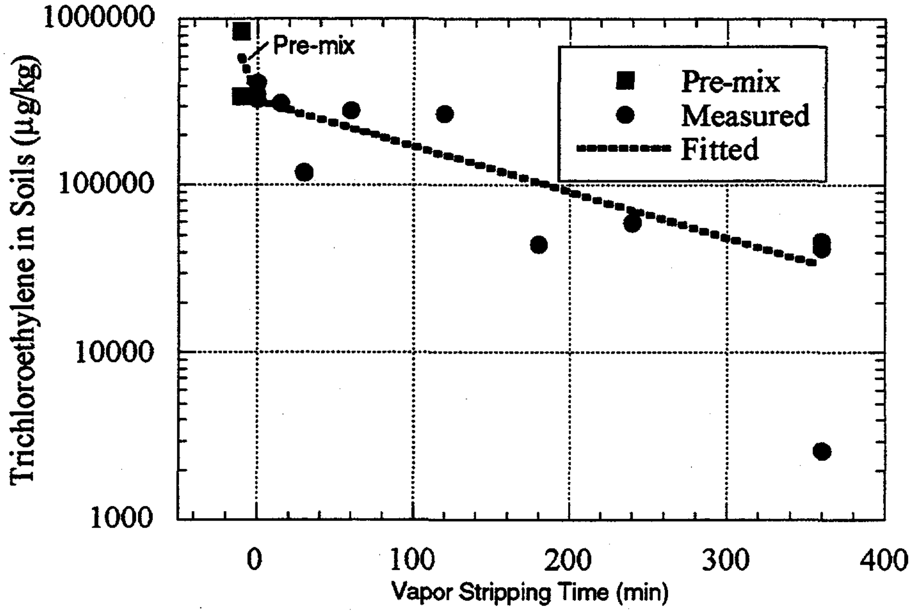


Fig. 8. Example of a single trichloroethylene vs treatment time curve. Data shown taken from core B10,11.0-11.5. Line represents a first-order kinetic curve fit through the data, with one rate constant governing removal from 0 to 360 minutes.

Table 6. Trichloroethylene removal rate constants compared at different flow rates for cores treated with the same amount of CaO

CaO Loading	Core	Flow rate (mL/min)	Trichloroethylene removal rate constant during first 30-min of vapor stripping (min^{-1})
91.5-100 g	B9 8.0-8.5	600	0.0263
	B9 8.5-9.0	300	0.0595
	B9 9.0-9.5	300	0.0383
65 g	B9 9.5-10.0	300	0.0363
	B10 10.0-10.5	300	0.0092
	B10 10.5-11.0	600	0.0964
	B10 11.0-11.5	300	0.0063
	B10 11.5-12.0	600	0.0870
242-250 g	B10 5.5-6.0	600	0.0379
	B10 6.0-6.5	600	0.1287
	B10 9.5-10.0	300	0.0909

We hypothesized that stronger sorption of TCE on partially dehydrated CaO-treated soil was the reason behind reduced removal rates after 30 to 60 min of vapor stripping. Water can compete with VOCs for sorption sites on mineral surfaces, such that higher VOC vapor phase partition coefficients have been measured at low soil moisture contents [*8*]. In the last core treated (B9,11.0-11.5), the stripping air was humidified by passing it through a heated water bath before it came in contact with the mixed soil. We thought that this would keep the soil partially moist to prevent higher sorption of TCE on dried soil. VOC removals were not dramatically improved with this approach (see Appendix A). Furthermore, residual VOC levels in the soil were more erratic compared to the previous cores that were treated with dry air.

The hypothesis of stronger TCE sorption on CaO-treated soil was also tested in an experiment where equal amounts of TCE were injected into vials containing equal masses of uncontaminated field-moist soil, CaO-treated soil, and pure CaO. The loading in the CaO-treated soil was equivalent to the 65-g CaO loadings in the core experiments (217 kg/m^3). After a 24-h equilibration in a 25°C water bath, TCE content in the headspace of the vials was measured by taking 20-µL vapor-phase samples that were then injected into a GC/ECD. No statistically significant differences were found between the headspace TCE concentrations in the vials with untreated and CaO-treated soil. However, a significant reduction of headspace TCE did occur in the vials with CaO alone. This experiment showed that higher TCE sorption may occur on pure CaO and that partitioning on soil treated with CaO (220 kg/m^3) was not different from untreated soil. This experiment still does not preclude the possibility of higher sorption at higher CaO loadings, especially where unreacted CaO may be present.

The apparent bi-phasic removal curves observed in a majority of the cores treated so far is an interesting phenomenon that may be attributed either to temperature or sorption effects. Further experimentation beyond the scope of this treatability work would be required to investigate the reasons for this. However, such a study may not be required for the field application of chemically enhanced MRVS. Results show that the technology can be expected to remove VOCs quite effectively within 1 to 2 h of treatment if the soil is amply mixed with an adequate amount of CaO and aggregate sizes are sufficiently small.

4. ASSESSMENT OF TECHNOLOGY FEASIBILITY

4.1 RECOMMENDED PROCESS CONDITIONS AND REMEDIATION COST ESTIMATES

The experiments described in the previous section have shown that chemically enhanced MRVS can effectively remove TCE and cis-1,2-DCE from the highly saturated, highly organic soils underlying the Michoud Rinsewater Impoundment. Treatment effectiveness depends on selecting adequate CaO loadings corresponding to the moisture content of the soil. CaO loadings required to achieve an aggregated mixed soil vary not only with depth but also with borehole [e.g. less CaO was required in B9 compared with B10 (see Fig. 9)]. CaO loadings ranged from 213 to 813 kg/m^3 in cores from B10, and 200 to 667 kg/m^3 in cores from B9. In an actual field application, metering the amount of CaO at different depths may be difficult. However, because the mixer can essentially homogenize a soil column over the mixing depth, the required CaO loading can be estimated from the average of the extreme loadings used in the experiments. By using this approach, the CaO required for Michoud soils is estimated to be 400-500 kg/m^3.

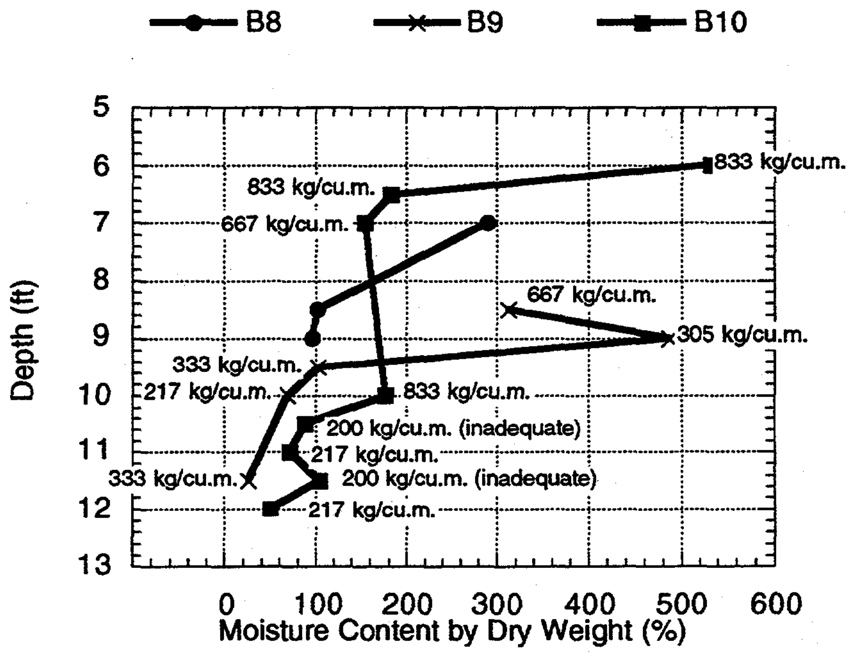


Fig. 9. Moisture content by dry weight as a function of depth. The locations of B9,11.0-11.5 and B9,8.0-8.5 have been switched. CaO loadings indicated beside data points.

One of the concerns when having to use such a high loading of CaO is the volumetric expansion that can result while mixing the soil. For the highly saturated cores, which required significant amounts of CaO, the soil did not expand substantially and maintained its slurry-like structure until the soil began to aggregate. At this point, enough CaO had been added to the soil. Volumetric expansion may not pose a significant problem in the field because of the unconsolidated nature of the Michoud soils. However, this can only be verified by a field application.

A second concern is the increase in soil pH when large amounts of CaO are added to the soil (Table 5). Before field testing chemically enhanced MRVS, the possibility of elevated soil pH should be discussed with environmental regulators. This may not be an issue since lime subsurface application is a common geotechnical and agricultural practice.

The costs associated with chemically enhanced MRVS include the following major components: (1) mobilization, (2) reagent cost, (3) operation of soil mixer, (4) demobilization, and (5) waste disposal. Of these five components, the cost for operating a soil mixer is the only one which is directly proportional to treatment time. For a given set of process conditions (i.e., CaO loadings and flow rates), the target residual contaminant level (or contaminant removal) is a function of treatment time. The required treatment time for a full-scale soil column to achieve a given percentage of TCE removal was estimated from the mixing experiments and is shown in Fig. 10. This estimate assumes that removal patterns observed in the mixing experiments can be used to predict field removals under similar CaO and normalized flow rate conditions. In the laboratory tests, the flow rates were 300 and 600 mL/min to vapor strip a soil volume of ~300 cc. Hence, the removal curve in Fig. 10 would be applicable to an 8-ft-diameter, 15-ft-deep soil column (~750 ft^3) that is vapor stripped with air at 750 to 1500 cfm. The removal curve was assumed to consist of three parts, corresponding to the observed trend in TCE vs treatment time data from the mixing experiments. The first portion of this curve (0-10 min) corresponds to the removals measured immediately after CaO was blended into the cores. TCE residual after 10 min was taken from the average of the ratio between the $t = 0$ and pre-mix TCE concentrations (excluding values from B10,10.0-10.5 and B10,11.0-11.5 for which CaO loading was inadequate). The second ($10 \text{ min} < t < 40 \text{ min}$) and third ($t > 40$ min) parts of the curve correspond to the removals observed during and after 30-minutes of vapor stripping, respectively. These are modeled as first-order kinetic curves, with rate constants taken from the average of the rate constants measured in the experiments (excluding values from B10,10.0-10.5 and B10,11.0-11.5).

The removal model in Fig. 10 predicts that percentage removals increase rapidly within the first 40-min of treatment. Additional removals gained after 40 min of MRVS are not expected to be significant. The cost for remediating a full-scale soil column can be estimated by assuming a daily cost for operating the soil mixing equipment (e.g., an 8-ft-diam soil mixer), and the time per day that the mixer is in use for remediation (e.g., 4 h or 240 min). At a daily cost of \$10,000, the cost per minute of treatment is ~\$42. This cost was combined with the removal model in Fig. 10, to produce a curve that defines the cost per soil column as a function of percentage TCE removed (Fig. 11). Treatment costs change gradually for target percentage removals < 95%, but escalate rapidly at removals > 95%. For example, it would cost \$1000 per soil column for a target removal of 90% (see Fig. 9). At 95%, this cost increases to \$2000. At 99%, the cost increases 6 times to \$12,000. This cost trend is an effect of the reduced removal rates that were observed in the experiments after 60 min of treatment.

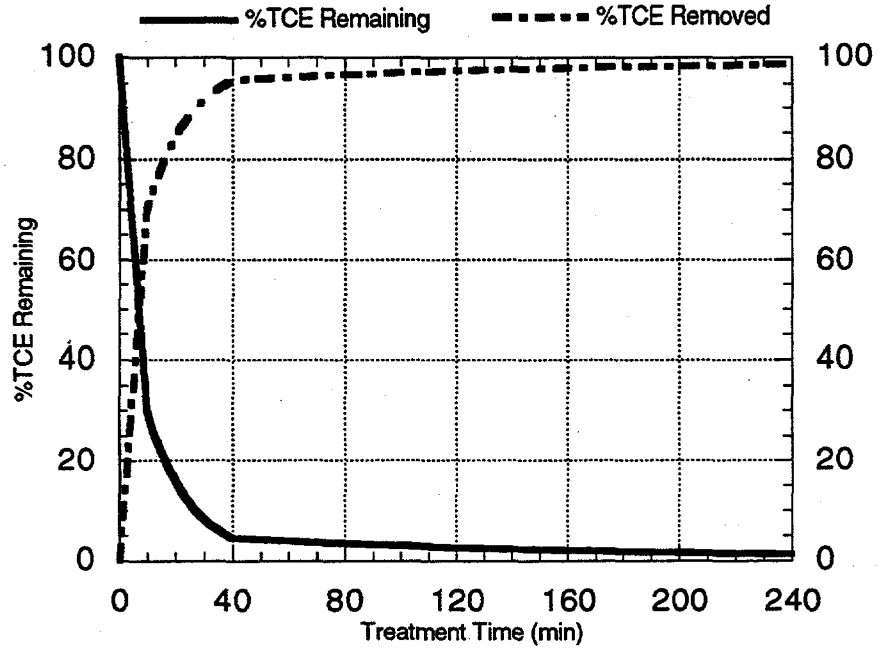


Fig. 10. Percent of trichloroethylene remaining and removed as a function of treatment time for chemically-enhanced mixed region vapor stripping.

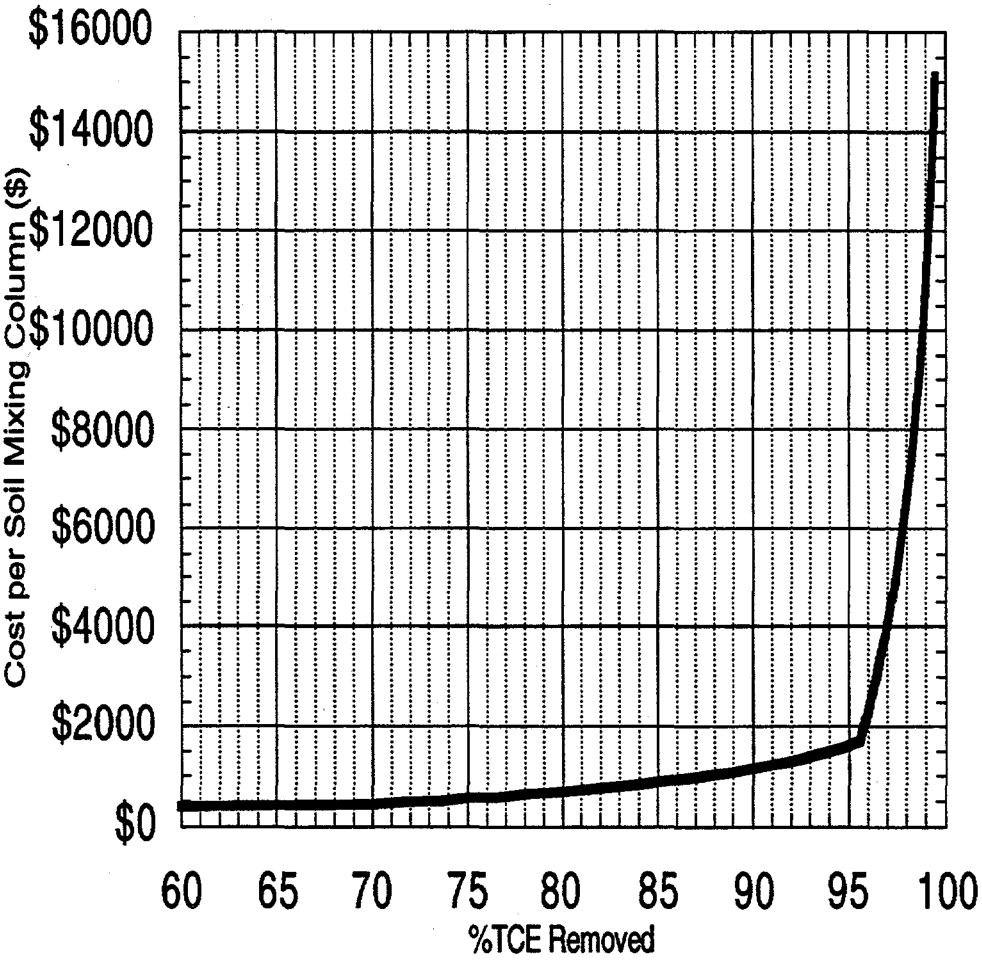


Fig. 11. Cost per soil column for chemically enhanced mixed region vapor stripping as a function of percentage trichloroethylene removed. (See text for assumptions)

The cost for remediating the entire Michoud Rinsewater Impoundment will depend on the treatment goals, which may take one of the following forms:

(1) a minimum percentage removal over a region of interest. Since removal rates appear to be independent of initial concentrations, this kind of treatment goal can be achieved by subjecting the entire region of interest to the same treatment time. The disadvantage of this approach is that regions with initially high contaminant levels may

still have relatively elevated post-treatment levels. However, the overall effect of these "hot spots" to the environment may be minimal if the volume of these hot spots is small.

(2) a minimum percentage removal of total contaminant mass over a region of interest. This approach, which is similar to what was used at the full-scale cleanup of the X-231B Unit, is equivalent to saying that the average contaminant concentration within the region of interest must be reduced by a minimum amount. This average may be decreased either by remediating the entire site for the same amount of time to achieve an overall percentage reduction [the same as no. (1)], or, remediation may be limited to the "hot spots." In the latter approach, more time may be spent remediating the hot spots, but the total amount of time spent would be the same or less than the time spent using approach no. (1). Estimating the time required to remediate a region of interest would require that the distribution of contaminants be known a priori.

(3) a target maximum residual concentration within the entire region of interest. As in no. (2), the required total treatment time would depend very strongly on the distribution of contamination within the region of interest.

The cost for treating a cubic yard of soil for specified target percentage removals (remediation goal no. (1) above) can be directly calculated from costs per soil column shown in Fig. 11 (Table 7).

Table 7. Cost per cubic yard of soil for chemically enhanced mixed region vapor stripping (MRVS) for given target percentage trichloroethylene (TCE) removals

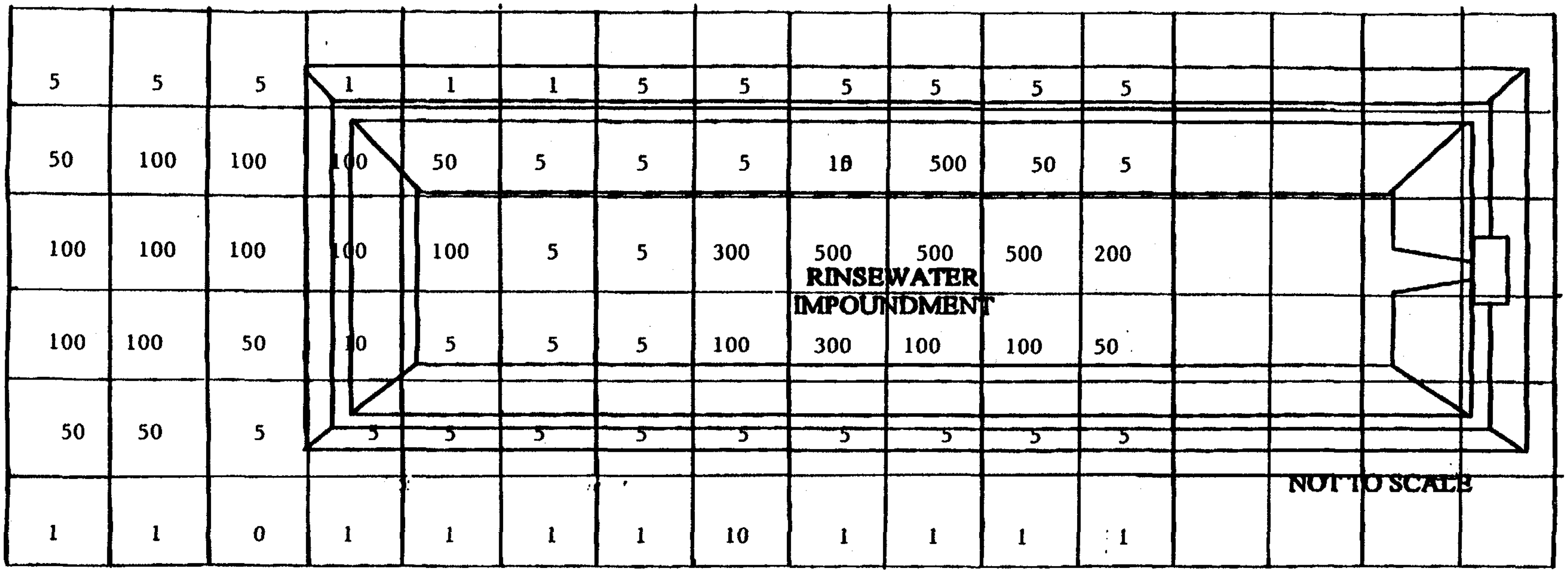
Target percentage TCE removal (%)	Cost per soil column for operating soil mixer[a]	Cost per cubic yard of soil for operating soil mixer [b]	Remediation cost per cubic yard of soil[c]	Residual TCE concentration (mg/kg) assuming initial level of 3000 mg/kg	Residual TCE concentration (mg/kg) assuming initial level of 300 mg/kg
90	\$1000	\$36/yd^3	\$63/yd^3	300	30
95	\$2000	\$71/yd^3	\$98/yd^3	150	15
99	\$12000	\$429/yd^3	\$456/yd^3	30	3

[a] Taken from Fig. 11 of this report.

[b] An 8-ft-diam, 15-ft-deep soil column has a volume of 28 yd^3.

[c] Includes reagent cost = \$27/yd^3 assuming \$80/ton of CaO

The cost for remediating the Michoud Rinsewater Impoundment given a specified target residual TCE concentration (approach no. (3)) was estimated from the removal curve in Fig. 10, and from contaminant contour maps derived from existing site characterization data [*6, 9*]. A grid consisting of 30-ft by 30-ft squares (see Fig. 12) was overlaid on a map of the Michoud Rinsewater Impoundment. TCE concentrations at three depth ranges within each square sub-area were then read off of the contaminant contour maps (see Appendix C for contour maps), and the highest concentration was assumed to be the initial TCE concentration within the entire depth of the sub-area (see Fig. 12). Knowing the initial concentration for a square sub-area and the target residual concentration, the treatment time required for each square sub-area can be estimated from the removal curve in Fig. 10. The total treatment time required for remediation is the sum of the treatment times for all the square sub-areas. Total cost for the operation of the soil mixer can be calculated from this total treatment time, assuming that an 8-ft-diam soil mixer is used and that the cost for operating this mixer is $10,000 per day. Costs for CaO can be calculated based on the amount of soil that requires treatment. This is then added to the total cost for soil mixer operation to arrive at a final estimate for remediation cost of the Michoud Rinsewater Impoundment as a function of the target residual TCE concentration (see Fig. 13, detailed calculations are contained in Appendix D of this report). The large increase with lower target residuals is due to longer treatment times as well as higher soil volumes that would require treatment.



5	5	5	1	1	1	5	5	5	5	5	5				
50	100	100	100	50	5	5	5	10	500	50	5				
100	100	100	100	100	5	5	300	500	500	500	200				
100	100	50	10	5	5	5	100	300	100	100	50				
50	50	5	5	5	5	5	5	5	5	5	5				
1	1	0	1	1	1	1	10	1	1	1	1				

Fig. 12. Grid used to estimate required time and cost for remediating the Michoud Rinsewater Impoundment given a target residual trichloroethylene concentration. Square subareas are 30 ft x 30 ft. Numbers in squares are assumed initial trichloroethylene concentrations (in mg/kg) within each sub-area.

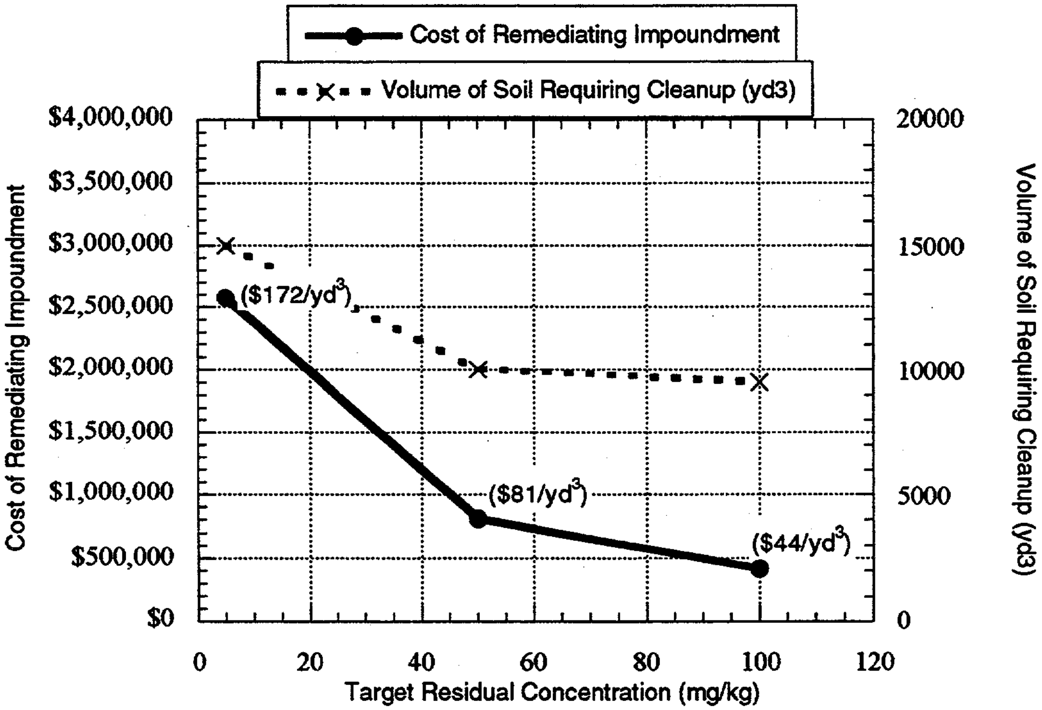


Fig. 13. Cost for remediating Michoud Rinsewater Impoundment vs target residual trichloroethylene concentrations. Effective remediation cost per cubic yard shown in parentheses.

4.2 COMPARISONS WITH ALTERNATIVE TECHNOLOGIES

Tables 8 and 9 contain lists of alternative in situ and ex situ technologies, respectively, for remediating TCE-contaminated soils. The tables also include (1) a description of the treatment mechanism; (2) the status of each technology (bench-, pilot-, or full-scale); and (3) anticipated feasibility for remediating the highly organic, highly saturated soil underlying the Michoud Rinsewater Impoundment. Technologies that were unlikely to achieve remediation goals were given a "low" feasibility rating. "Medium" feasibility was assigned to technologies that are potentially applicable to the site. A "high" rating would have been given to technologies that have a high probability of achieving remediation goals, but because of uncertainties in treatment performance brought about by difficult in situ conditions (high moisture and organic soil content), none of the technologies listed in Tables 8 or 9 were given this rating.

Of the eight in situ technologies listed in Table 8, electroosmosis and 2-Phase extraction were considered to be potentially capable of overcoming the difficult soil conditions underlying the Michoud Rinsewater Impoundment. Both of these technologies are fairly new (<2 years) and have not been tested under a wide variety of conditions. Hence, laboratory and/or field pilot tests at the Michoud Rinsewater Impoundment may have to be conducted to establish technical feasibility with a higher degree of certainty. Better estimates for costs associated with these technologies can also be obtained from pilot tests.

Information regarding the four ex situ technologies in Table 9 was found in the VISITT 4.0 database [*11*], a compilation of vendor information developed by the U.S. Environmental Protection Agency. For thermal desorption, some vendors listed in the VISITT 4.0 database state that moisture contents greater than 20-30% and high clay/silt content significantly reduce process throughput [*11*]. Thus, costs for treating the Michoud soil by thermal desorption are expected to be on the higher end of the $50-400/ton range contained in the database. The reduced throughput is likely a result of the higher energy required to heat soils with a high water content, as well as difficulties in handling very wet soils. Soil dewatering before thermal desorption is possible but would also add to treatment cost. Solvent extraction is an alternative to thermal desorption, with costs listed in database ranging from $100-400/ton. One of the vendors states that costs increase with moisture contents >70%; this cost increase may occur in the remediation of

Michoud soils which have moisture contents as high as 500% (see Fig. 11). Chemical oxidation by Fenton's reagent was offered by one vendor in the database. This vendor mentioned that reaction rates may be significantly reduced if soils have a high clay content, which is also true for the Michoud soils.

Table 8. In situ technologies for remediating trichloroethylene (TCE)-contaminated soils

Technology	Technology description and treatment mechanism	Technology status	Feasibility at Rinsewater Impoundment (low, medium, high)
Mixed region chemical oxidation [*6,10*]	TCE degraded by strong oxidizers ($KMnO_4$ or H_2O_2).	Full-scale for H_2O_2 Bench-scale for $KMnO_4$	(Low to Medium) Natural soil organics will compete with TCE for oxidants; larger amounts of oxidants may be needed.
Mixed region reductive dechlorination by iron filings [*6*]	TCE dechlorinated by zero-valence iron.	Preliminary bench-scale	(Technology has not been explored sufficiently) Incomplete dechlorination produces vinyl chloride, which is more toxic than TCE.
Mixed region bioremediation [*11*]	TCE aerobically or anaerobically degraded either by indigenous or engineered microorganisms.	Bench- to full-scale	(Low) Extremely high levels of TCE may be toxic to degrading organisms.
Mixed region steam stripping [*11*]	TCE volatilized by increasing soil temperature through steam injection	Full-scale	(Low) High soil moisture content will require large amounts of energy (i.e., steam) to increase soil temperature. Condensed steam will add water to a soil that already has a very high moisture content.
Soil vacuum extraction (SVE) enhanced by hydraulic or pneumatic fracturing [*11*]	TCE volatilized by SVE; low-permeability formations are fractured hydraulically or pneumatically to increase air conductivities.	Full-scale	(Low) Due to high-plasticity and moisture content, soils are not likely to fracture. Hydraulic or pneumatic pressures used to induce borehole fracturing would probably result in plastic deformations around the borehole instead.
Soil vacuum extraction (SVE) enhanced by AC- or radio-frequency heating [*11,12*]	TCE volatilized by SVE; soil is heated to increase fugacity of TCE.	Full-scale	(Low) The heat capacity of water is ~5 times the heat capacity of dry soil particles [*13*], therefore, large amounts of energy will be required to heat high-moisture content soil.

Table 8. (continued)

Technology	Technology description and treatment mechanism	Technology status	Feasibility at Rinsewater Impoundment (low, medium, high)
Electroosmosis: "Lasagna" process [*14*]	Electrokinetics used to induce migration of water/TCE through trapping (carbon adsorption) or degradation (zero-valence iron) barriers.	Pilot-scale	(Medium) This technology has been pilot-tested recently but data are currently unavailable. Since treatment is at ambient temperature, treatment time may be lengthy as a result of the high organic content of the soil.
2-Phase Extraction [*15*]	TCE volatilized by high-vacuum pumps (as much as 28-in. Hg), which draw soil water and vapor from low-permeability soils	Full-scale	(Medium) Soil appears to have a high water-holding capacity so dewatering may be difficult even at high vacuums. Since treatment is at ambient temperature, treatment time may be lengthy as a result of the high organic content of the soil.

Table 9. Ex situ technologies for remediating trichloroethylene-contaminated soils

Technology	Treatment mechanism	Technology status	Feasibility at Rinsewater Impoundment (low, medium, high)
Thermal desorption [*11*]	TCE volatilized from soil, which is heated in rotary kilns to temperature above boiling point of contaminants.	Full-scale	(Low to Medium) Some thermal desorption units can only handle soils with moisture contents <20-30% so that soil must be dewatered prior to treatment. For undewatered soils, energy requirements will be high to heat soil to desired temperatures.
Chemical oxidation [*11*]	TCE degraded by strong oxidizers (H_2O_2).	Full-scale for H_2O_2	(Low to Medium) Natural soil organics will compete with TCE for oxidants; larger amounts of oxidants may be needed.
Solvent extraction [*11*]	TCE is extracted from the soil by liquefied gas solvents.	Full-scale	(Low to Medium) One vendor claims it can be used for sludge. Another vendor states that costs become high with moisture contents >70%. Mostly used for semi-volatile organics, probably due to cost.
Biodegradation [*11*]	TCE is biodegraded by indigenous or non-native bacteria.	Full-scale	(Low) High levels of TCE may be toxic to bacteria. TCE degradation rates may not be rapid enough to achieve high soil throughput.

Based on the rough-order-of-magnitude estimates given in the previous section, chemically enhanced MRVS compares favorably with the ex situ methods listed in Table 9 if remediation goals are set to 95% removal. The estimated cost for chemically enhanced MRVS is ~\$100/ton (1 ton is ~1 cu.yd. of soil) This is lower than costs for the ex situ methods given in Table 9, which may range from \$200 to \$400/ton given the high moisture and clay content of the Michoud soil.

Comparing chemically enhanced MRVS with electroosmosis and 2-Phase extraction is more difficult because of the lack of data from applications of the latter technologies at other sites. TCE removal with chemically enhanced MRVS may be more rapid since temperatures are elevated and moisture contents are reduced, both due to the hydration reaction of CaO. However, without testing equivalent to the experiments described in this report, saying with certainty that chemically enhanced MRVS would achieve remediation goals faster and at a lower cost than electroosmosis or 2-Phase vacuum extraction is not feasible at this point.

5. CONCLUSIONS AND RECOMMENDATIONS

Chemically enhanced mixed region vapor stripping is a viable technology for in situ remediation of TCE-contaminated soils underlying the Michoud Rinsewater Impoundment. This conclusion is based on laboratory simulations of MRVS performed on 16 field-contaminated cores collected from the study site. Residual levels of predominant VOCs (TCE and cis-1,2-DCE) measured as a function of treatment time showed that TCE and cis-1,2-DCE removals were very rapid in the first 60 minutes after the cores were amended with a sufficient amount of CaO. Removal rates were significantly lower when vapor stripping was continued beyond 60 minutes. A TCE removal curve (percent TCE removed as a function of treatment time) was developed by averaging the removal curves obtained from the MRVS tests. Based on this curve, it is estimated that ~30 and ~300 minutes of treatment is needed to remove 90% and 99% of initial TCE contamination. For example, starting with an initial concentration of 3000 mg/kg, only 30 minutes of chemically enhanced MRVS is required to achieve a target residual of 300 mg/kg. The same amount of time would be needed to go from 300 to 30 mg/kg of contamination. However, a significantly longer time (300 minutes) would be required to achieve a residual level of 30 mg/kg if the initial contaminant level were 3000 mg/kg. This substantial increase in treatment time when remediation goals for TCE increase beyond 95% is a reflection of the bi-phasic removal patterns observed in the MRVS tests (i.e., rapid followed by slower TCE removal beyond 60 minutes of treatment). Rapid removals were accompanied by increased soil temperatures ranging from 40°C to 75°C. The more gradual removals observed beyond 60 min of treatment may be a result of temperatures returning to ambient levels, as well as increased sorption on drier soils.

The amount of CaO required to achieve high removal rates was found to be dependent on the initial moisture content of the soil; a 400-500 kg/m^3 CaO loading is expected to be sufficient for the Michoud soils, which have moisture contents ranging from 26 to 534% dry weight. This high CaO loading is needed to dehydrate the soil sufficiently and to achieve temperature increases necessary for rapid TCE removal. Some concerns exist regarding the volumetric expansion of the soil when this much CaO is added in situ. However, this may not occur due to the unconsolidated nature and low density of the contaminated soil under the Michoud Rinsewater Impoundment. This concern can be best addressed through a field test.

Chemically enhanced MRVS was estimated to cost ~\$100/ton for a remediation goal of 95% TCE removal. This is lower than anticipated costs for ex situ methods (e.g., excavation followed by on-site treatment), which are potentially more costly than normal to implement due to the extremely high moisture content of the Michoud soils. Two other technologies were identified as having the potential for remediating the highly saturated, low-permeability soils underlying the Rinsewater Impoundment. These technologies, electroosmosis and 2-Phase extraction, are fairly new and have not been applied to a wide variety of sites. Specific performance and cost data for remediating the Rinsewater Impoundment using these methods can only be obtained if laboratory and/or field tests are conducted.

On the issue of addressing existing contamination at the Michoud Rinsewater Impoundment, we recommend the following:

(1) Vendors that can provide soil mixing and calcium oxide delivery should be contacted to obtain more accurate cost estimates for chemically enhanced MRVS on the basis of the removal curve generated from this work. Once better cost estimates for this technology are established, NASA Michoud can make a decision on whether the technology should be field tested.

(2) Field testing of chemically enhanced MRVS can be provided by ORNL. ORNL can design the field experiment, hire and supervise a contractor to conduct soil mixing and CaO delivery, and collect samples for performance assessment. The scope of this field test can be adjusted to accommodate NASA Michoud's budget constraints. Alternatively, NASA Michoud can hire a soil-mixing vendor who would be willing to work with ORNL staff to develop process parameters in the field. In the latter case, ORNL can assist NASA Michoud in evaluating the field performance of the technology. The possibility of continuing the full-scale cleanup should be considered when contracting the services of the soil mixing vendor in case the field test is successful. This way, mobilization and de-mobilization costs would not have to incurred twice like they would be if the full-scale cleanup were not done immediately after field testing.

(3) Vendors who provide 2-Phase extraction and electroosmosis services should be contacted to explore the possibilities of field testing these technologies. Some of these

vendors may be willing to provide order-of-magnitude estimates given some information regarding the Michoud site.

6. REFERENCES

[1] West, O. R., R. L. Siegrist, J. S. Gierke, S. W. Schmunk, A. J. Lucero, and H. L. Jennings. 1995. In situ mixed region vapor stripping in low permeability media: 1. Process features and laboratory experiments. Environ. Sci. Technol. 29:2191-2197.

[2] Siegrist, R. L., O. R. West, M. I. Morris, D. A. Pickering, D. W. Greene, C. A. Muhr, D. T. Davenport, and J. S. Gierke, . 1995. Environ. Sci. Technol. 29:2198-2207.

[3] Gierke, J. S., C. Wang, O. R. West, and R. L. Siegrist. 1995. In situ mixed region vapor stripping in low-permeability media. 3. Modeling of field tests. Environ. Sci. Technol. 29:2208-2216.

[4] West, O. R.; James, B. R.; Bayne, C. K.; Siegrist, R. L. 1994. Performance verification in soil mixing and vapor stripping of VOC contaminated soils. pp. 497-499. In D. W. Tedder (ed.), Emerging Technologies in Hazardous Waste Management VI. American Chemical Society, Washington, D. C.

[5] CH^{2}M Hill Southeast, Inc. 1989. Field investigation and contaminant assessment, rinsewater impoundment and appurtenant structures, NASA Michoud Assembly Facility. Prepared for Martin Marietta Manned Space Systems, Facilities Engineering Department.

[6] Lucero, A. J., Gilbert, V. P.; Hewitt, J. D.; Koran, L. J. Jr.; Jennings, H. L.; Donaldson, T. L.; West, O. R.; Cline, S. R.; Marshall, D. S. 1995. Treatability of TCE-contaminated clay soils at the rinsewater impoundment, Michoud Assembly Facility. ORNL/TM-12931. Oak Ridge National Laboratory.

[7] Martin Marietta Manned Space Systems. 1995. Statement of Work, IDOD No. 3100-94-001M, rev. C.

[8] Ong, S. K. and L. W. Lion. 1991. Mechanisms for trichloroethylene vapor sorption onto soil minerals. J. Environ. Qual. 20:180-188.

[9] CH^{2}M Hill Southeast, Inc. 1990. Supplemental closure investigation: Field investigation and contaminant assessment, rinsewater impoundment and appurtenant structures, NASA Michoud Assembly Facility. Prepared for Martin Marietta Manned Space Systems, Facilities Engineering Department.

[10] Gates, D. D., Siegrist, R. L. 1993. X-231B technology demonstration for in situ treatment of contaminated soils: Laboratory evaluation of chemical oxidation using hydrogen peroxide. ORNL/TM-12259. Oak Ridge National Laboratory.

[11] U. S. Environmental Protection Agency Office of Solid Waste and Emergency Response. 1994. VISITT 4.0 database.

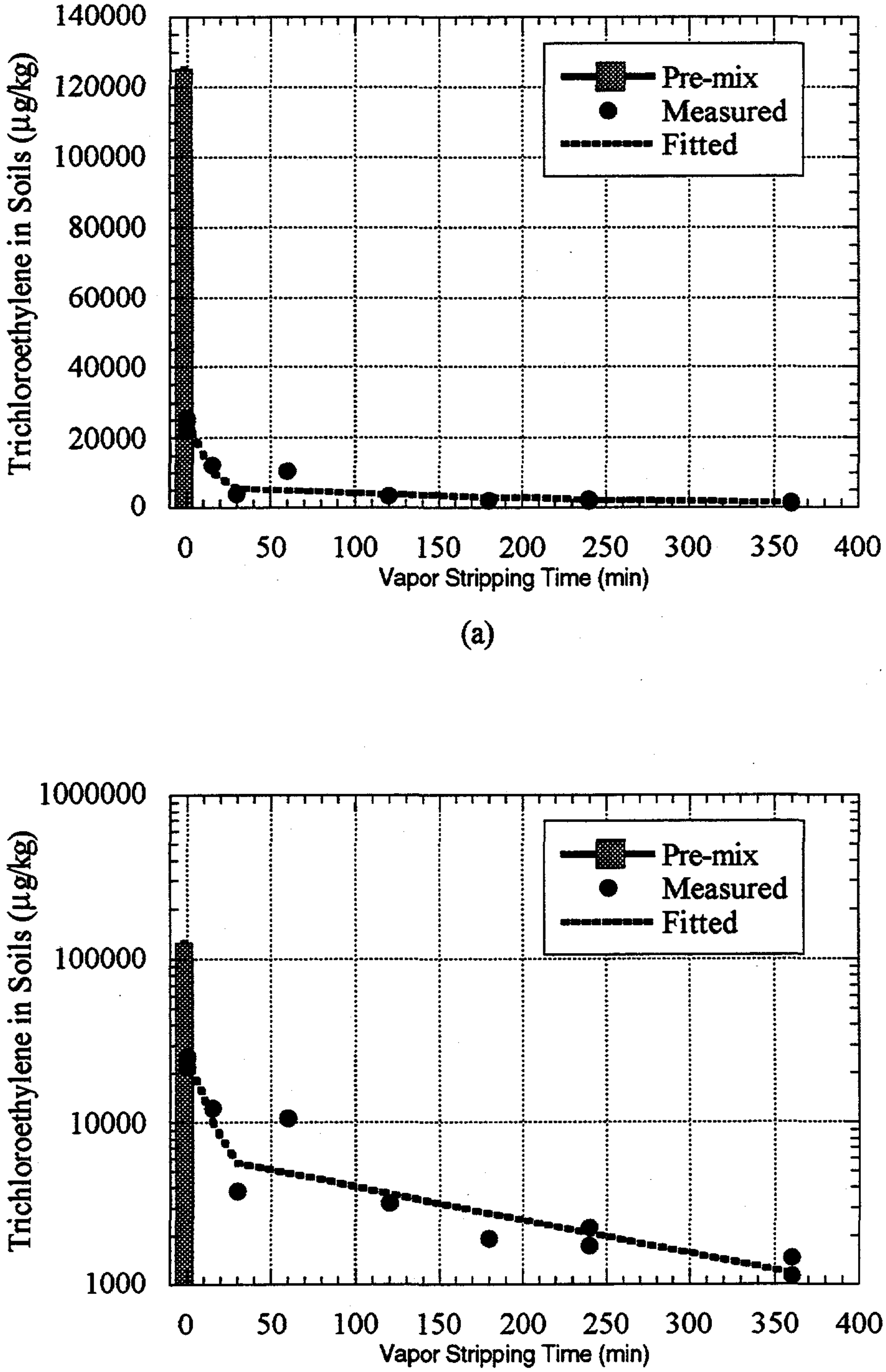
[12] Siegrist, R. L., Morris, M. I., Donaldson, T. L., Palumbo, A. V., Herbes, S. E., Jenkins, R. A., Morrissey, C. M., Harris, M. T. 1993. X-231B technology demonstration for in situ treatment of contaminated soils: Technology evaluation and screening. ORNL/TM-12257. Oak Ridge National Laboratory.

[13] Foth, H. D. 1978. Fundamentals of Soil Science. 6th ed. John Wiley and Sons, New York.

[14] Ho, S. V. and P. H. Brodsky. 1994. Integrated in situ technology for soil remediation -- The lasagna process. In D. W. Tedder (ed.), Emerging Technologies in Hazardous Waste Management VI. American Chemical Society, Washington, D. C.

[15] Duffney, E. N., Gayle, B. P., Narkunas, J., and Siegfried, J. E. 1994. Accelerated environmental remediation by the 2-PHASE extraction process, Case study: Xerox CRC Facility. Xerox Corporation, Atlanta, GA.

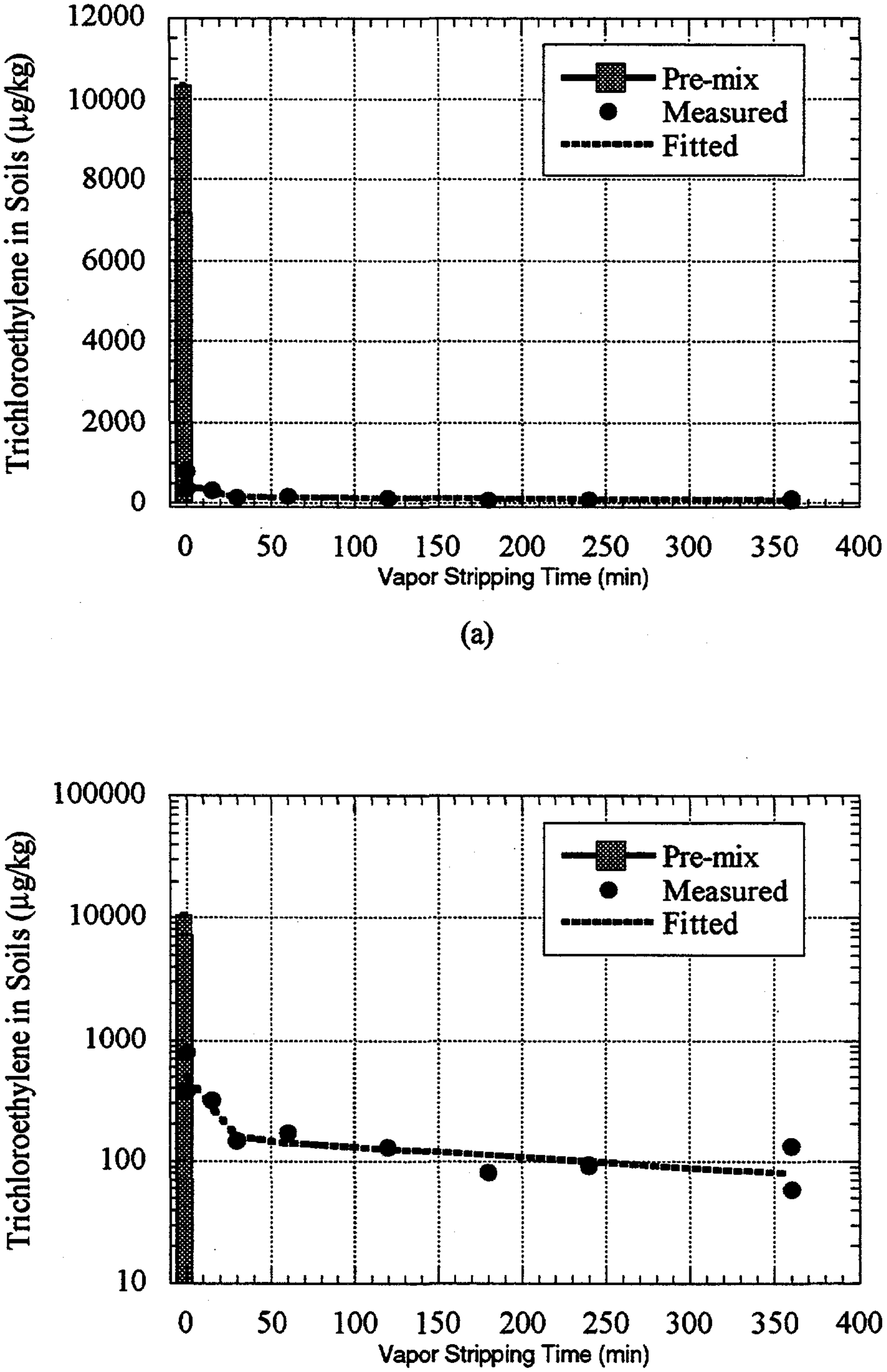
APPENDIX A.
RESIDUAL TRICHLOROETHYLENE VS VAPOR STRIPPING TIME



(a)

(b)

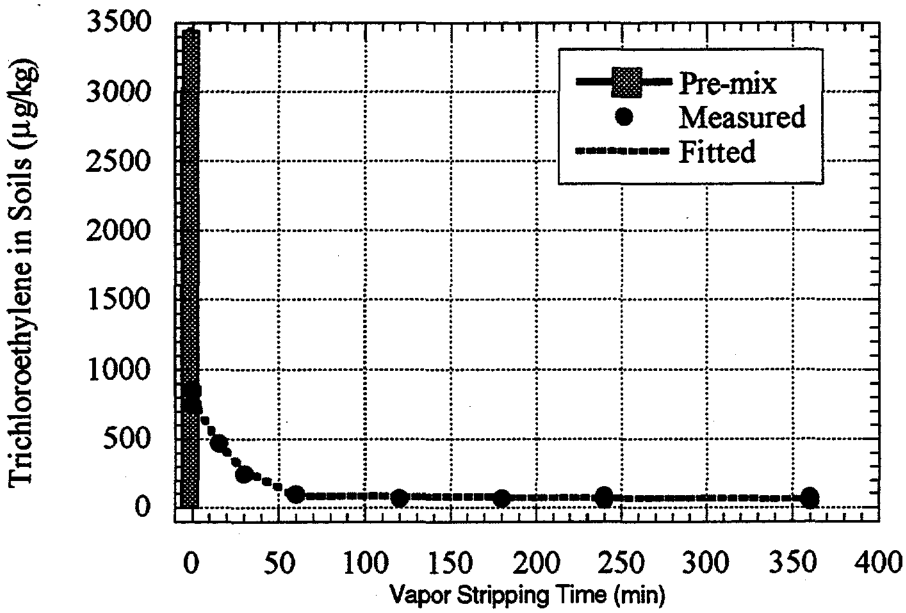
Fig. A.1. Residual trichloroethylene (TCE) in soil vs vapor stripping time in core B9,8.5-9.0; (a) TCE plotted on a normal scale, (b) TCE plotted on a log scale.



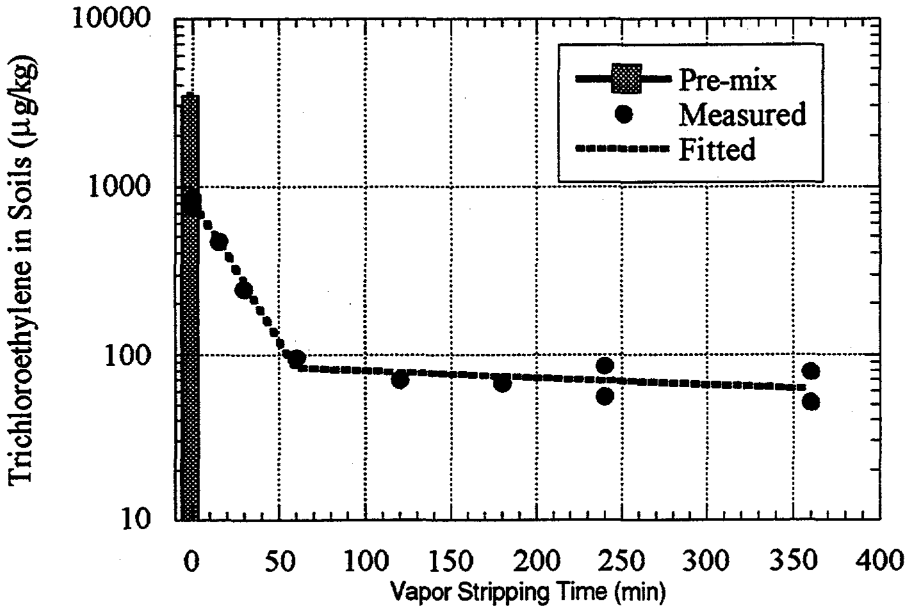
(a)

(b)

Fig. A.2. Residual trichloroethylene (TCE) in soil vs vapor stripping time in core B9, 9.0-9.5; (a) TCE plotted on a normal scale, (b) TCE plotted on a log scale.

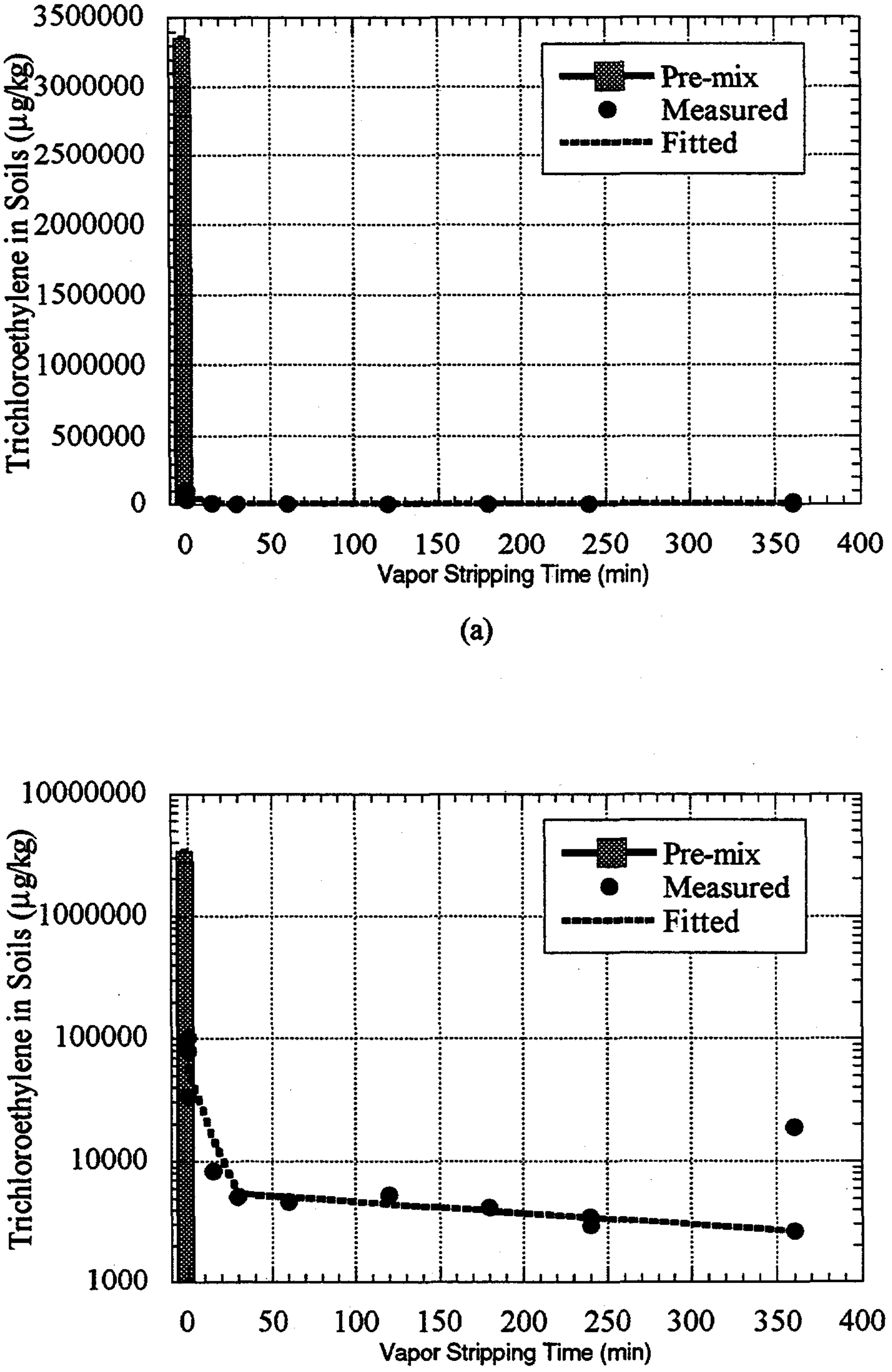


(a)



(b)

Fig. A.3. Residual trichloroethylene (TCE) in soil vs vapor stripping time in core B9,9.5-10.0; (a) TCE plotted on a normal scale, (b) TCE plotted on a log scale.



(a)

(b)

Fig. A.4. Residual trichloroethylene (TCE) in soil vs vapor stripping time in core B10,9.5-10; (a) TCE plotted on a normal scale, (b) TCE plotted on a log scale.

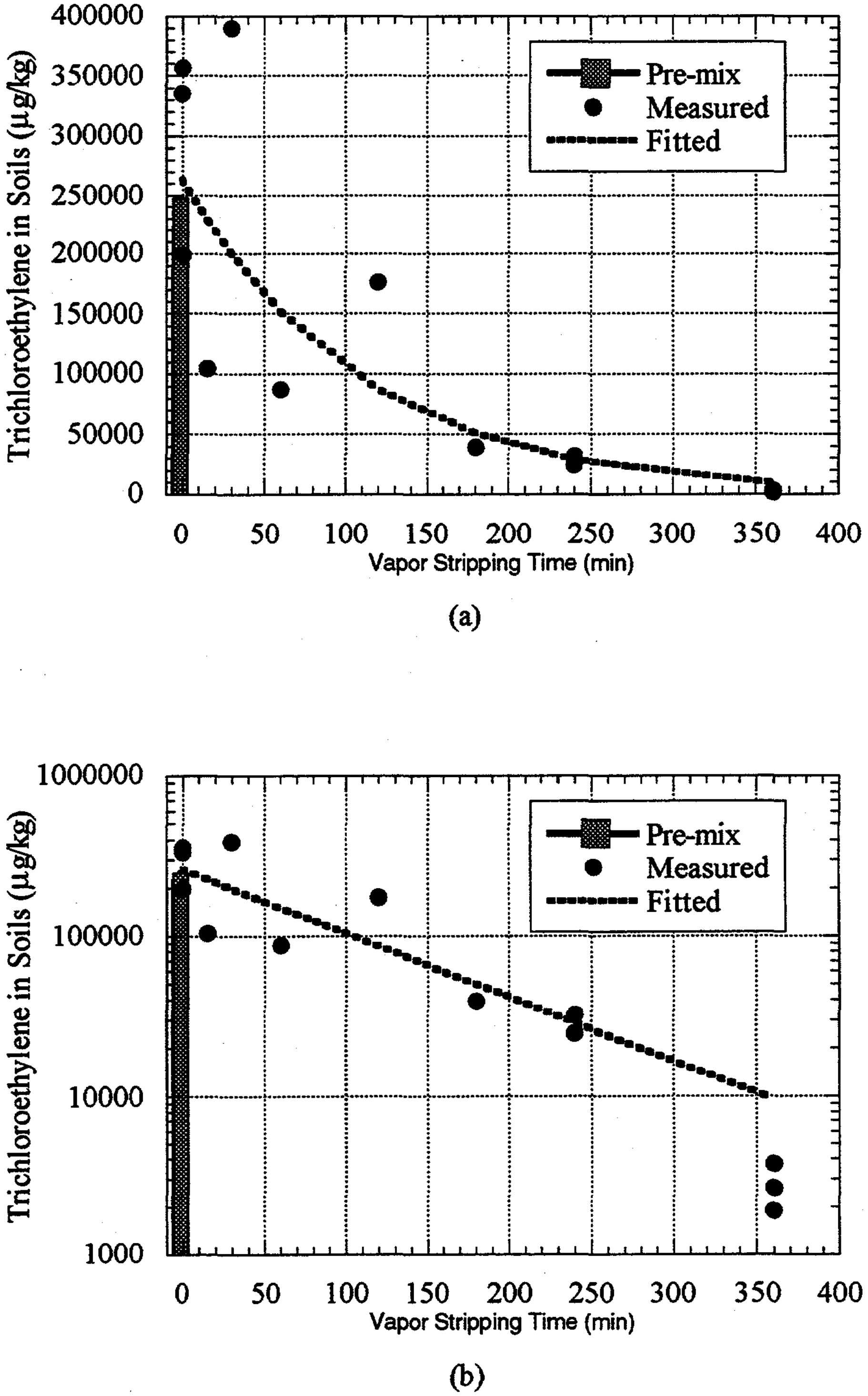
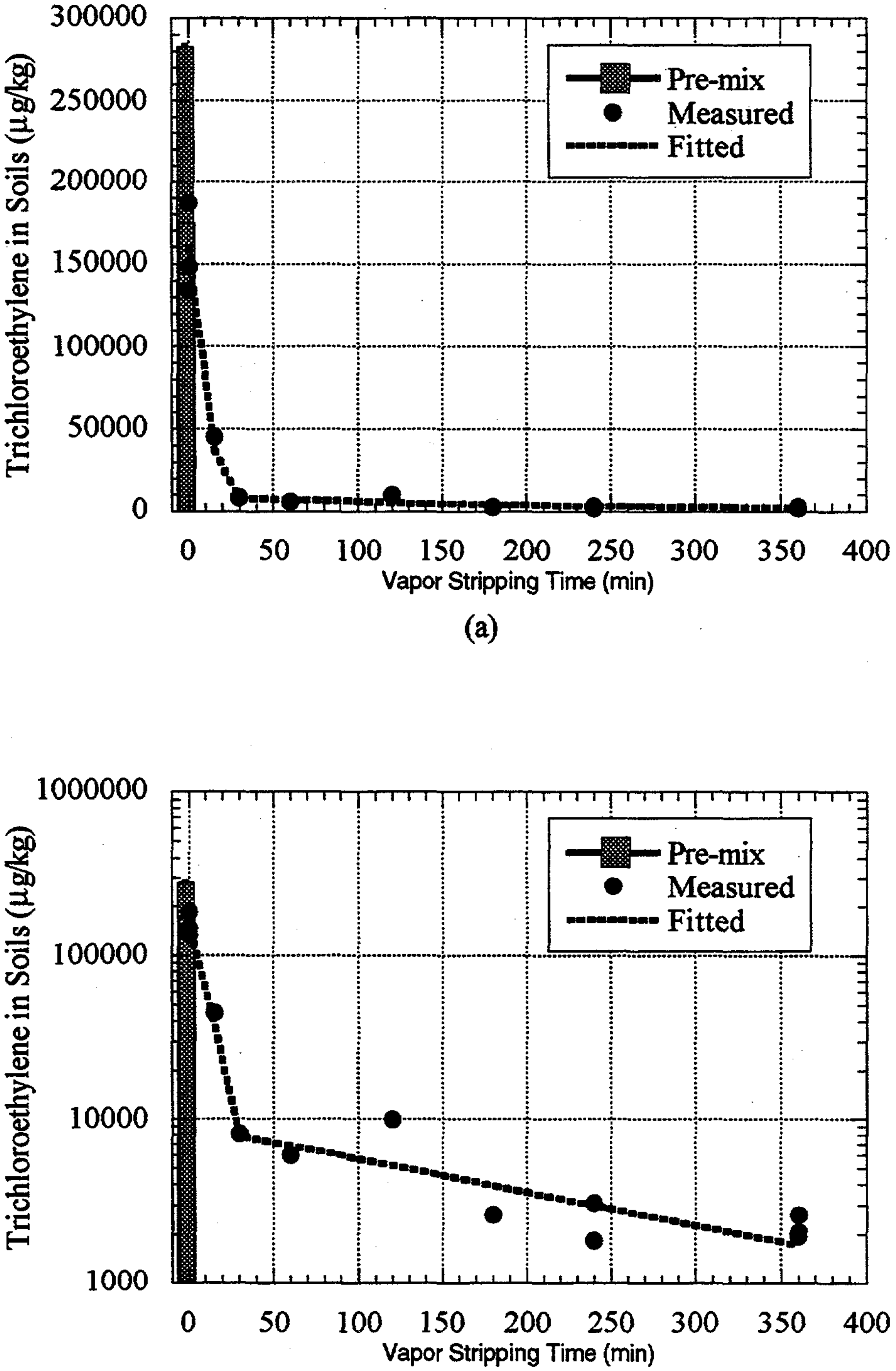


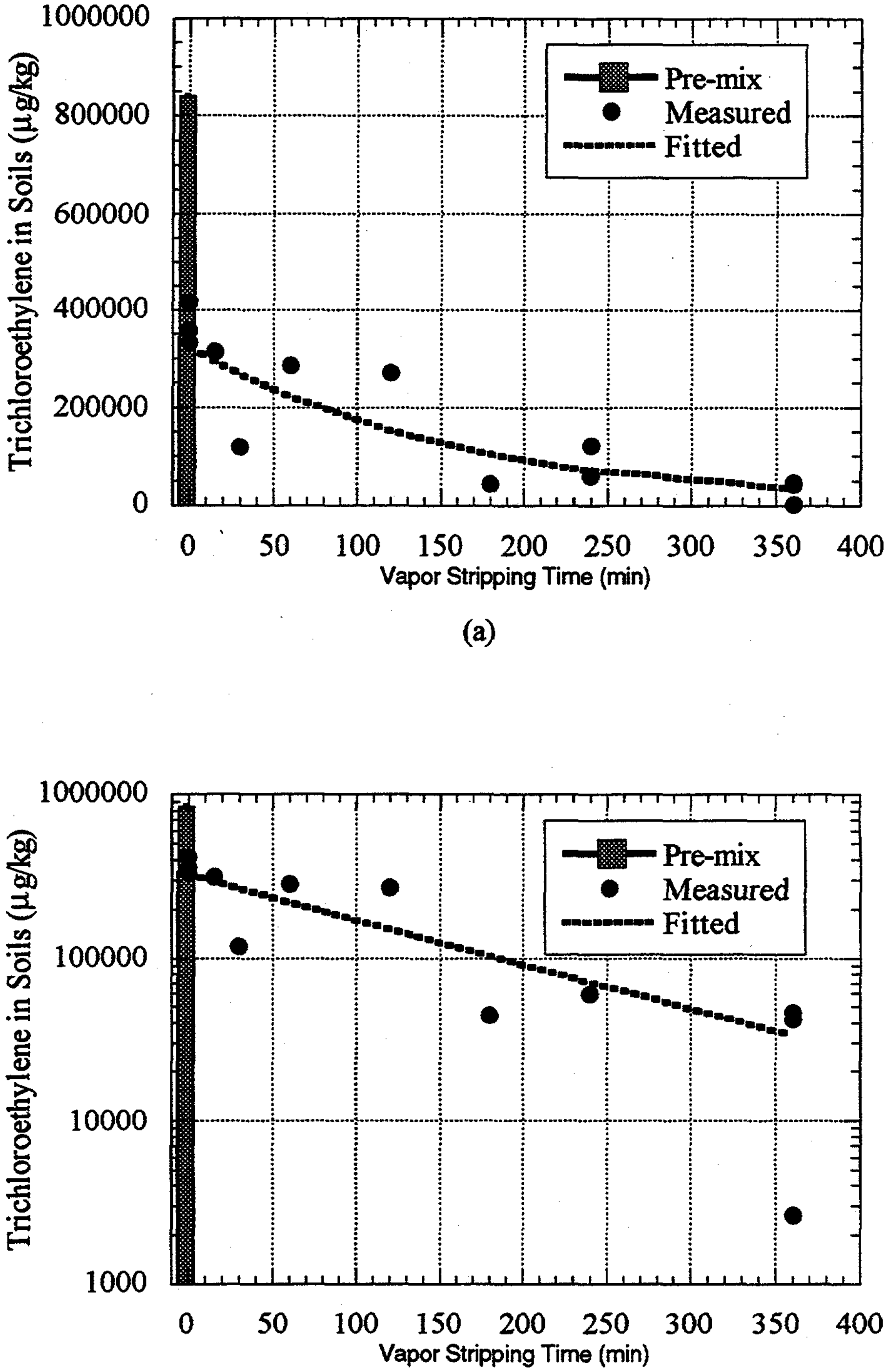
Fig. A.5. Residual trichloroethylene (TCE) in soil vs vapor stripping time in core B10,10.0-10.5; (a) TCE plotted on a normal scale, (b) TCE plotted on a log scale.



(a)

(b)

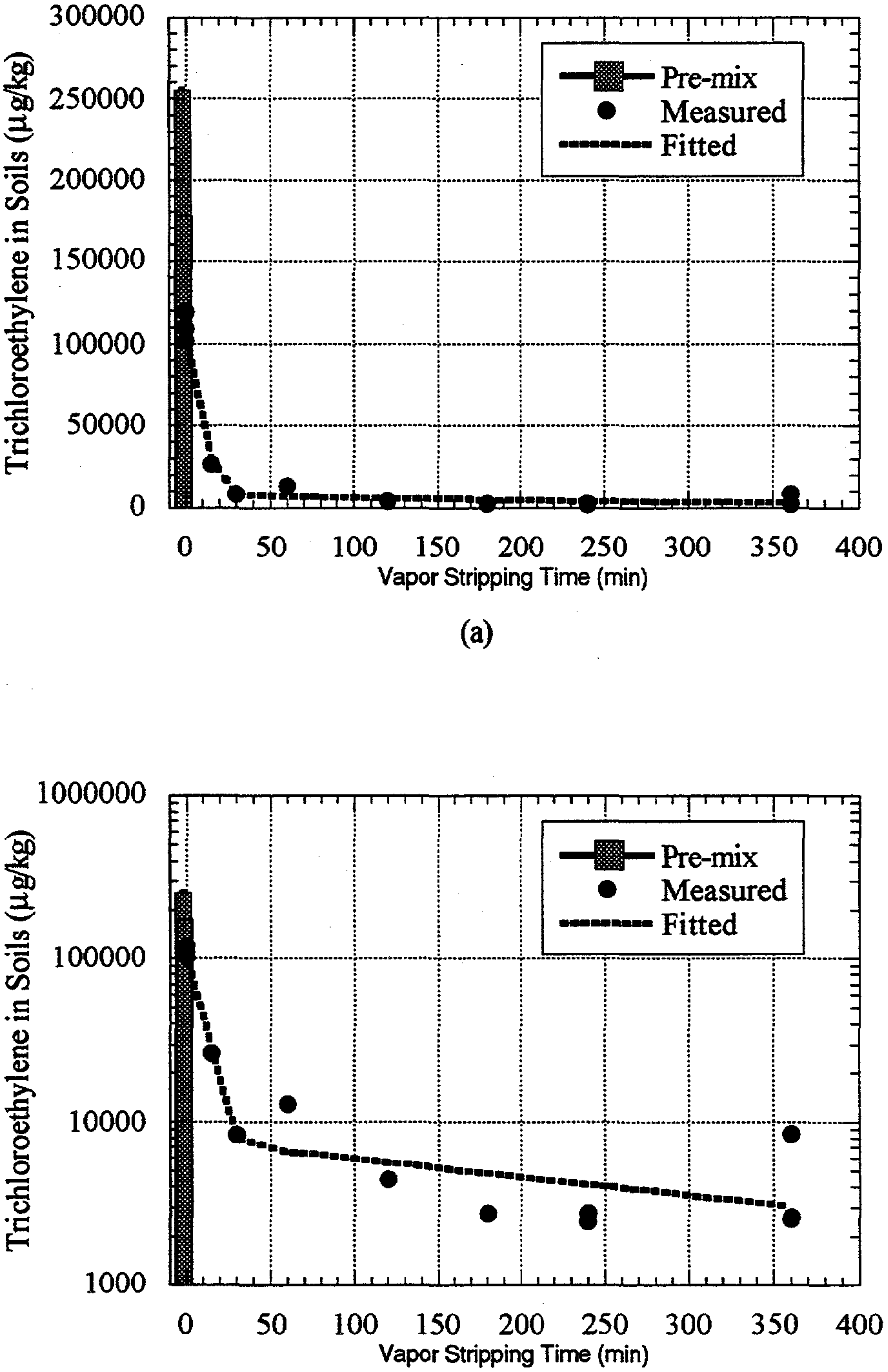
Fig. A.6. Residual trichloroethylene (TCE) in soil vs vapor stripping time in core B10,10.5-11.0; (a) TCE plotted on a normal scale, (b) TCE plotted on a log scale.



(a)

(b)

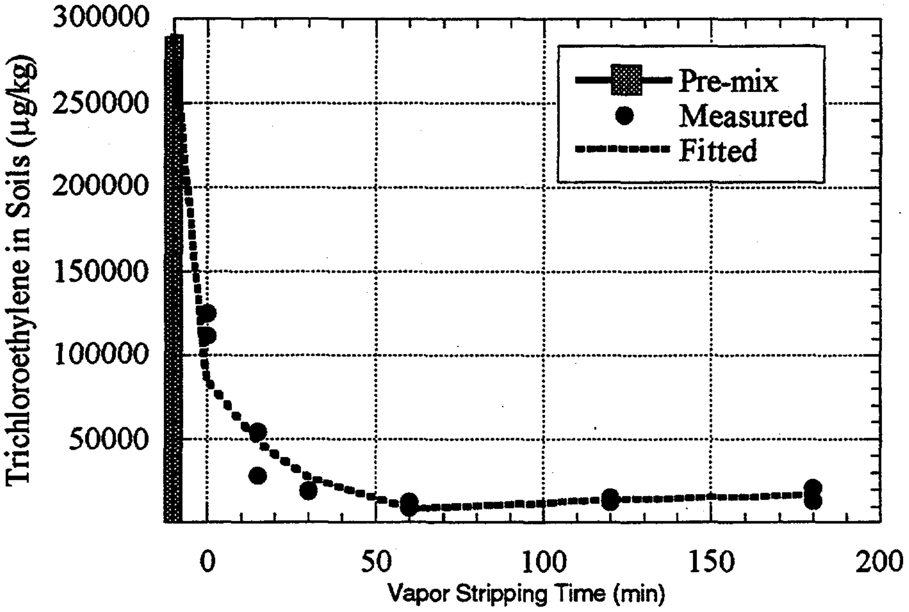
Fig. A.7. Residual trichloroethylene (TCE) in soil vs vapor stripping time in core B10,11.0-11.5; (a) TCE plotted on a normal scale, (b) TCE plotted on a log scale.



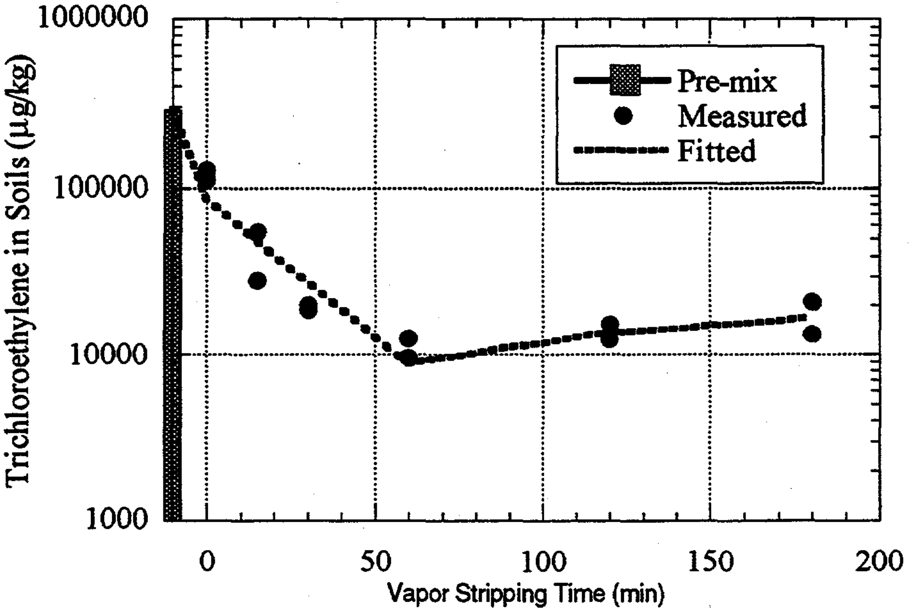
(a)

(b)

Fig. A.8. Residual trichloroethylene (TCE) in soil vs vapor stripping time in core B10,11.5-12.0; (a) TCE plotted on a normal scale, (b) TCE plotted on a log scale.

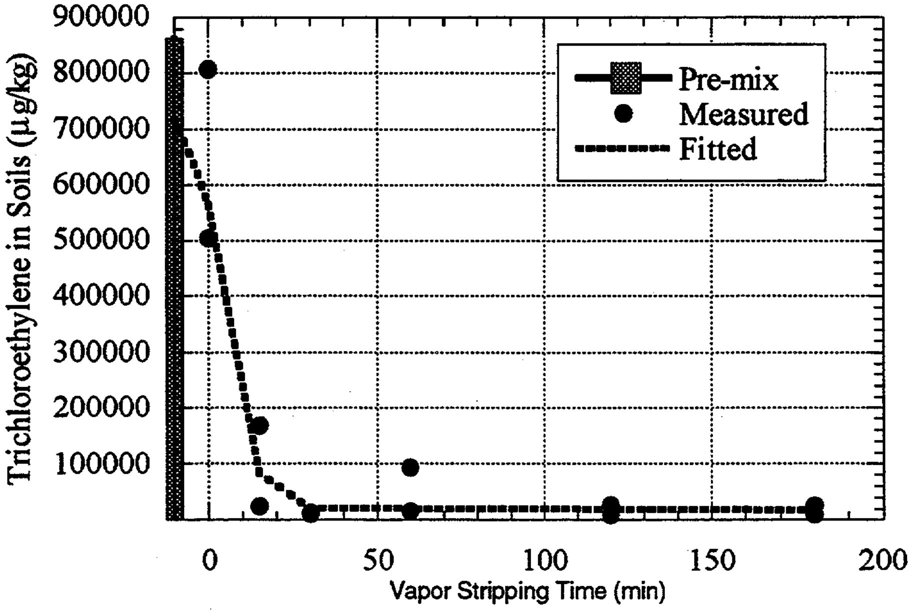


(a)

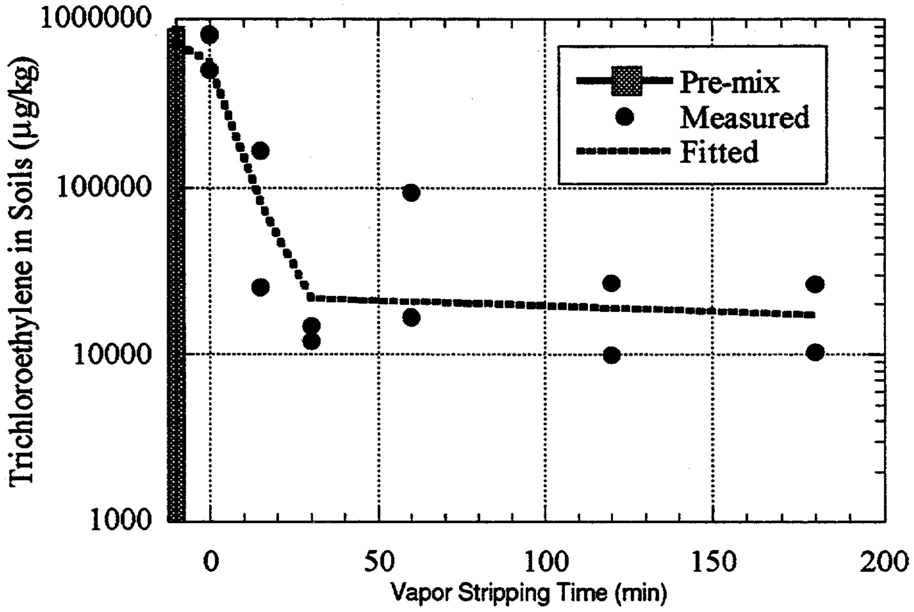


(b)

Fig. A.9. Residual trichloroethylene (TCE) in soil vs vapor stripping time in core B10,5.5-6.0; (a) TCE plotted on a normal-scale, (b) TCE plotted on a log-scale.

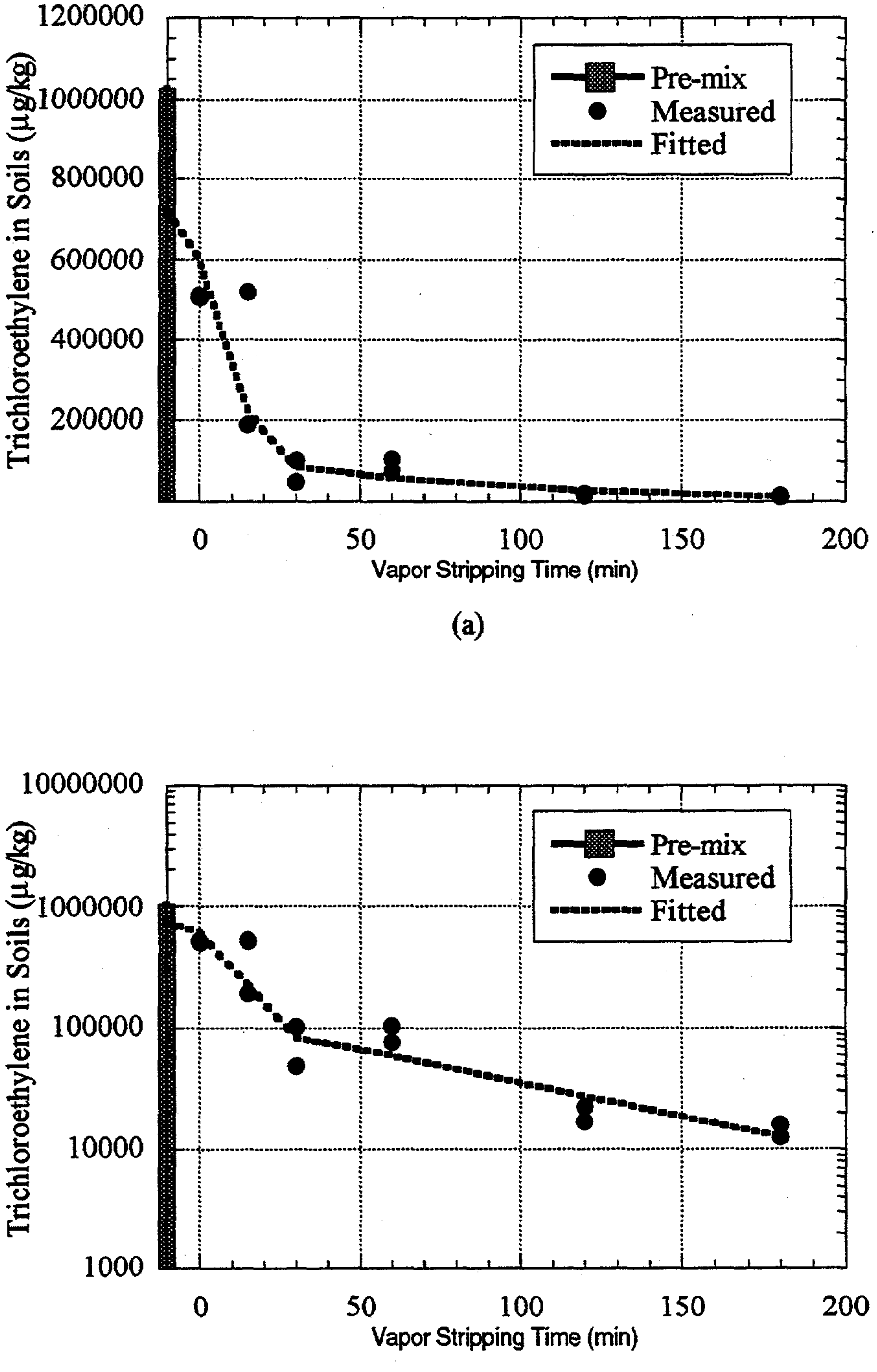


(a)



(b)

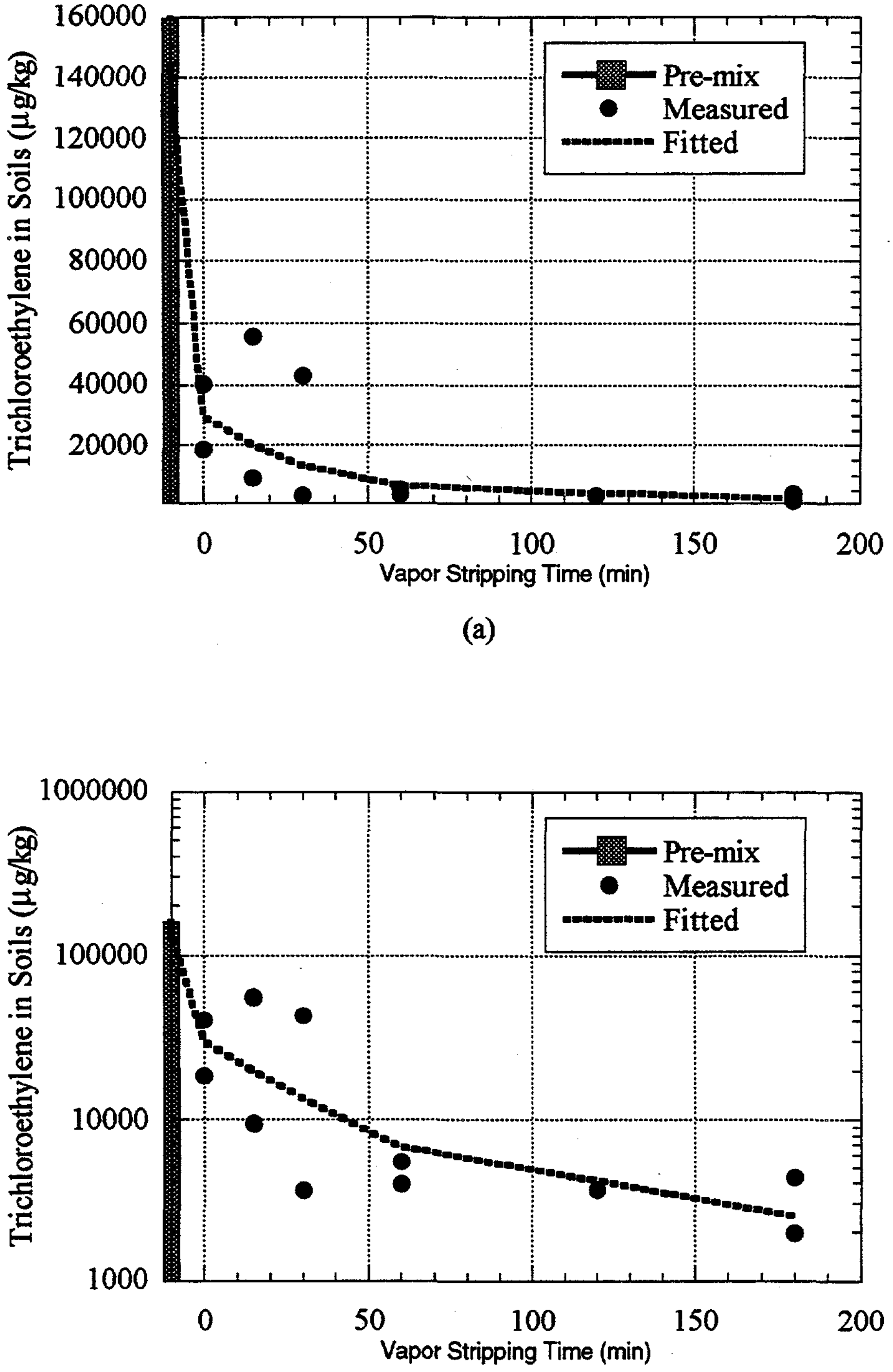
Fig. A.10. Residual trichloroethylene (TCE) in soil vs vapor stripping time in core B10,6.0-6.5; (a) TCE plotted on a normal scale, (b) TCE plotted on a log scale.



(a)

(b)

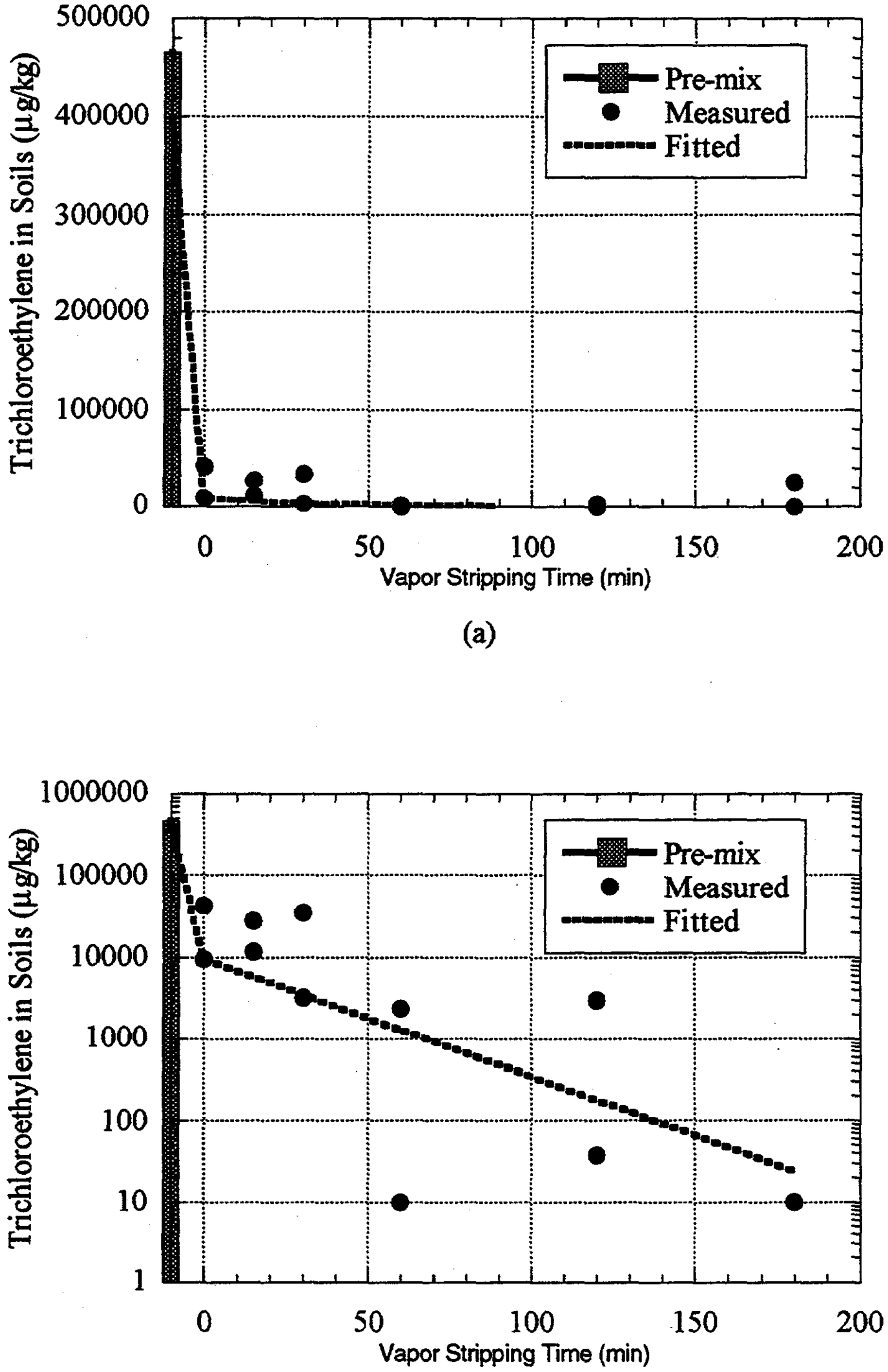
Fig. A.11. Residual trichloroethylene (TCE) in soil vs vapor stripping time in core B10,6.5-7.0; (a) TCE plotted on a normal scale, (b) TCE plotted on a log scale.



(a)

(b)

Fig. A.12. Residual trichloroethylene (TCE) in soil vs vapor stripping time in core B9,8.0-8.5; (a) TCE plotted on a normal scale, (b) TCE plotted on a log scale.



(a)

(b)

Fig. A.13. Residual trichloroethylene (TCE) in soil vs vapor stripping time in core B9,11.0-11.5; (a) TCE plotted on a normal-scale, (b) TCE plotted on a log-scale.

APPENDIX B.
TEMPERATURE AND TRICHLOROETHYLENE REMOVAL VS VAPOR STRIPPING TIME

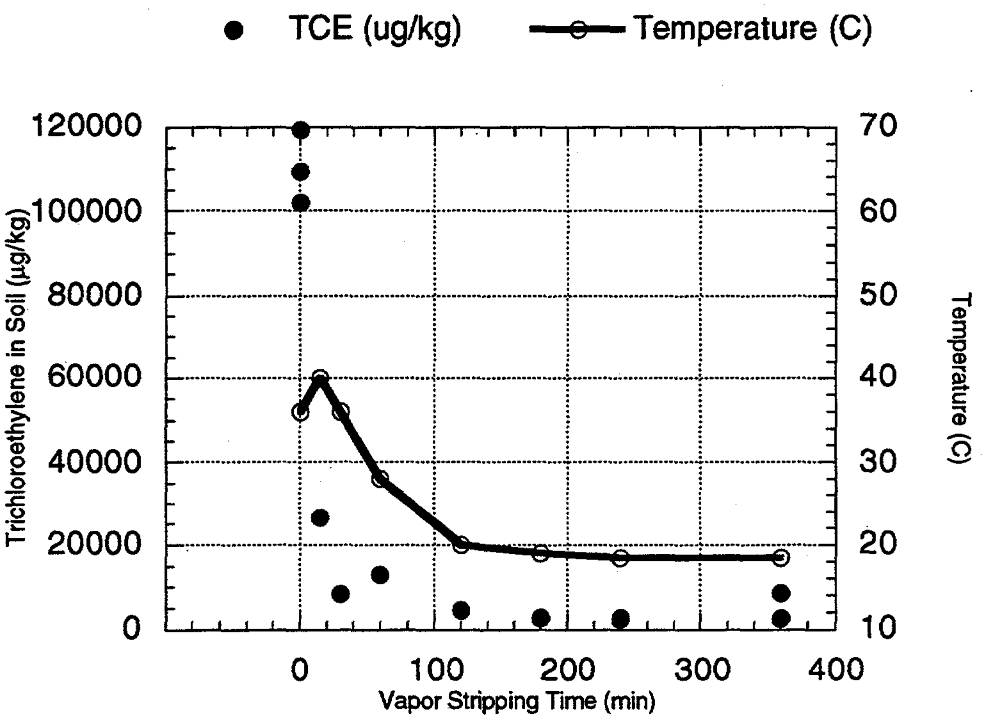


Fig. B.1. Temperature and residual trichloroethylene in soil vs vapor stripping time, core B10,11.5-12.

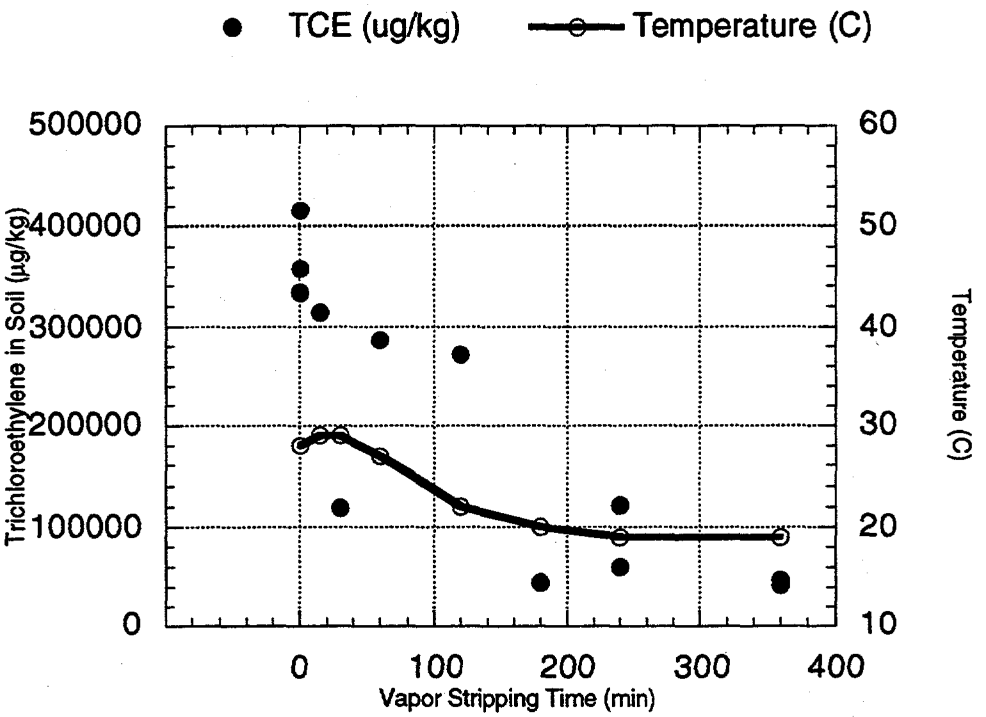


Fig. B.2. Temperature and residual trichloroethylene in soil vs vapor stripping time, core B10,11.0-11.5.

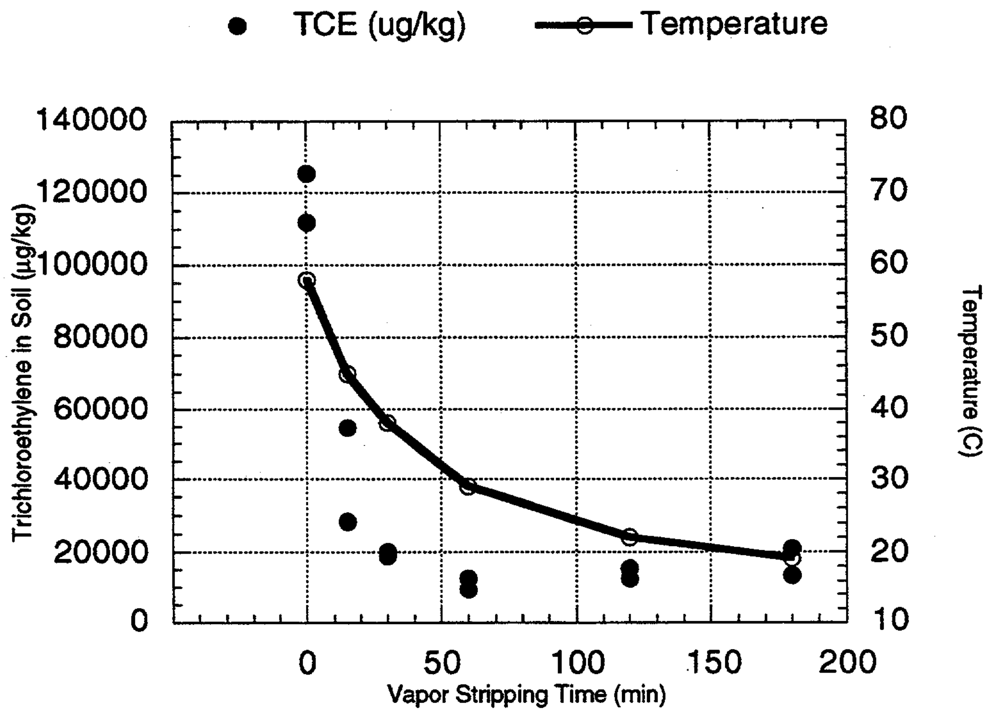


Fig. B.3. Temperature and residual trichloroethylene in soil vs vapor stripping time, core B10,5.5-6.0.

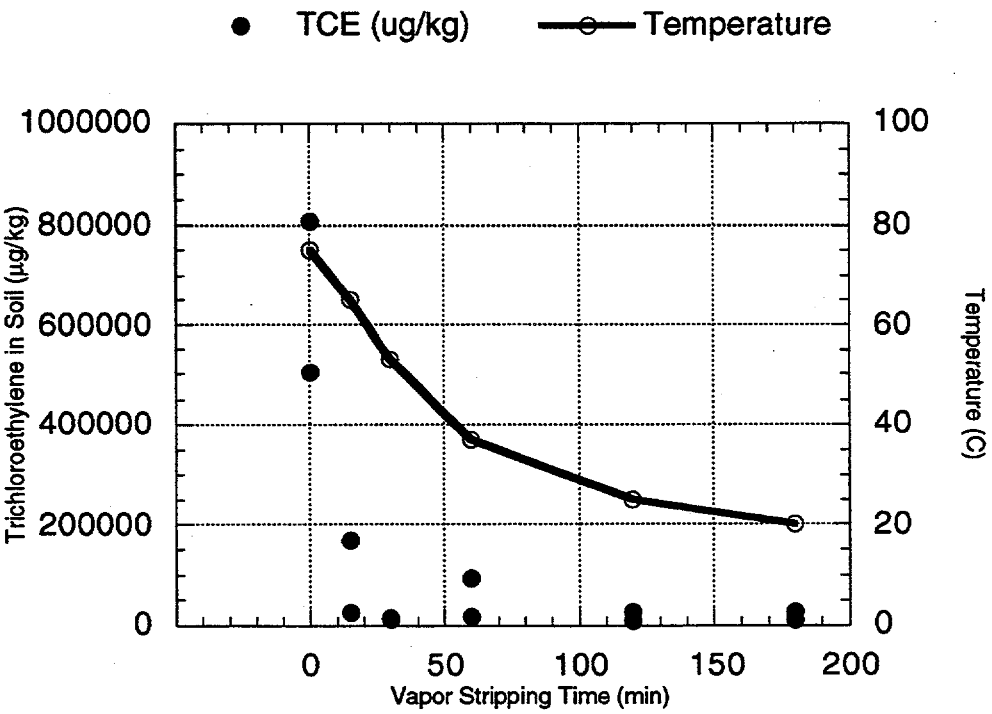


Fig. B.4. Temperature and residual trichloroethylene in soil vs vapor stripping time, core B10,6.0-6.5.

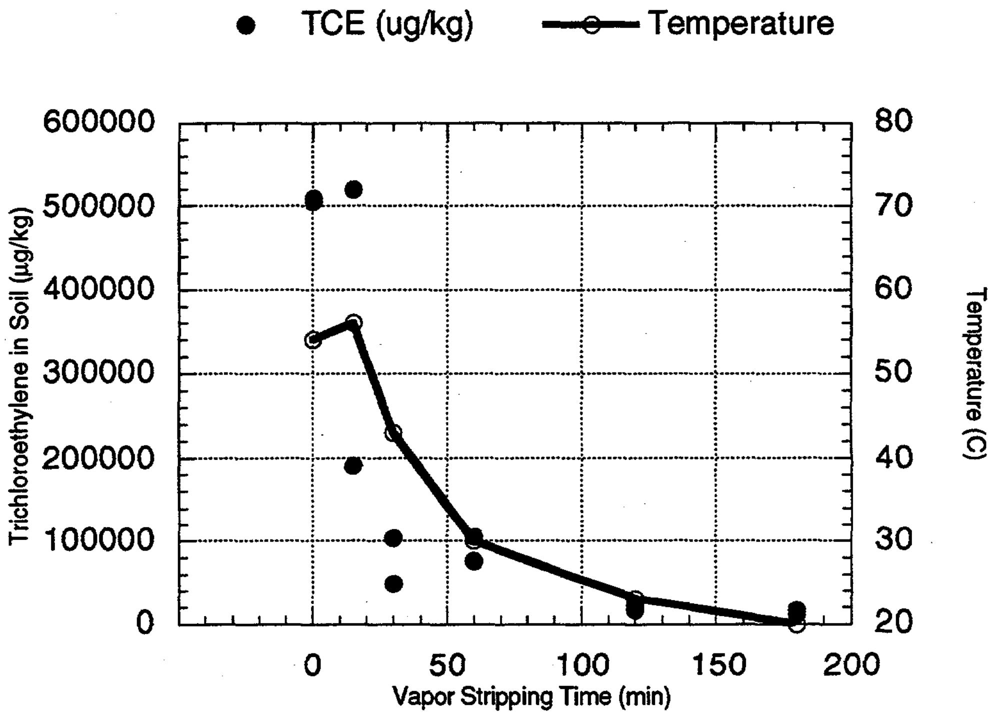


Fig. B.5. Temperature and residual trichloroethylene in soil vs vapor stripping time, core B10,6.5-7.0.

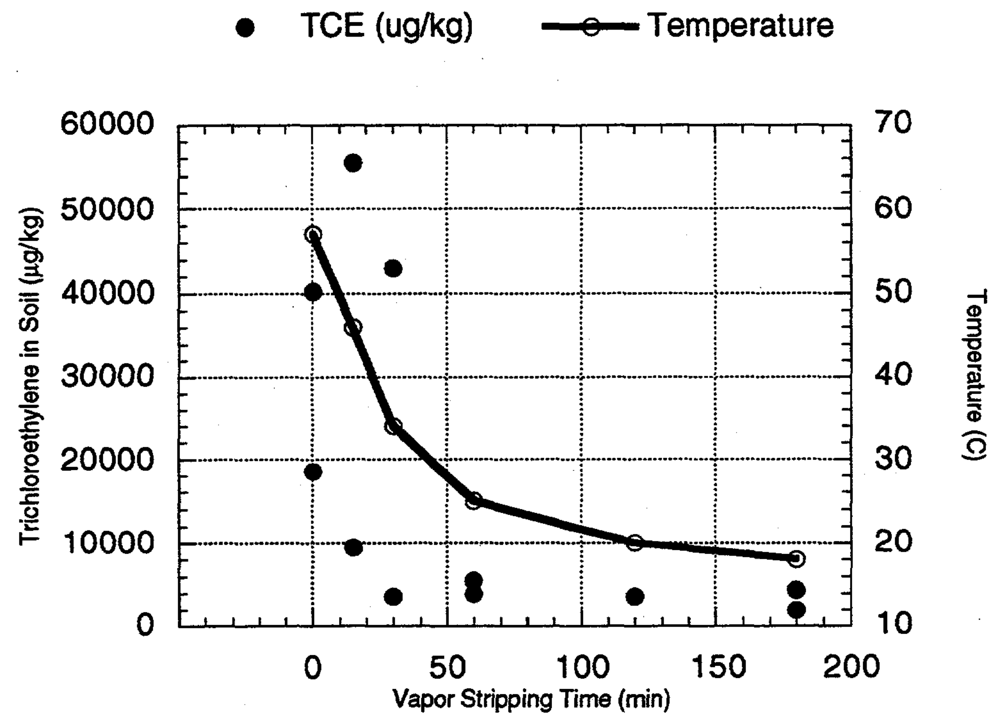


Fig. B.6. Temperature and residual trichloroethylene in soil vs vapor stripping time, core B9,8.0-8.5.

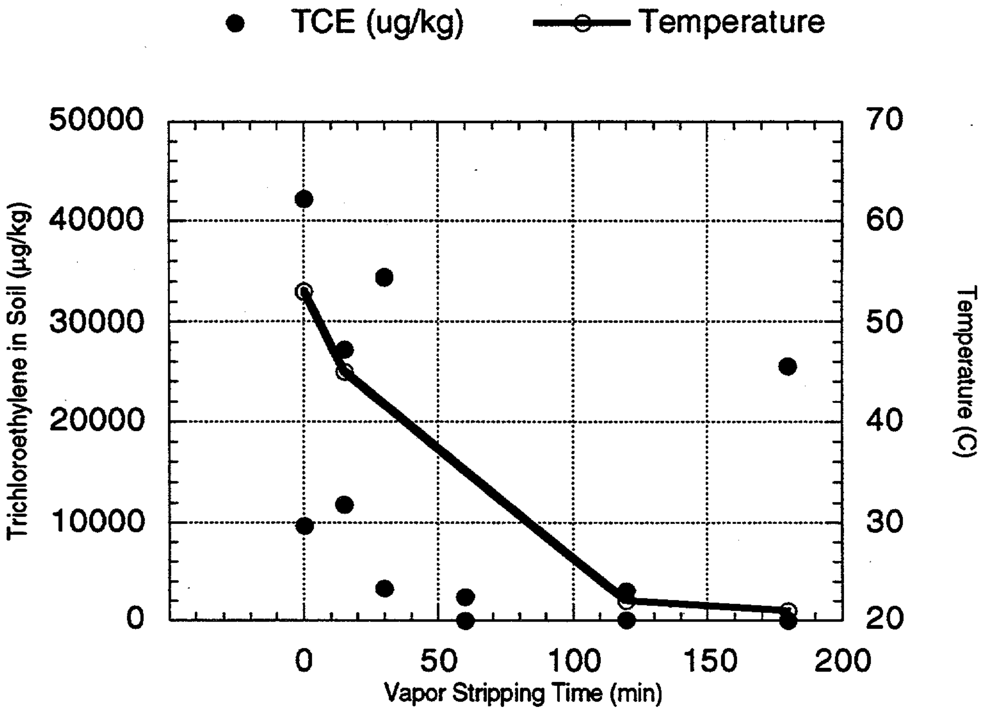


Fig. B.7. Temperature and residual trichloroethylene in soil vs vapor stripping time, core B9,11.0-11.5.

APPENDIX C.

CONTOUR MAPS OF TRICHLOROETHYLENE CONTAMINATION IN SOILS UNDERLYING THE MICHOUD RINSEWATER IMPOUNDMENT

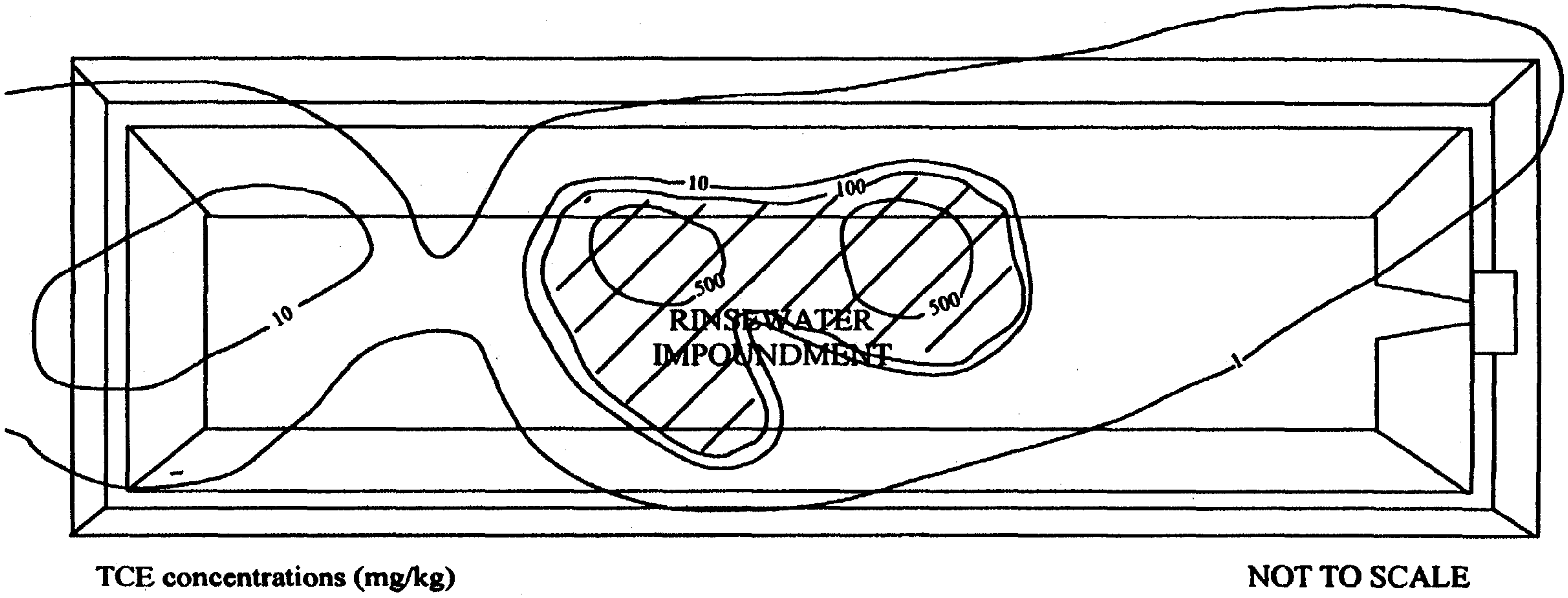


Fig. C.1. Trichloroethylene contamination in subsurface soils from 0 to 4 ft below the bottom of the impoundment concrete liner.

Sources:

1. Lucero, A. J., Gilbert, V. P.; Hewitt, J. D.; Koran, L. J. Jr.; Jennings, H. L.; Donaldson, T. L.; West, O. R.; Cline, S. R.; Marshall, D. S. 1995. Treatability of TCE-contaminated clay soils at the rinsewater impoundment, Michoud Assembly Facility. ORNL/TM-12931. Oak Ridge National Laboratory.
2. CH^2M Hill Southeast, Inc. 1990. Supplemental closure investigation: Field investigation and contaminant assessment, rinsewater impoundment and appurtenant structures, NASA Michoud Assembly Facility. Prepared for Martin Marietta Manned Space Systems, Facilities Engineering Department.

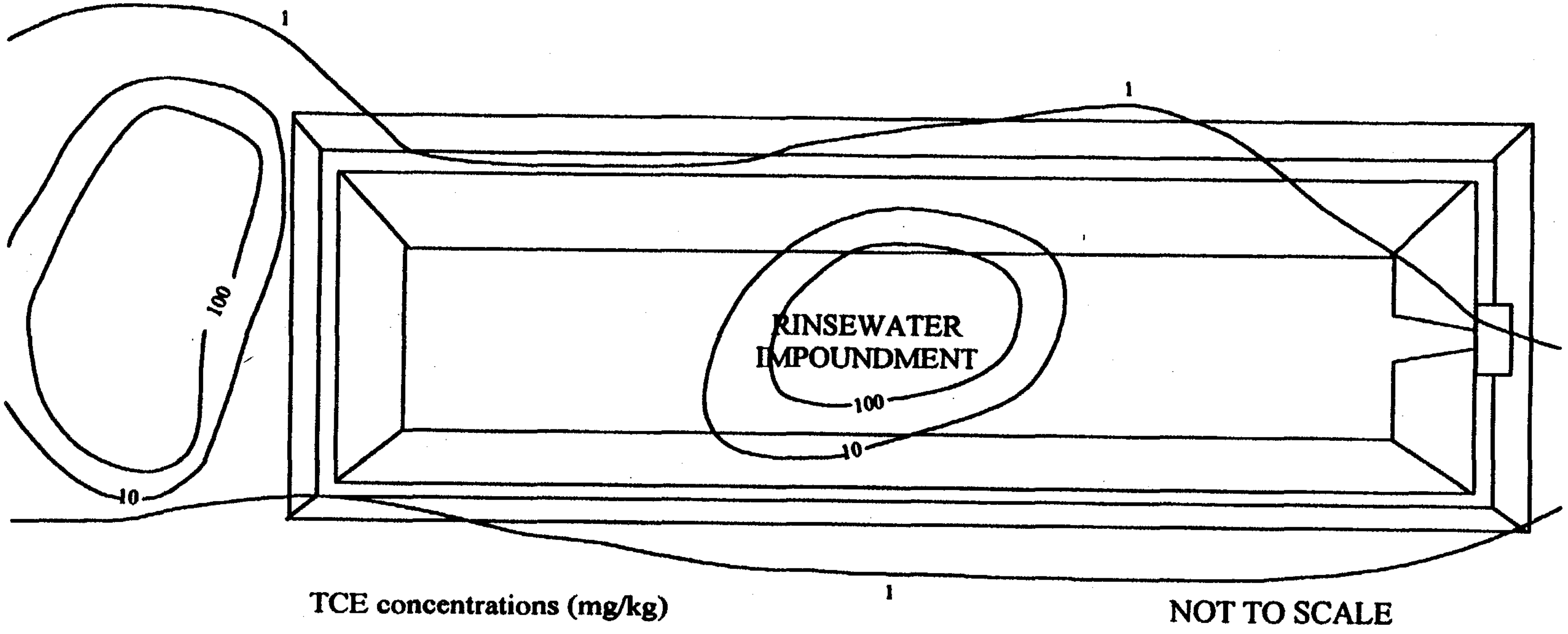


Fig. C.2. Trichloroethylene contamination in subsurface soils from 4 to 10 ft below the bottom of the impoundment concrete liner.

Sources:

1. Lucero, A. J., Gilbert, V. P.; Hewitt, J. D.; Koran, L. J. Jr.; Jennings, H. L.; Donaldson, T. L.; West, O. R.; Cline, S. R.; Marshall, D. S. 1995. Treatability of TCE-contaminated clay soils at the rinsewater impoundment, Michoud Assembly Facility. ORNL/TM-12931. Oak Ridge National Laboratory.

2. CH^2M Hill Southeast, Inc. 1990. Supplemental closure investigation: Field investigation and contaminant assessment, rinsewater impoundment and appurtenant structures, NASA Michoud Assembly Facility. Prepared for Martin Marietta Manned Space Systems, Facilities Engineering Department.

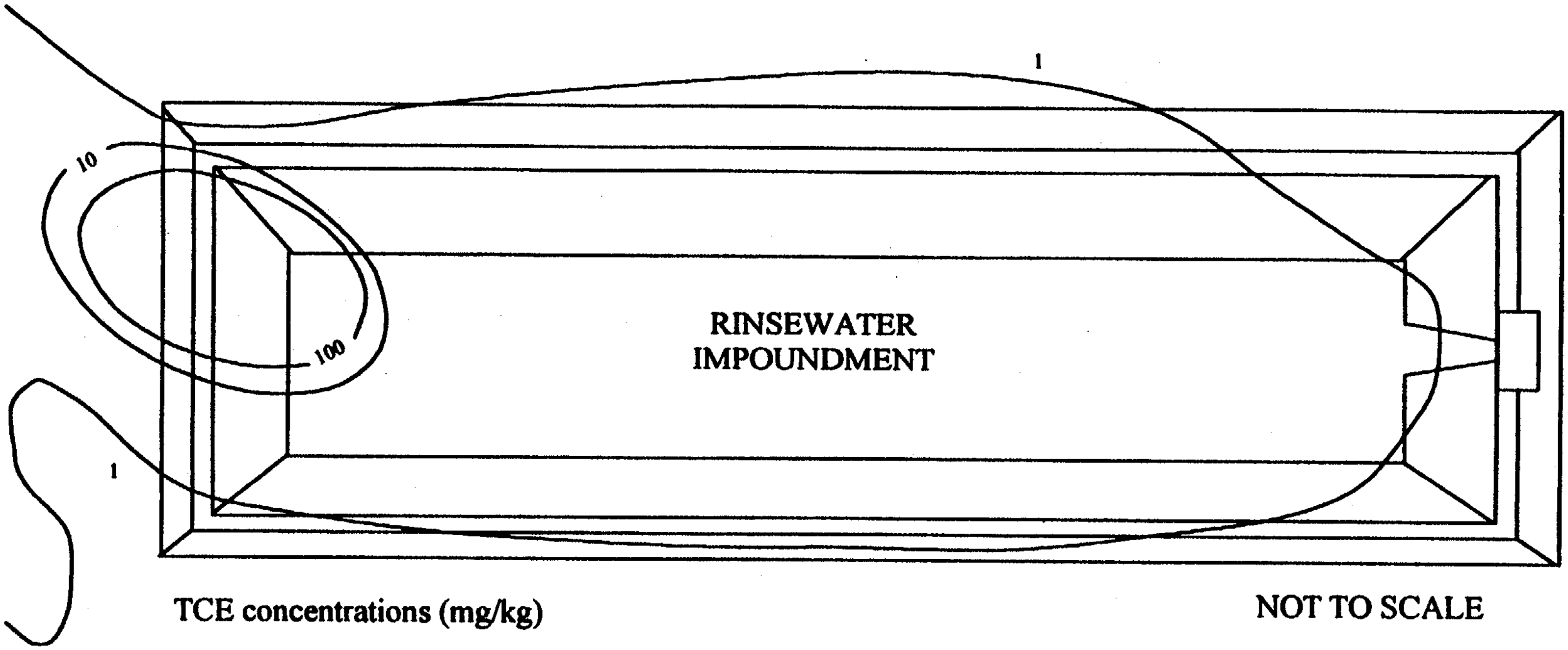


Fig. C.3. Trichloroethylene contamination in subsurface soils from 10 to 15 ft below the bottom of the impoundment concrete liner.

Sources:

1. Lucero, A. J., Gilbert, V. P.; Hewitt, J. D.; Koran, L. J. Jr.; Jennings, H. L.; Donaldson, T. L.; West, O. R.; Cline, S. R.; Marshall, D. S. 1995. Treatability of TCE-contaminated clay soils at the rinsewater impoundment, Michoud Assembly Facility. ORNL/TM-12931. Oak Ridge National Laboratory.
2. CH^{2}M Hill Southeast, Inc. 1990. Supplemental closure investigation: Field investigation and contaminant assessment, rinsewater impoundment and appurtenant structures, NASA Michoud Assembly Facility. Prepared for Martin Marietta Manned Space Systems, Facilities Engineering Department.

APPENDIX D.
CLEANUP COST CALCULATIONS FOR REMEDIATION GOAL SPECIFIED AS A TARGET RESIDUAL TRICHLOROETHYLENE CONCENTRATION

The following describes how remediation costs were estimated for cleanup goals specified as a target residual trichloroethylene concentration (Fig. 13). For a given target residual concentration and using the grid and the initial concentrations shown in Fig. 12:

1. For each 30 ft x 30 ft sub-area, the percentage of TCE removal required to achieve the target residual concentration (*P*) was calculated. For example, an initial concentration of 500 mg/kg would require a 99% to achieve a target residual concentration of 5 mg/kg.

2. For each sub-area, the time required per soil column (T_{col}) to achieve *P* was estimated using Table D.1. Treatment times in Table D.1 are partially based on the removal curve shown in Fig. 10. Treatment times for some target percentage removals are longer than what would have been obtained from Fig. 10.

Table D.1 Treatment times to achieve specified percentages of trichloroethylene removal

Target Percentage Removal (%)	Treatment Time per Soil Column (min)
0	0
60	30
80	30
90	60
95	60
98	180
99	300

3. The time required to cleanup a square sub-area ($T_{sub\text{-}area}$) was calculated as follows:

$$T_{sub-area} = T_{col} * N_{col}$$

where N_{col} is the number of soil columns per sub-area. The latter is equal to 28 for an 8-ft-diam soil mixer.

4. The total time required to cleanup the Impoundment is calculated by summing T_{col} over all the sub-areas ($\sum T_{col}$). Assuming that the cost for operating a soil mixer per day is $10,000, and that 4 h of a day is effectively used for treatment, the cost for operating a soil mixer per minute is ~$42. The total operational cost is then:

$$C_{oper} = \$42 \times \sum T_{col}$$

5. The total volume of soil requiring treatment (V_{soil}) is estimated from Fig. 12, and the total reagent cost is obtained as follows:

$$C_{reagent} = \$27 \times V_{soil} \ ,$$

where $27/yd^3 is the cost for a CaO loading of 400-500 kg/m^3.

6. Finally, the total cost for remediation is obtained by adding C_{oper} and $C_{reagent}$.

INTERNAL DISTRIBUTION

1. L. D. Bates
2. B. A. Berven
3. P. A. Cameron
4. R. B. Cook
5. A. G. Croff
6. J. H. Cushman
7. V. H. Dale
8. T. L. Donaldson
9. N. T. Edwards
10. D. E. Fowler
11. S. G. Hildebrand
12. G. K. Jacobs
13. P. Kanciruk
14. K. T. Klasson
15. L. J. Koran, Jr.
16. N. E. Korte
17. J. M. Loar

18.-32. A. J. Lucero (15)

33. A. P. Malinauskas
34. L. E. McNeese
35. M. I. Morris
36. C. A. Muhr
37. D. E. Reichle
38. S. M. Robinson
39. M. K. Savage
40. F. E. Sharples
41. D. S. Shriner
42. R. L. Siegrist

43.-52. O. R. West (10)

53. Central Research Library

54.-68. ESD Library (15)

69.-70. Laboratory Records Dept. (2)

71. Laboratory Records, ORNL-RC
72. ORNL Patent Section
73. ORNL Y-12 Technical Library

EXTERNAL DISTRIBUTION

74.-88. M. A. Rowland, Lockheed Martin Manned Space Systems, 13800 Old Gentilly Road, New Orleans, LA 40189

89. M. Broido, Acting Director, Environmental Sciences Division, Department of Energy, 19901 Germantown Road, Germantown, MD 20874

90. F. A. Donath, Director, Institute for Environmental Education, Geological Society of America, 1006 Las Posas, San Clemente, CA 92673

91. D. W. Freckman, Director, College of Natural Resources, 101 Natural Resources Building, Colorado State University, Fort Collins, CO 80523

92. A. Patrinos, Associate Director, Office of Health and Environmental Research, Department of Energy, G-165, Germantown, MD 20874

93. G. S. Sayler, Professor, 10515 Research Drive, Suite 100, The University of Tennessee, Knoxville, TN 37932-2567

94. F. J. Wobber, Environmental Sciences Division, Office of Health and Environmental Research, ER-74, Department of Energy, 19901 Germantown Road, Germantown, MD 20874

95. Office of Assistant Manager for Energy Research and Development, U.S. Department of Energy Oak Ridge Operations, P.O. Box 2001, Oak Ridge, TN 37831-8600

96.-97. Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831