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Thermal desorption of hazardous and toxic organic compounds from soil matrices : dichloromethane, chloroform, benzene, toluene, 1-chloronaphthalene, 1, 2, 4-trichlorobenzene

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ABSTRACT

Title of Thesis: Thermal Desorption of Hazardous and Toxic
Organic Compounds from Soil Matrices:
Dichloromethane, Chloroform, Benzene,
Toluene, 1-Chloronaphthalene,
1,2,4-Trichlorobenzene

Arun Chemburkar, Master of Science, 1987

Thesis Directed By: Dr. Joseph W. Bozzelli,
Principal Investigator

This research project was undertaken to understand the process of desorption/removal of organic compounds from soil matrices under the influence of temperature and gas purging. The project was divided in two parts :

A. Plug deposition experiments: Columns packed with soil matrices were purged with an inert gas under isothermal conditions. Organic compounds were then introduced as a plug on the front of the column by on-line injection. The rate of passage (due to sequential adsorption/desorption) of the plug through the various soil matrices was measured by a gas chromatograph equipped with a flame ionization detector (FID). The compounds studied were methylene chloride, chloroform, benzene, toluene and 1-chloronaphthalene. The soil matrices used

were sand, soil, gaschrom R and propak T. For a given combination of organic compound and a soil matrix the process was studied at different temperatures at a fixed flow of the inert gas. The plug deposition process was mathematically modeled and the model can be used to predict desorption of these compounds at any temperature in soil matrices under the same gas flow rate conditions. The sand column showed the weakest and the Poropak T column the strongest affinity for the pollutants. An increase in operating temperature also decreased the retention time of the compound.

B. Desorption experiments with uniformly contaminated Soil: A desorption system was built to study a uniformly contaminated soil columns. It incorporated purge flow controls, an oven, valve switching system, temperature probes and a gas chromatograph (FID). The organic compounds studied were 1,2,4-trichlorobenzene (BP = 214°C) and 1-chloronaphthalene (BP = 263°C). Columns containing soil uniformly contaminated with a known concentrations of toxic organic compounds were placed into the oven at isothermal conditions. An inert gas (N₂) at a constant flow of 30 ml/min was used to desorb the compounds from the soil. Vapors were directed by means of a 6-way switching valve either to an FID for analysis, or to activated carbon adsorbers for collection. Solvent

extractions of the soil samples and adsorber columns provided a mass balance for the compound in the system. The desorption rate of the toxic organic compound was analyzed as a function of oven temperature. Mathematical models were developed and curves plotted that can be used to determine desorption-time for the removal of compounds from the soil at isothermal condition. At 200°C and at N₂ flow of 30 cc/min the TCB concentration was 84 ppm after 69 minutes showing 92% removal. At 220°C and at N₂ flow of 30 cc/min the CNAP concentration was 143 ppm after 70 minutes showing 84% removal. Based on an analysis of the results design suggestions are made for a pilot scale soil decontamination system.

**THERMAL DESORPTION OF HAZARDOUS AND TOXIC ORGANIC
COMPOUNDS FROM SOIL MATRICES:
DICHLOROMETHANE, CHLOROFORM, BENZENE, TOLUENE,
1-CHLORONAPHTHALENE, 1,2,4-TRICHLOROBENZENE**

by

Arun Chemburkar

**Thesis submitted to the Faculty of the Graduate School of
the New Jersey Institute of Technology
in partial fulfillment of the requirements for the
degree of Master of Science-Toxicology Option in the
Environmental Engineering Graduate Program**

1987 *f*

APPROVAL SHEET

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I. INTRODUCTION

A. Purpose of Research Project

The purpose of this research project was to develop and model a technique for decontaminating and/or removing hazardous/toxic organic pollutants from soil matrices. The available technologies for decontamination are complete Incineration of soil mass and On-site Leachate Collection & Treatment¹. The drawbacks of the Incineration technology are high capital cost and lack of mobility. The drawbacks of On-site Leaching are the need to fabricate leachate collection and treatment systems on the site, the process in addition depends on the leachability of the organics and most importantly often takes long time periods. Thermal desorption is a physical separation process¹. Applying heat and a flow or purge of inert gas to the soil increases volatilization of organic species adsorbed on the soil and therefore facilitates removal of the organic compounds from soil¹. The main advantage of the technique is that moderately low temperatures and energy inputs to the system are required relative to complete Incineration and the use of inexpensive carrier gas such as CO₂ or N₂ are often sufficient to thoroughly desorb the

organic compounds allowing reuse of soil. Toxicity and exposure potential is also reduced by concentrating the hazardous constituents into a small volume of activated carbon which is easier to treat. The goal of the project is ultimately to completely destroy the desorbed gases by a low energy consumption catalytic oxidation system.

Two different sets of experiments were performed: Plug Deposition Experiments and Uniform Desorption Experiments.

The compounds studied in the Plug Deposition Experiments were

- dichloromethane (methylene chloride)
- chloroform
- benzene
- toluene
- 1-chloronaphthalene

The compounds studied in the Uniform Desorption Experiments were,

- 1,2,4-trichlorobenzene
- 1-chloronaphthalene.

Physical constants for selected compounds⁴ appear in Table I.

Accomplishment of objectives also required:

- i. Data evaluation and mathematical modeling of thermal desorption for interpretation.
- ii. Accurate and thorough determination of the composition, material characteristics, and particle size distribution of the specific soil studied.
- iii. Preparation of soils with known concentration of contaminants.
- iv. Development of analytical techniques for collection and quantitative measurement of the organic vapors which are thermally evolved from the soil matrices.
- v. Determination of the quantity of organic materials remaining on the soil after desorption.

TABLE 1. PHYSICAL CONSTANTS OF SELECTED
ORGANIC COMPOUNDS

| COMPOUND | BOILING POINT °C | DENSITY gm/cc | MOLECULAR WEIGHT | EMPIRICAL FORMULA |
|-----------------------------|------------------------|------------------|---------------------|---|
| Toluene | 111 | 0.87 | 92.0 | C ₇ H ₈ |
| Benzene | 80 | 0.87 | 78.1 | C ₆ H ₆ |
| Dichloromethane | 40 | 1.33 | 84.9 | CH ₂ Cl ₂ |
| 1,2,4-Trichloro -benzene | 214 | 1.45 | 128.4 | C ₆ H ₃ Cl ₃ |
| Trichloro -methane | 61.7 | 1.48 | 119.4 | CHCl ₃ |
| Chlorobenzene | 132 | 1.06 | 112.6 | C ₆ H ₅ Cl |
| 1-Chloro -naphthalene | 263 | 1.94 | 162.6 | C ₇ H ₁₀ Cl |
| Hexachloro -benzene | 322 | 1.57 | 284.8 | C ₆ Cl ₆ |
| Acetone | 56 | 0.79 | 58.1 | CH ₃ COCH ₃ |

B. Previous Studies

There have not been many studies done on the thermal desorption of contaminated soil; however the Superfund Amendments and Reauthorization Amendments (SARA) Act of 1986 has placed emphasis on developing new and effective technologies for the treatment of Superfund sites¹. The authorization by SARA of \$8.5 billion for the clean-up over the next 5 years will have a profound effect on the further developments in on-site thermal and other types of contaminated soil treatment technologies. The major number of the previous studies were done for the United States

Environmental Protection Agency (USEPA), and the pertinent one's are described below.

R.A. Miller et al., studied thermal desorption and heat transfer characteristics of soil contaminated with 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) to establish operating parameters for EPA's Mobile Incineration System at Times Beach, Missouri². They used different types of soil and covered a wide range of moisture content, pH, hydraulic conductivity, organic matter content, and particle size distribution. In the laboratory oven soil trays were maintained at isothermal conditions for a specified period of time and were purged with either air or nitrogen. Their results showed that there was no correlation between oven atmosphere and desorption rate. There was also no correlation between desorption rates and soil moisture or oven atmosphere observed. Temperature and time were the primary desorption parameters. Linear regression analysis produced two mathematical relationships which enabled the prediction of final 2,3,7,8-TCDD concentrations at different times and under different temperature conditions. Material flow models were developed, partially based on the heat transfer characteristics of the soil. The soil was cleaned up to a 2,3,7,8-TCDD concentration of less than 0.2 ppb.

Freeman and Schroy developed a model to describe the vaporization and diffusion of low volatility organic compounds through a column of soil³. The model was used to predict the transport of 2,3,7,8-TCDD at Times Beach site in Missouri. The model determines the rate of vapor phase transport by solving material and energy balance around the soil column. The model predicted that 57 percent by mass of dioxin will be vaporized in the first year and most of that will occur during the summer months. The complex transport and destruction mechanisms indicate that a simple half life model is inadequate to describe movements of low volatility organics.

Cudahy, J.J. et al. of IT Corporation have developed a mobile thermal desorber system⁴. This unit has a capacity for treating soil at the rate of 10 tons per hour at a moisture content of 10 to 15 percent. The primary chamber of the system is at the temperature required to volatilize the organic contaminant in the soil. This ensures a minimum auxiliary fuel consumption. The mobile unit has also the provision for operation with a thermally fired secondary combustion chamber or a flue gas treatment system which will condense, recover and concentrate the volatilized organic compounds for final disposal.

The USEPA announced a Record of Decision (ROD), choosing thermal desorption as the remedial alternative selection at a Superfund site, given to Metaltech/Aerosystems in Franklin Borough, New Jersey⁵. The regional groundwater table will be lowered to excavate the soil. Ten thousand cubic yards of soil are slated for excavation. The contaminants are 1,1,1-trichloroethylene and many other similar volatile organics. The technologies implemented will be either an asphalt drier or an incinerator, operated at 300 - 500 °C. The emission from the operating unit will be trapped on activated carbon.

C. Outline of Experiments

Two basic types of experiments were performed:

1) Plug Deposition Experiments, which consisted of on-line injections with a syringe of selected organic compounds into a heated column containing soil matrices under isothermal conditions.

2) Quantitative desorption experiments under isothermal conditions; utilizing uniformly precontaminated soil packed in glass columns.

In the Plug Deposition experiments, 12.3 cm long by 0.44 cm I.D. stainless steel columns were used. Soil matrices were either sand, soil, Poropak T or Gaschrom R. These were chosen to represent various naturally occurring soils with a wide range of differing adsorptive affinities for organic compounds. The elution of compounds with an inert gas purge through different soil matrices under isothermal conditions was observed with a gas chromatograph (G.C.) equipped with a flame ionization detector (FID). 1.0 ul of benzene(BZ), methylene chloride(MET), toluene(TOL), chloroform(FOM) or 1-chloronaphthalene(CNAP) were separately injected as a Plug onto head of the soil columns. The time required for 50% and 90% removal of the compound was observed at various temperatures and fixed carrier gas flow of 30 cc/min.

The quantitative desorption experiments utilized soil that had been pre-contaminated with known quantities of trichlorobenzene(TCB) and chloronaphthalene. The soil was packed into columns and placed in a pre-heated oven with a constant flow of nitrogen through it. The desorbed gases were analyzed to determine the effluent concentration of the contaminant by an on-line GC (FID). Gases were either directed to the flame ionization detector, or to activated carbon adsorbers. GC analysis of liquid extracts was performed on the contaminated soil, the desorbed soil and

the activated carbon to provide a mass balance throughout the system.

D. Mathematical Modeling

Two different mathematical models were developed to describe the desorption processes of both experiments. The models were based upon the properties of the organic compound such as structure, heat of vaporization and dipole moment. The models will be helpful in scaling up the system to a pilot plant study. They will also be useful in the prediction of the desorptive behavior of different organic compounds in the studied soil matrices and in determining temperature and flow rate needed for complete desorption. They will be discussed in detail in the appropriate experimental section.

E. Software for Modeling

The software used for the mathematical modeling and curve plotting of the desorption process was developed for the scientific use by the Engineering and Science Division of Omicron Inc. (copyright 1982, 1983). For a line plot the data is fed and stored as X and Y coordinates. The stored data file can be statistically processed for different curve or model fitting.

The different models in which the data can be fitted are linear, exponential, power function, logarithmic, inverse X, inverse Y, inverse X & Y and polynomial (up to 6th order). For each curve-fit, the software gives the value of the constants and the regression coefficient of the fit. The given data can be regressed for different curve-fits. The mathematical model can be developed for a particular process based upon the satisfactory and consistent values of the regression coefficient.

The software is also capable of plotting Line Graphs, Pie Charts and Bar Charts. In line graphs, it can draw smooth curves through the data points for up to four different correlations on a pair of coordinates.

An input data file for the software use is shown in Appendix 23. The data in this file is 50% Retention Time versus Temperature for dichloromethane in soil matrix.

II. EXPERIMENTAL

A. Plug Deposition Experiments

1. System Description and Operation

The plug deposition experiments were carried out to establish a relationship between the temperature and the required time for the transport of a plug of organic compound across a given type of soil column at a constant flow-rate of the carrier gas. The molecules of compound are successively adsorbed onto soil particles, then are desorbed and thus migrate to the adjoining particles in the direction of the purge gas flow. The plug deposition refers to the entrance, passage and exit of a collective mass of organic vapors through a soil column while maintaining the plug form to some extent.

A Varian Model 1200 Gas Chromatograph⁷ equipped with a FID was used for the analysis. The GC was connected to channel B of a Varian Model 4290 Reporting Integrator⁸. The standard GC column was replaced with 12.3 cm by 0.44 cm I.D. stainless steel tubes, packed with one of four packings listed in Table II. The N₂ flow through the packing was 30 ml/min.

TABLE II. COLUMN PACKINGS FOR PLUG DEPOSITION EXPERIMENTS

| Packings | Mass (gm) | Mesh | Material |
|------------|-----------|---------|--------------------------------|
| Soil | 2.95 | 35-45 | dried organic top soil |
| Sand | 3.84 | 45-80 | silicone oxide |
| Poropak T | 2.38 | 100-120 | ethylene glycol dimethacrylate |
| Gaschrom R | 2.14 | 60-70 | aluminium and silicone oxide |

The five packings were chosen to represent natural soils with a range of retentive tendencies. Adsorption grade alumina of 80-200 mesh was rejected after trying because it was found to hold the high boilers very tightly. It was decided that the behavior of this packing was too extreme to represent a "worst case" soil expected to be found at hazardous sites. Sand was the least retentive packing. Poropak T was chosen to represent a claylike or "worst case" soil because it represented a highest retentive tendency. Soil found at a hazardous waste site was expected to retain organic compounds less strongly than Poropak T.

One microliter (ul) samples of methylene chloride, chloroform(trichloromethane), benzene, toluene and 1-chloronaphthalene were separately injected into the head

of column. The compounds were selected because they present a range of boiling points with the lowest for methylene chloride and highest for 1-chloronaphthalene.

The desorption times were studied in 20°C increments under isothermal conditions. For each compound the lowest temperatures, at which runs were made was 40°C below the boiling point of the compound (except for methylene chloride). The maximum temperatures used were those that caused the compound to desorb in less than a minutes time. In all cases, at least 4 temperatures were studied for each compound. Injector and detector temperatures were set at 40 degrees C above the boiling point of the compound so that no condensation or holdup would occur on the injector/detector surface.

The time required for 50% removal of the compound from the column was taken as the peak time indicated on the integrator report. The time for 90% removal of the compound from the soil was taken as the point where the FID output signal dropped to 10% of its maximum or peak value. Although the FID output voltage level (height from the baseline) indicated by the integrator is not always directly equated to the concentration of contaminant remaining in the soil (the area under the curve should be the correct measure); comparisons to total area under the desorption curve at different times showed that this level

(10% of Peak level) gives reasonable estimate, was readily measurable and reproducible. It was then decided to utilize the method.

The data sets are summarized in Appendices 1 through 5. The desorption curves are presented in Appendices 6 through 13. Appendices 6 through 13 show two types of graphs: Temperature vs. 50% Retention Time; and Temperature vs. 90% Retention Time. The retention time refers to the time at which 50% or 90%, respectively, of the compound has been removed from the column. Two formats were used to present the data:

(1) Multiple compound fixed soil matrix,

- soil column, temperature vs. retention time
- sand column, temperature vs. retention time
- gaschrom R column, temperature vs. retention time
- poropak T column, temperature vs. retention time

(2) Fixed compound multiple soil matrices.

- 1-chloronaphthalene, temperature vs. retention time
- toluene, temperature vs. retention time
 - benzene, temperature vs. retention time
- dichloromethane, temperature vs. retention time
- chloroform, temperature vs. retention time

2. Mathematical Modeling

The mathematical expression used to model the retention time versus temperature at a constant flow of carrier gas is an exponential decay type. After trying to fit the retention time versus temperature data into different models such as Power Function, the following equation was utilized :

$$t = A_i \times \exp (-b_i \times T)$$

Where A_i and b_i are parameters to be fit for the i^{th} compound;

T is the temperature and t is the retention time.

This model was used to fit data obtained on a combination of five target organic compounds and four different types of soils which resulted in twenty sets of parameters. The equation fit all the data with a correlation coefficient always greater than 0.95. A summary of results appears in Appendices 13-16. The parameter b_i was the indicator of the rate of removal of a given organic compound from the given soil matrix at a given temperature and purge gas flow rate. The parameter b_i is a function of Heat of Vaporization of the compound

plus the porosity, the grain size and the surface properties of the soil matrix. The parameter A_i is the function of molecular size and diffusion coefficient of the organic compound. The model is useful in determining the desorption time required for quantitative removal of a select compound, at a given temperature and flow rate, from a known soil matrix. Thus direct calculation of the time would result from using appropriate A_i and b_i into the equation for the corresponding soil and compound combination.

3. Discussion of Results

The results of the Plug Deposition experiments gave suggestions regarding the parameters that will effect the thermal desorption of organic pollutants from soil. The results showed that the heat of vaporization and molecular weight of the organic compound are important parameters which affect the thermal desorption process. As expected, the sand column shows the weakest and the Poropak T column the strongest affinity for the pollutants. Also, an increase in operating temperature drastically decreases the retention time of the compound. The results also were consistent with the calculations based on the mathematical model. The Exponential Decay model which was used to fit

data obtained on a combination of five target organic compounds and four different types of soils showed an average correlation coefficient was 0.975. All the parameters for the model were established and presented in Appendices 14 through 17. The results show that the target compounds move through a soil column like analytes through a GC column (refer Appendices 6 to 9). The organic compounds could eventually be completely desorbed from the soil in a similar full scale design. Results showed that for the compounds in this phase of the study, the 90% removal was achieved relatively easily. For example, for toluene (BP=111°C) at 120°C the 90% removal was possible in 2.55 minutes at N₂ flow rate of 30 cc/min. This clearly shows that thermal desorption with purge can be utilized for cleansing soils contaminated with these compounds.

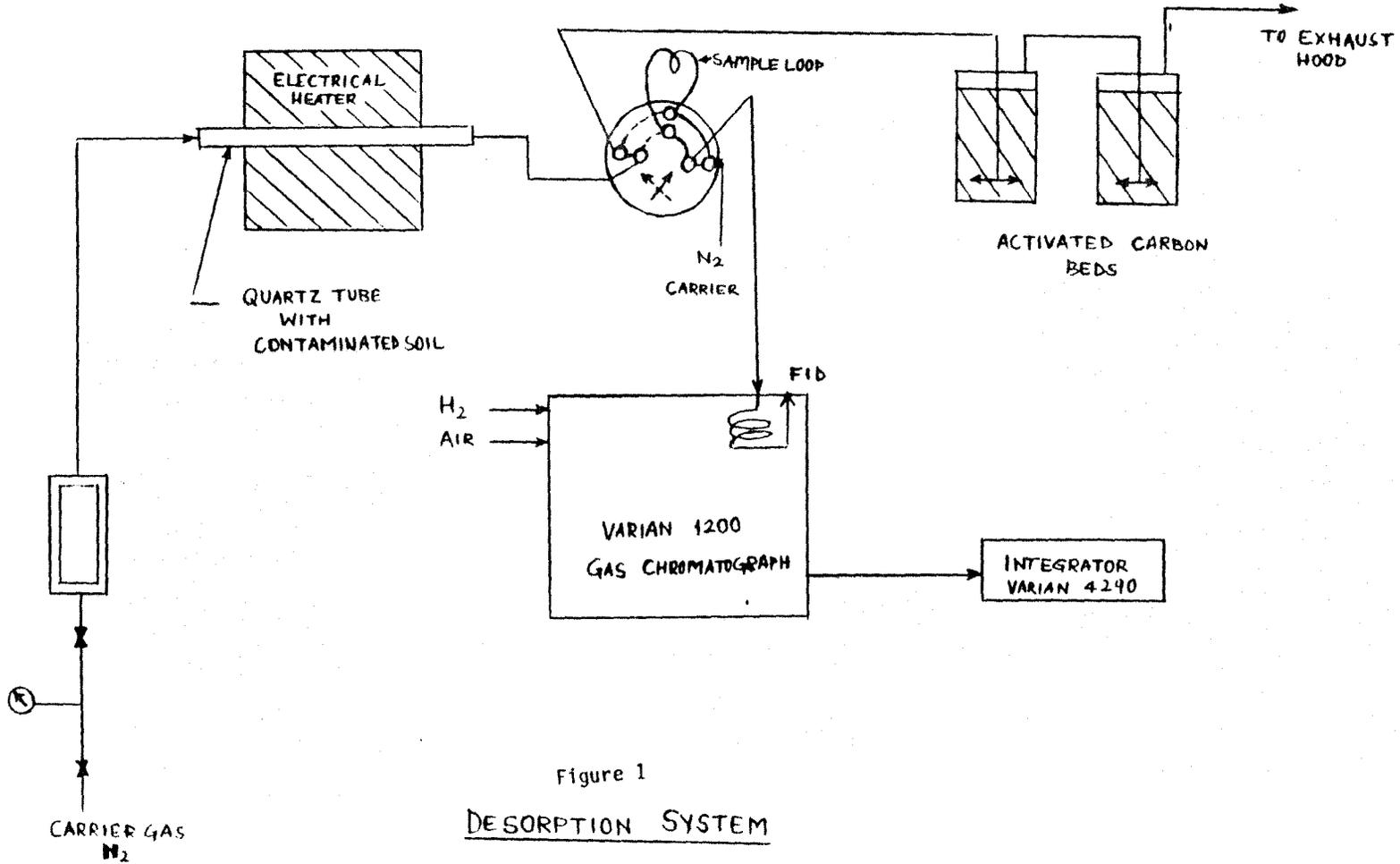


FIGURE I

Figure 1
DESORPTION SYSTEM

B. Desorption Experiments With Uniformly
Contaminated Soil

1. System Description and operation

The equipment used for this second experimental setup are as follows: a) Gas Chromatograph, Model 1200 GC (Varian Instruments, Texas). b) Reporting Integrator, Model 4290, (Varian Instruments, Texas). c) The Desorption Oven of 1" ID and 30 cm in length tube was Model 55031-S (Lindberg Corporation, Watertown, Wisconsin). d) Six Port High Temperature Valve (Valco Corporation, Houston, Texas). e) Digital Thermometer, Model 115 KC (Omega Engineering, Stamford, Connecticut). f) GC Column, 2 meter x 1/8 inch O.D., 10% OV-101 Chrom W-HP 80/100. (Alltech Associates, Arlington Heights, Illinois). g) Heating Tape, Model 5954H (Thomas Scientific). i) Variac Autotransformer 0 - 120 volts at 10 amps, General Radio Corporation, New York, New York. j) Rotameter, 0 - 60 cc/min at STP. (Brooks Rotameter Corporation, Lansdale, Pennsylvania). k) SS Tubing/Fitting, (Components and Control, Carlstadt, New Jersey). l) Graphite Ferrules. (Scientific Glass Engineering, Austin, Texas). m) Gases, H₂ and N₂, technical grade (Liquid Carbonic, Harrison, New Jersey).

n) Activated Carbon of grade JXC 4/10X, (Chemical dynamics, South Plainfield, New Jersey).

The desorption system setup is shown in Figure I. The pre-contaminated soil was placed into a quartz tube (1 cm I.D. and 30 centimeter in length). The soil (15 grams) was loosely packed by gentle tapping and retained in the column by means of a quartz wool plug on both ends. The quartz tube was connected to a stainless steel tube at both ends by means of a 1/2 inch x 1/4 inch stainless steel reducing union equipped with 1/2 inch graphite ferrules for the Quartz connections, stainless steel back ferrules and two polytetrafluoroethylene (PTFE) gaskets. Quartz was chosen as a tube material because of it's ability to withstand temperatures around 550°C, it's inertness and to insure that tubing walls do not catalyze the decomposition of the organic compound at the operating temperatures. The tube was secured inside a tubular housing of the desorption oven.

The temperature of the desorption tube was monitored with chromel/alumel thermocouples attached to a common digital display via rotary selector switch. The temperature sensing ends of thermocouples were housed inside the oven but not inside the desorption quartz tube. To protect the brittle end of thermocouples, they were sheathed by a thin quartz tubing and placed along side the

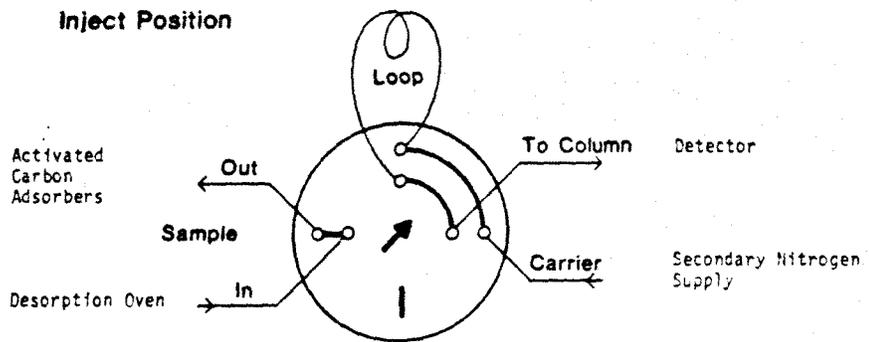
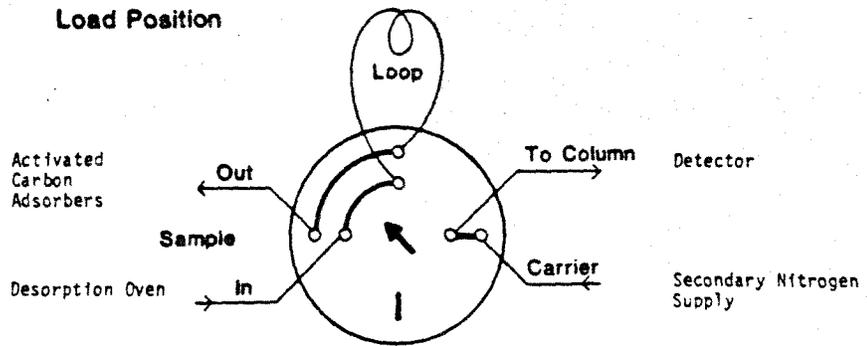
desorption tube. A steady-state temperature profile was measured for the length of the desorption tube with the thermocouple probe inside the oven, corresponding to the set voltage (60, 80, 100 volts) of the Variac. Also a temperature correlation was measured to compensate for any temperature difference between the soil in the desorption tube, which had nitrogen flowing through it, and the thermocouple tube which was outside adjacent to it. All reported temperatures reflect the actual temperature that the soil was exposed to.

In the desorption oven, there was a temperature decrease of 6 degrees from the center to each end. Only the central part of the oven showed isothermal conditions corresponding to a set voltage. 15.0 grams of the soil were used for each of the desorption runs to fill the central 15 centimeters of the oven where the optimum isothermal conditions existed. The bulk density of the soil was found to be 1 gm/cc. The oven temperature was controlled by the Variac Transformer; also the oven door could be manually opened for temperature reduction if the actual temperature rose above the desired operating temperature.

Nitrogen (technical grade) was used as the inert purge gas. The flow rate was held at a constant 30 cc/min. The flow was controlled with a needle valve and a two

stage constant pressure regulator on the gas cylinder. The flow was monitored using a rotameter from 0 to 30 cc/min. The rotameter was calibrated using a soap bubble meter. The hydrogen flow rate was also held constant at 30 cc/min and controlled by the means of a rotameter. Air supply to GC FID was from the building air compressor. The air flow rate was 300 cc/min. The air flow was controlled by two pressure regulators and purified by an activated carbon column measuring 2 cm I.D. by 60 cm length. The air-line also had a rotameter, a shut off valve and a needle valve for monitoring and control respectively.

FIGURE II



The high temperature stainless steel six port valve (Figure II) housed inside the GC oven controlled the flow direction of the desorbed vapors. The desorbed vapors were either directed through a 240 ul sample loop to an FID for a periodic concentration analysis or to activated carbon adsorbers for mass balance. Two 26 gram activated carbon tubes, placed in series, collected the desorbed organic vapors. The effluent from the adsorbers was released into the laboratory exhaust hood.

To determine the concentration of the target compound in the desorbed vapors, the sample from the loop was directed to a FID through a chromatographic column. It was packed with 10% OV-101 Chrom W-HP 80/100. The column separated the target compound from the solvent. The output signal from the FID was fed to the Reporting Integrator.

All of the metal connecting tubes and fittings were wrapped with the Heater Tape and held at constant a temperature of atleast 40°C above the boiling point of the target compound to prevent condensation of the target compound as well as the solvent.

The desorption oven assembly was mounted on raised platform adjacent to the GC so that the vapors desorbing from the soil bed would be directed into the the six port valve, with minimum length of connecting tubes.

2. Preparation and Contamination Of Soil

Soil preparation procedures were used to provide a matrix with consistent adsorbing properties. Thirty kilograms of soil were taken from a location within the New Jersey Institute of Technology campus at Newark, New Jersey. The soil was washed in running water which removed the finest particles, salts and possibly polar organic compounds. A small particle size of the matrix would have caused a large pressure drop across the desorbing soil bed and would have damaged the six port valve and the chromatographic column.

The soil was dried at 200°C overnight. This procedure removed water and volatile species. It was essential to have no "background signal" from any compound other than the target compound and the solvent.

A sieve analysis was performed so that particle size distribution would be known. The sieve set was purchased from Soil Test, Inc., Evanstown, Illinois. The Sieve Set was placed in a mechanical shaker (Humboldt Manufacturing Company).

Soil of mesh size 40 to 70 was selected for the experiments. The Particle Size Distribution of the soil appears in Appendix 17. Analysis by Emission Spectrography and an X-ray diffraction analysis was also done for a

representative sample of the prepared soil for complete chemical and elemental characterization. This was performed by Labtech Corp., Fairfield, NJ. This data appears in the Appendix 18 and Appendix 19.

Two methods of soil contamination were adapted from the description in Chemistry 5139 Laboratory Manual¹⁴ prepared by the University of Minnesota. The methods are : Filtration Technique and Evaporation Technique. The techniques are commonly used in the preparation of GC column packing.

In the Filtration Technique a known mass of soil is placed in a vacuum flask. An excess volume of a standard solution of a volatile organic solvent and a target organic compound is added to obtain a slurry. One hour contact is allowed with a periodic shaking. The slurry is then poured into a Buchner funnel and a slight vacuum was applied till the solution stops flowing out of the funnel. The soil is then transferred to a watch glass for complete drying. The technique was discontinued in favor of the evaporative method. The reasons were: The filter paper absorbs a significant portion of the target compound (as determined by solvent extraction), the target compound evaporates under the influence of vacuum, and because many glass vessels were involved transfer losses are experienced.

In the Evaporative Technique a known volume of standard solution is added to a known mass of soil. The solution was allowed to dry for at least 48 hours at room temperature under the exhaust hood. The drying soil mass was stirred occasionally for better distribution of the target compound. The solvents tested to distribute target compound in the soil were: methylene chloride, acetone and toluene. Methylene chloride was tried first as it's a good solvent with a low boiling point but its use was discontinued because it created peak tailing on the chromatograms due to it's polar nature. Acetone's use was discontinued because it presented difficulties in the extraction of the target compound from the activated carbon. Toluene was found to be the most suitable solvent for both distribution and extraction of target compound.

The initial soil contaminant concentration was based on the volume and known concentration of the standard solution added. It was also used as a guide in subsequent experiments. The actual initial concentration was determined by performing the solvent extraction.

The initial 1,2,4-trichlorobenzene (TCB) soil concentration was calculated as follows: The standard solution of 1000 ppm (gm TCB/ gm acetone) TCB in acetone was used to contaminate the soil. For 500 gm of soil 250 ml of the standard solution was used.

Let X be the concentration of TCB on the soil then,
gm of TCB in 250 ml Standard Solution

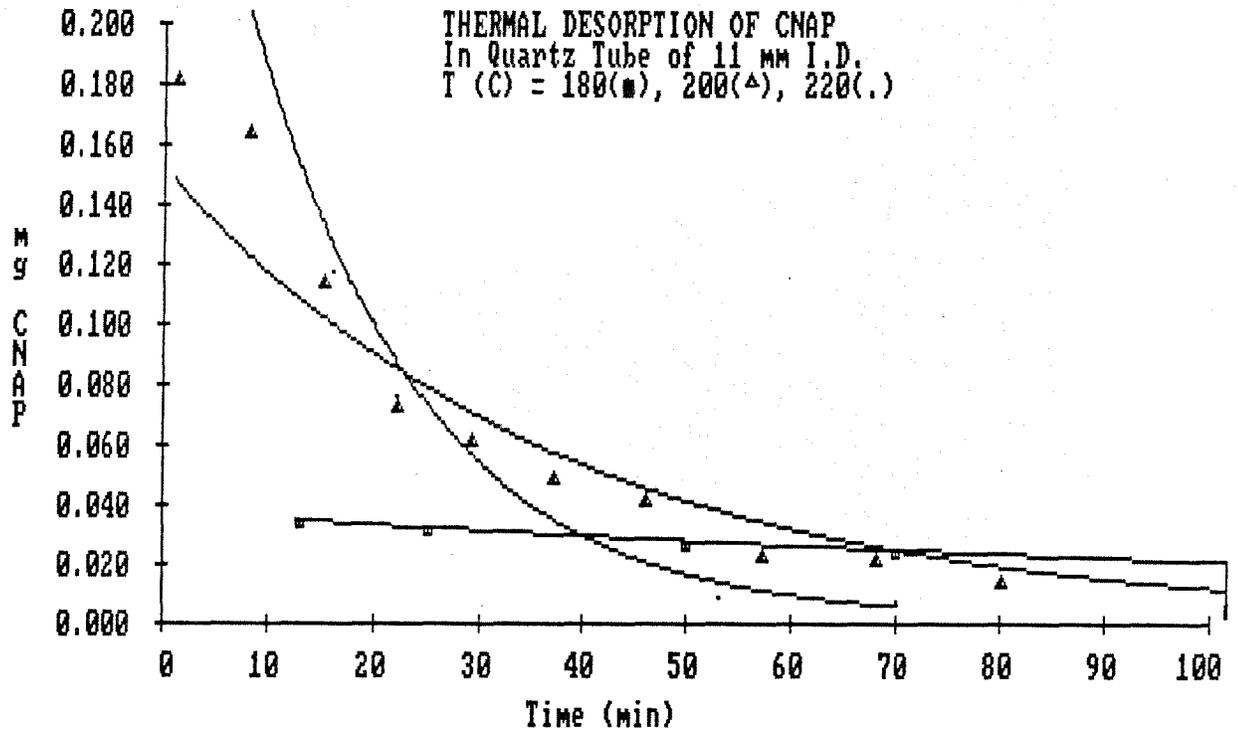
$$\begin{aligned} X &= \frac{\text{-----}}{\text{500 gm of soil}} \\ &= \frac{1.972 \text{ gm TCB}}{\text{-----}} \\ &= \frac{500 \text{ gm Soil}}{\text{-----}} \\ &= 4 \text{ mg TCB/gm Soil} \end{aligned}$$

Similarly for 1-chloronaphthalene (CNAP),

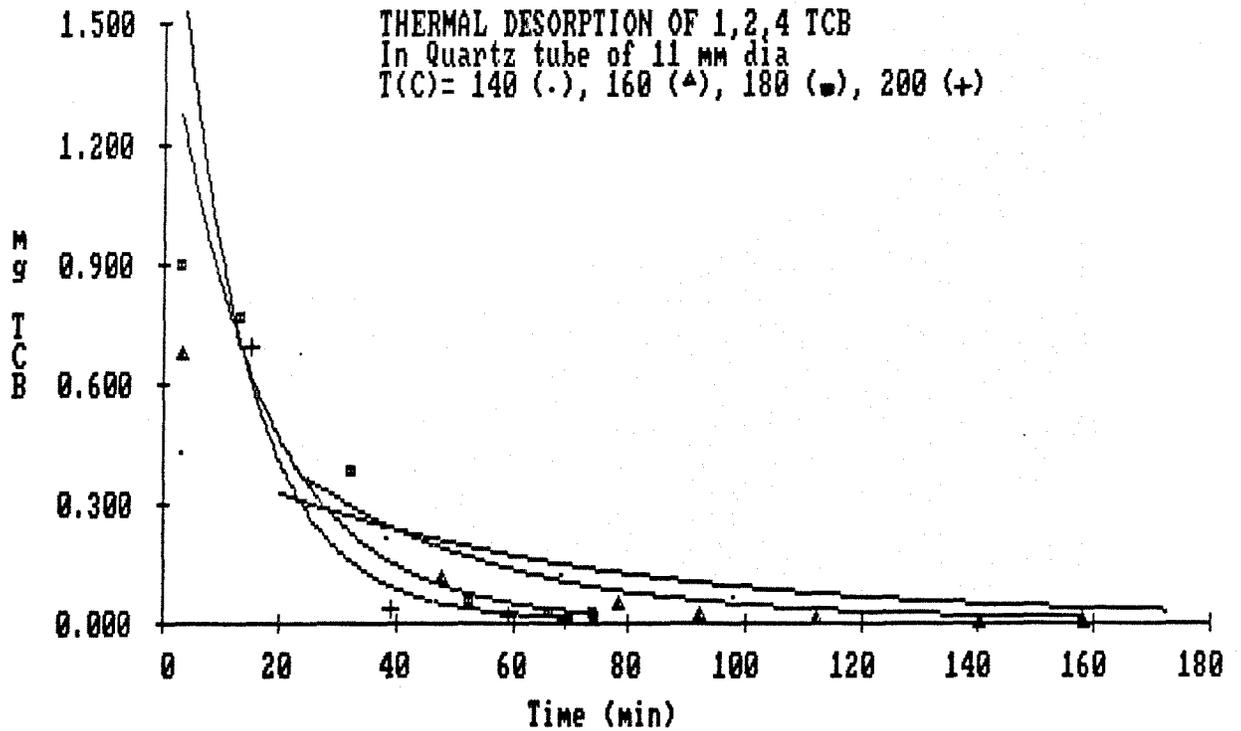
The standard solution of 1000 ppm (gm CNAP/ gm toluene) CNAP in toluene was used to contaminate the soil. For 200 gm of soil 250 ml of the standard solution was used.

$$\begin{aligned} X &= \frac{\text{gm of CNAP in 250 ml Standard Solution}}{\text{-----}} \\ &= \frac{200 \text{ gm of Soil}}{\text{-----}} \\ &= \frac{0.0867 \text{ gm CNAP}}{\text{-----}} \\ &= \frac{200 \text{ gm Soil}}{\text{-----}} \\ &= 0.4335 \text{ mg CNAP/gm Soil} \end{aligned}$$

Graph I



Graph II



3. Desorption Procedure

A 12.5 cm OD quartz tube packed with the contaminated soil was placed in the oven. After the soil had reached the desired isothermal conditions nitrogen flow was started. After waiting 2 minutes for the nitrogen flow rate to stabilize at 30cm³/min the six port valve was switched from the load position to the inject position (See Figure 2). This causes a GC carrier nitrogen supply to direct the first desorbed gas sample from the sample loop into the GC column and FID. It also causes a loss of some of the desorbed vapors. This was accounted for via extrapolation. The chromatographic column in Varian GC provided satisfactory separation of the target compound from the accompanying solvent. When, at the end of the run, the chromatograph recording returned to baseline from the target compound peak, the six port valve was reset and another sample was injected. The procedure repeated periodically until the integrator area of the target pollutant fell to approximately to 1% of the targets largest peak area. The experimental run was stopped as the concentration values fell below detection by this analysis procedure.

The periodic injections produced a series of chromatograms. Typical desorption chromatogram series for TCB and CNAP are presented in Appendices 20 and 21, respectively. Tables III and IV are compilations of elapsed time and unit area for each compound.

TABLE III. ELAPSED TIME AND UNIT AREAS FOR TCB
DESORPTION

| Run Time (min) | Area 10^3 | Run Time (min) | Area 10^3 |
|-------------------|----------------|-------------------|----------------|
| 140 °C | | 160 °C | |
| 0 | 0 | 0 | 0 |
| 3 | 284 | 3 | 276 |
| 38 | 141 | 25 | 333 |
| 54 | 126 | 47 | 51 |
| 68 | 81 | 78 | 22 |
| 84 | 49 | 92 | 13 |
| 98 | 44 | 112 | 7 |
| 154 | 23 | 140 | 5 |
| | | 158 | 5 |
| 180 °C | | 200 °C | |
| 0 | 0 | 0 | 0 |
| 3 | 986 | 1 | 1800 |
| 13 | 842 | 15 | 514 |
| 32 | 421 | 39 | 27 |
| 52 | 60 | 59 | 12 |
| 66 | 30 | 69 | 8 |
| 74 | 18 | | |

TABLE IV. ELAPSED TIME AND UNIT AREAS FOR CNAP

DESORPTION

| Run Time (min) | Area 10 ⁴ | Run Time (min) | Area 10 ⁴ |
|-------------------|-------------------------|-------------------|-------------------------|
| 180 °C | | 220 °C | |
| 0 | 0 | 0 | 0 |
| 13 | 58.07 | 1 | 151.3 |
| 25 | 53.9 | 7 | 94.1 |
| 50 | 46.246 | 16 | 45.8 |
| 70 | 40.91 | 22 | 29.8 |
| 361 | 6.9 | 38 | 11.5 |
| 377 | 5.99 | 53 | 3.33 |
| | | 70 | 2.73 |
| 200°C | | | |
| 0 | 0 | | |
| 1 | 71.35 | | |
| 8 | 64.7 | | |
| 15 | 45.2 | | |
| 22 | 29.1 | | |
| 29 | 24.51 | | |
| 37 | 19.65 | | |
| 46 | 16.53 | | |
| 57 | 9.5 | | |
| 68 | 8.83 | | |
| 80 | 5.89 | | |
| 126 | 3.09 | | |

Numerous batches of soil were contaminated, extracted and desorbed on a trial basis to establish operating parameters. Only successful experiments are included in this report. The contaminant area units, and the their peak times were entered into the statistical software package for regression. The output was an equation representing a mathematical model of the desorption rate. To convert the integrator area units into contaminant concentration units, the area under the curve was obtained by integration of signal between $t = 0$ min. and $t = t_f$. At $t = t_f$, the height reached 1% of the largest peak height. The area was then equated to the milligrams of the target compound which were extracted from the activated carbon adsorber. These calculations are explained under the section II(B:4). The milligrams of target compound per unit integrator area was calculated and graphs were plotted as concentration versus time.

4. Extractions

The purpose of extraction is to obtain a mass balance of the contaminant through the system. Extractions were performed with the same solvent as the one which was used to make stock solutions with the target compound to contaminate the soil. This minimized the number of

components to be separated in an extract calibration chromatogram. The extractions were performed on the following entities: uncontaminated soil, contaminated soil, desorbed soil and activated carbon. The purpose of extracting clean soil was to ensure that there is no "background signal" in the extract chromatogram.

The mass balance of contaminant through the system for each column run is:

$$\text{mass on soil} = \text{mass undesorbed} + \text{mass desorbed (mass collected on adsorbers)}$$

The equipment used was 1. Shimadzu GC FID (Model 8A, Shimadzu Instrument Corporation, Baltimore, Maryland). 2. Reporting Integrator, Model 4290 (Varian Instruments, Walnut Creek, California). 3. Mechanical Agitator, Model 37A (Eberbach Corporation, Ann Arbor, Michigan). and 4. Hamilton Microliter Syringes, Model 7000.

The three different solvents used for extraction were, methylene chloride, acetone, toluene. Methylene chloride's use was discontinued as it was not a good extracting solvent and showed peak tailing. Acetone did not cause peak tailing but was not a good extracting solvent both TCB and CNAP as compared to toluene as determined by the extraction of the identical soil sample using both solvents.

For soil extractions, 15 gm of soil were extracted with 50 ml of solvent. For activated carbon extraction, 26 gm of carbon were extracted with 50 ml of solvent. Narrow mouth screw cap bottles (125 ml) equipped with (PTFE) polytetrafluoroethylene liners were used. The bottles were placed in a mechanical agitator for thirty minutes for good interphase contact and high extraction efficiency. The bottles were allowed to stand for at least 24 hours optimal contact time and also to allow time for the settling of fine particulates so that clear supernatant solution could be decanted. Particulates might have damaged the syringes used to inject the samples into the GC.

All extracts were analyzed on a Shimadzu GC (equipped with dual columns and FIDs). All injections had internal standards to quantify the mass of contaminant. The volume injected for each of the extract sample was 1 ul.

TABLE V

TCB EXTRACTIONS

| SAMPLE | SOLVENT STANDARD | AV. AREA RATIO | PPM | MASS | TOTAL |
|------------------------|---------------------|-------------------|------|-----------------|--------|
| Adsorber 1 | Toluene | | | | |
| 1 ^o Extract | | 1.36 | 2800 | 83.7 | |
| 2 ^o Extract | | 2.7 | 1320 | 39.46 | 24.9/ |
| 3 ^o Extract | | 6.15 | 580 | 17.34 | column |
| 4 ^o Extract | | 13.1 | 300 | 8.96 | |
| | | | | | |
| | | | | (for 6 columns) | 149.47 |
| Adsorber 2 | Toluene CNAP | | | | |
| 1 ^o Extract | | - | - | - | - |
| Conta. Soil | Acetone CB | | | | |
| 1 ^o Extract | | 1.97 | 850 | 23 | |
| 2 ^o Extract | | 12.3 | 136 | 3.68 | 27.27/ |
| 3 ^o Extract | | 77 | 22 | 0.59 | column |
| Desorbed Soil | Acetone CB | | | | |
| 1 ^o Extract | | 55 | 40 | 1.09 | 1.26/ |
| 2 ^o Extract | | 90 | 6.4 | 0.17 | column |
| 3 ^o Extract | | - | - | - | |

Note : All the masses are in milligrams.

TABLE VI.

CNAP EXTRACTIONS

| SAMPLE | SOLVENT STANDARD | AV. AREA RATIO | PPM | MASS | TOTAL |
|------------------|---------------------|-------------------|-----------------|--------|--------|
| Adsorber 1 | Toluene TCB | | | | |
| 1° Extract | | 3.3 | 254 | 11.01 | |
| 2° Extract | | 8.2 | 92.5 | 4.01 | 5.38/ |
| 3° Extract | | 41 | 23 | 0.99 | column |
| | | | | ----- | |
| | | | (for 3 columns) | 16.018 | |
| Adsorber 2 | Toluene TCB | | | | |
| 1° Extract | | 0.0 | 0.0 | 0.0 | 0.0 |
| Conta. Soil | Toluene TCB | | | | |
| 1° Extract | | 5.35 | 150 | 6.5 | |
| 2° Extract | | 66.5 | 15 | 0.65 | 7.28/ |
| 3° Extract | | 120 | 3 | 0.13 | column |
| | | | | ----- | |
| | | | | 7.28 | |
| Desorbed Soil | Toluene TCB | | | | |
| 1° Extract | | 31.5 | 30 | 1.14 | 1.27/ |
| 2° Extract | | 120 | 3 | 0.13 | column |
| 3° Extract | | 0.0 | 0.0 | 0.0 | |

Note : All the masses are in milligrams.

TABLE VII TARGET COMPOUND MASS BALANCE

| COMPOUND | I | II | III | IV | CONTA. SOIL | % R | % RM |
|----------|------|-----|-------|-------|----------------|------|------|
| TCB | 24.9 | 0.0 | 1.26 | 26.16 | 27.27 | 96.3 | 95.4 |
| CNAP | 5.34 | 0.0 | 1.313 | 6.653 | 7.28 | 91.4 | 81.9 |

where, I = Mass collected on Adsorber 1
 II = Mass collected on Adsorber 2
 III = Mass remaining on Soil
 IV = I + II + III
 Mass on contaminated soil - III

$$\% \text{ RM (Removal)} = \frac{\text{Mass on contaminated soil} - \text{III}}{\text{Mass on contaminated soil}} \times 100$$

$$\% \text{ R (Recovery)} = \frac{\text{IV}}{\text{Mass on contaminated soil}} \times 100$$

Note : All the masses are in milligrams.

5. Quality Control

Quality control checks were done on the following aspects of research to generate true and reproducible data.

Soil : Physical and chemical properties of the soil were determined by X-ray diffraction, emission spectrophotometry and sieve analysis.

Bulk density and actual density were also determined. A large quantity of soil was prepared for the experiments as described in Section IIb, so that it would last for the entire duration of the project. This stock soil was desorbed and the effluent was analysed in GC to ensure that no volatiles were present and the soil was also subject to periodic solvent extraction for background level determination. Injection of the extract yielded no peaks other than those of the solvent.

Chemicals : All the organic chemicals used in the study were subject to GC analysis prior to use. They were checked for the impurities. If any unidentified or interfering peaks were found, the chemical was discarded.

Extraction : Replicate extractions (labeled R) were performed upon samples. Multiple injections of each extract was performed to ensure reproducibility. The syringes were equipped with Chaney adapters so that the injector error was minimized.

6. Standard Concentration Curves

Standard concentration curves were prepared to quantify the contaminants in the extracts. For TCB, six standard solutions were prepared: 10, 50, 100, 250, 500 and 1000 ppm w/w (gm TCB/gm acetone) of TCB in acetone. A constant quantity or internal standard of 1000 ppm (w/w) of chlorobenzene CB in acetone was added to each standard solution. Injection of each standard in the Shimadzu GC for analysis produced a ratio of CB area to TCB area. Each ratio corresponds to a specific concentration of TCB. A standard curve was constructed of area ratios vs. concentration of TCB. In the same fashion, Standard Concentration Curves for CNAP were also developed. Standard solutions prepared of 10, 50, 100, 500, 1000 ppm (w/w) CNAP in toluene were prepared. The internal standard used was TCB. These graphs appear in Appendices 22 and 23, respectively.

To determine the actual concentration of contaminant in the solvent extract, the following steps were taken : From each extract, five mls were decanted. 1000 ppm (w/w) of internal standard was added to it. Injection of this in the Shimadzu GC yielded an internal standard area and contaminant area on the chromatogram. The ratio of these areas could then be compared to the standard curve and the concentration of the contaminant (ppm) can be read from

the curve. Once the concentration of contaminant was determined, its mass in the sample could be easily calculated. A summary of extraction results for TCB and CNAP are presented in Tables V and VI, respectively. The mass of the contaminant collected on the activated carbon adsorber was divided by the number of soil columns desorbed during the experiment so a mass balance can be made around the system. For TCB, the desorbed gases from six soil columns (15 gm each) were collected on a pair of activated carbon adsorber tubes. For, CNAP three soil column's desorbed vapors were collected on a pair of activated carbon adsorber tubes. The mass balance and final soil concentration summary appears in Table VII.

7. Mathematical Modeling For Desorption Process

The data obtained from the desorption experiments was fed to Plotrax program for Statistical Analysis as described in Section I. The exponential fit was selected from the different options of curve-fitting was the most suitable one. The desorption process is a function of the heat of vaporization, dipole moment, mass of contaminant molecule plus the soil properties, temperature and purge gas flow rate. At constant soil properties, temperature and gas flow rate, the process is a function of heat of vaporization, molecule mass and dipole moment only. Therefore, for a soil similar in properties to the one in the study and if the temperature and gas flow rate conditions are identical then this model can be used to predict its removal rates of different organic compounds. The data needed to predict the desorption rate would be the heat of vaporization, mass of molecule and dipole moment of the compound.

The selected model was a direct function of the heat of vaporization in the exponential part of the equation, and of the dipole moment or polarizability in the linear portion of the equation.

The overall form of the equation expresses concentration removed from the soil matrix as a function of time at a given temperature and flow rate of 30 cc/min of N₂. The change in concentration with time is expressed as:

$$dC_i/dt = -kC_i$$

Where C is concentration of species i adsorbed on the soil

This equation can be integrated to yield:

$$C(t)/C(0) = \exp(-kt)$$

Where C(t) is concentration remaining on the soil at time t.

The coefficient k is a function of temperature and Heat of Vaporization.

TABLE VIII. SUMMARY OF PARAMETERS FOR MATHEMATICAL MODELING OF TCB DESORPTION

| Temperature °C | C ₀ | k | R |
|----------------|----------------|-----------------------|-----|
| 140 | 0.384 | 1.59x6 ⁻² | .98 |
| 160 | 0.500 | 2.663x6 ⁻² | .97 |
| 180 | 1.52 | 6.03x6 ⁻² | .98 |
| 200 | 2.06 | 8.23x10 ⁻² | .98 |

Where, C₀ = initial concentration of TCB

k = rate constant

R = correlation coefficient

TABLE IX. SUMMARY OF PARAMETERS FOR MATHEMATICAL MODELING OF CNAP DESORPTION

| Temperature °C | C ₀ | k | R |
|----------------|----------------|------------------------|------|
| 180 | 0.0365 | 6.176x10 ⁻³ | 0.99 |
| 200 | 0.1513 | 2.650x10 ⁻² | 0.96 |
| 220 | 0.3343 | 6.129x10 ⁻² | 0.99 |

Where, C₀ = initial concentration of TCB

k = rate constant

R = correlation coefficient

8. Results and Discussion of Desorption Experiments

The desorption system constructed for the project proved to be operationally satisfactory for the study the of desorption of different organic compounds from the soil over a wide range of temperature. The operational methods allowed precise and reproducible desorption data.

The evaporative method of soil contamination was a suitable procedure for uniformly distributing the target compounds on the soil.

For the extraction of activated carbon the solvent should be chosen such as it is at least structurally similar to the target compound. It was found that during the experiments, toluene extracts TCB from activated carbon more efficiently than acetone because it is structurally similar to TCB.

The exponential decay mathematical model was found to fit the desorption data with uniformly contaminated soil most satisfactorily. The decay constants were determined for each compound for a specific isothermal condition. The data fit the equation with an average correlation coefficient of 0.98 for both TCB and CNAP. The desorption curves for these compounds at each studied temperature were plotted in Figures III.

Mass balance was performed on the entire system. Table VII shows that 96% of the TCB and 91% of the CNAP was accounted for. The percent removals were 95% for TCB and 82% for CNAP. From the initial TCB soil concentration of 940 ppm the TCB soil concentration reduced to 84 ppm after desorption at 200 degrees for 69 minutes. From the initial CNAP soil concentration of 760 ppm the CNAP soil concentration reduced to 143 ppm after desorption at 220 degrees for 70 minutes.

Pentachlorophenol was also tried as one of the target compounds but these experiments were abandoned because the compound was found to decompose during the thermal desorption at the temperature of 220 °C.

9. Conclusion

This research project was undertaken to understand the process of desorption/removal of organic compounds from soil matrices under the influence of temperature and gas purging.

In the first part of the project columns packed with soil matrices were purged with an inert gas under isothermal conditions. Organic compounds were then introduced as a plug on the front of the column by on-line injection. The rate of passage (due to sequential adsorption/desorption) of the plug through the various soil matrices was measured. The compounds studied in this system were methylene chloride, chloroform, benzene, toluene and 1-chloronaphthalene. The soil matrices used were sand, soil, gaschrom R and propak T. For a given combination of organic compound and a soil matrix the process was studied at different temperatures ranging from 40 to 260 °C at a constant 30 cc/min flow of the inert gas. The plug deposition process was mathematically modeled. It was decided to use the exponential decay model to fit the retention time versus temperature data. This model fit all the data with a correlation coefficient greater than 0.95. The model can be used to predict desorption of these compounds at any temperature in soil matrices at 30 cc/min of inert gas flow. The sand column

showed the weakest and the Poropak T column the strongest affinity for the pollutants. An increase in operating temperature also decreased the retention time of the compound.

In the second set of experiments a desorption system was built to study a uniformly contaminated organic top soil columns. It incorporated purge flow controls, an oven, valve switching system, temperature probes and a gas chromatograph (FID). The organic compounds studied were 1,2,4-trichlorobenzene (BP=214°C) and 1-chloronaphthalene (BP=263°C). Columns containing soil uniformly contaminated with a known concentrations of toxic organic compounds were placed into the oven at isothermal conditions. An inert gas (N₂) at a constant flow of 30 ml/min was used to desorb the compounds from the soil. Vapors were directed by means of a 6-way switching valve either to an FID for analysis, or to activated carbon adsorbers for mass balance calculations. The desorption rate of the toxic organic compound was analyzed as a function of oven temperature. Mathematical models were developed and curves plotted that can be used to determine desorption-time for the removal of compounds from the soil at isothermal condition. At 200°C and at N₂ flow of 30 cc/min the TCB concentration was 84 ppm after 69 minutes showing 92% removal. At 220°C and at N₂ flow of

30 cc/min the CNAP concentration was 143 ppm after 70 minutes showing 84% removal.

The two compounds studied here viz. 1,2,4-trichlorobenzene and 1-chloronaphthalene have significantly higher boiling points than those studied in the first phase of the research. They are clearly more difficult to desorb and complete removal from soil requires higher temperature and higher purge flow.

10. Suggested Areas For Further Studies

- a. Determination of the limits of the mathematical model and analyzing the possibility of different model fits.
- b. Determination of the desorption rates from soil with multiple organic compounds.
- c. Determination of the desorption rates of organic compounds from multi-layered soil.
- d. Construction and testing of a bench scale continuous feed unit.
- e. Determination of the effects of using different types of purge gases, such as carbon dioxide, under the same operating conditions.
- f. Incorporating soil properties into the development of the desorption model.

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APPENDIX 1

Compound : 1-Chloronaphthalene

Retention Time Vs. Temperature Data
in different Soil Matrices

| Temp °C | SOIL | | SAND | | GASCHROM. | | POROPAK | |
|------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| | RT ₅₀ | RT ₉₀ |
| 140 | - | - | 0.43 | 4.75 | - | - | - | - |
| 160 | - | - | 0.37 | 2.96 | 0.49 | 4.79 | - | - |
| 180 | 7.71 | 58.67 | 0.31 | 1.84 | 0.36 | 3.33 | 1.98 | 8.90 |
| 200 | 7.51 | 38.86 | 0.27 | 1.15 | 0.27 | 1.83 | 1.42 | 4.09 |
| 220 | 7.31 | 25.74 | 0.23 | 0.71 | 0.20 | 0.98 | 1.02 | 1.88 |
| 240 | 7.11 | 17.05 | 0.20 | 0.44 | 0.14 | 0.34 | 0.73 | 1.26 |
| 260 | 6.93 | 11.29 | 0.17 | 0.28 | 0.11 | 0.24 | 0.40 | 0.70 |

Note : Times are in minutes.

RT₅₀ : 50% Removal Time of compound

RT₉₀ : 90% Removal Time of compound

APPENDIX 2

Compound : Toluene

Retention Time Vs. Temperature Data
in different Soil Matrices

| Temp! °C | SOIL | | SAND | | GASCHROM. | | POROPAK | |
|-------------|------|------|------|------|-----------|------|---------|------|
| | RT50 | RT90 | RT50 | RT90 | RT50 | RT90 | RT50 | RT90 |
| 60 | 1.70 | 9.42 | 1.82 | 6.15 | 0.48 | 2.21 | - | - |
| 80 | 1.14 | 4.78 | 1.6 | 4.34 | 0.39 | 2.08 | - | - |
| 100 | 0.77 | 3.29 | 0.82 | 3.49 | 0.33 | 1.87 | - | - |
| 120 | 0.52 | 2.55 | 0.63 | 3.05 | 0.27 | 1.5 | 0.94 | 6.46 |
| 140 | 0.35 | 1.85 | - | - | - | - | 0.60 | 3.78 |
| 160 | - | - | - | - | - | - | 0.38 | 2.21 |
| 180 | - | - | - | - | - | - | 0.25 | 1.29 |

Note : Times are in minutes.

RT50 : 50% Removal Time of compound

RT90 : 90% Removal Time of compound

APPENDIX 3

Compound : Benzene

Retention Time Vs. Temperature Data
in different Soil Matrices

| Temp °C | SOIL | | SAND | | GASCHROM. | | POROPAK | |
|------------|------|-------|------|-------|-----------|-------|---------|-------|
| | RT50 | RT90 | RT50 | RT90 | RT50 | RT90 | RT50 | RT90 |
| 40 | - | - | 0.35 | 13.81 | 0.45 | 17.97 | - | - |
| 60 | 0.67 | 32.86 | 0.30 | 10.11 | 0.40 | 13.74 | - | - |
| 80 | 0.51 | 23.58 | 0.26 | 7.40 | 0.34 | 10.51 | 1.37 | 12.12 |
| 100 | 0.39 | 16.92 | 0.23 | 5.42 | 0.30 | 8.04 | 0.82 | 6.28 |
| 120 | 0.30 | 12.14 | 0.20 | 3.96 | 0.26 | 6.15 | 0.49 | 3.25 |
| 140 | - | - | - | - | - | - | 0.29 | 1.68 |

Note : Times are in minutes.

RT50 : 50% Removal Time of compound

RT90 : 90% Removal Time of compound

APPENDIX 4

Compound : Dichloromethane

Retention Time Vs. Temperature Data
in different Soil Matrices

| Temp °C | SOIL | | SAND | | GASCHROM. | | POROPAK | |
|------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| | RT ₅₀ | RT ₉₀ |
| 40 | 0.74 | 3.60 | 0.09 | 1.13 | 0.49 | 1.49 | 10.28 | 47.16 |
| 60 | 0.63 | 2.61 | 0.03 | 0.97 | 0.46 | 1.37 | 6.37 | 25.37 |
| 80 | 0.53 | 1.88 | 0.01 | 0.83 | 0.43 | 1.26 | 3.95 | 13.65 |
| 100 | 0.45 | 1.36 | 0.01 | 0.72 | 0.40 | 1.15 | 2.45 | 7.34 |
| 120 | - | - | - | - | 0.38 | 1.06 | 1.52 | 3.95 |
| 140 | - | - | - | - | 0.36 | 0.97 | - | - |

Note : Times are in minutes.

RT₅₀ : 50% Removal Time of compound

RT₉₀ : 90% Removal Time of compound

APPENDIX 5

Compound : Chloroform

Retention Time Vs. Temperature Data
in different Soil Matrices

| Temp °C | SOIL | | SAND | | GASCHROM. | | POROPAK | |
|------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| | RT ₅₀ | RT ₉₀ |
| 40 | - | - | - | - | 0.52 | 1.66 | - | - |
| 60 | 2.52 | 8.54 | - | - | 0.50 | 1.41 | - | - |
| 80 | 1.16 | 3.72 | 0.38 | 1.60 | 0.48 | 1.19 | 4.92 | 10.75 |
| 100 | 0.53 | 1.62 | 0.35 | 1.39 | 0.47 | 1.01 | 3.18 | 7.12 |
| 120 | - | - | 0.31 | 1.21 | - | - | 2.06 | 4.72 |
| 140 | - | - | 0.28 | 1.05 | - | - | 1.33 | 3.12 |
| 160 | - | - | 0.26 | 0.92 | - | - | 0.86 | 2.07 |

Note : Times are in minutes.

RT₅₀ : 50% Removal Time of compound

RT₉₀ : 90% Removal Time of compound

APPENDIX 6

PARAMETERS FOR SOIL COLUMN

50% Compound Removal

| | R | A | -Bi | Temperature Range °C |
|---------------------|------|-------|------------------------|-------------------------|
| 1-Chloronaphthalene | 0.95 | 10.33 | -1.34×10^{-3} | 180 - 260 |
| Toluene | 0.93 | 5.99 | -1.98×10^{-2} | 60 - 140 |
| Benzene | 0.94 | 1.58 | -1.33×10^{-2} | 60 - 120 |
| Dichloromethane | 0.99 | 1.04 | -8.28×10^{-3} | 40 - 100 |
| Chloroform | 0.99 | 26.22 | -3.89×10^{-2} | 60 - 100 |

90% Compound Removal

| | R | A | -Bi | Temperature Range °C |
|---------------------|------|--------|------------------------|-------------------------|
| 1-Chloronaphthalene | 0.98 | 2441 | -2.06×10^{-2} | 180 - 260 |
| Toluene | 0.99 | 568.72 | -2.89×10^{-2} | 60 - 140 |
| Benzene | 0.99 | 89.87 | -1.66×10^{-2} | 60 - 120 |
| Dichloromethane | 0.97 | 7.1 | -1.62×10^{-2} | 40 - 100 |
| Chloroform | 0.99 | 104.01 | -4.15×10^{-2} | 60 - 100 |

APPENDIX 7

PARAMETERS FOR SAND COLUMN

50% Compound Removal

| | R | A | -Bi | Temperature Range °C |
|---------------------|------|------|------------------------|----------------------|
| 1-Chloronaphthalene | 0.97 | 1.32 | -7.83×10^{-3} | 140 - 220 |
| Toluene | 0.98 | 0.85 | -1.28×10^{-2} | 60 - 120 |
| Benzene | 0.97 | 0.47 | -6.87×10^{-3} | 40 - 120 |
| Dichloromethane | 0.95 | 0.60 | -4.70×10^{-2} | 40 - 100 |
| Chloroform | 0.95 | 0.59 | -4.85×10^{-3} | 80 - 160 |

90% Compound Removal

| | R | A | -Bi | Temperature Range °C |
|---------------------|------|-------|------------------------|----------------------|
| 1-Chloronaphthalene | 0.90 | 145.7 | -2.37×10^{-2} | 140 - 220 |
| Toluene | 0.98 | 60.59 | -2.07×10^{-2} | 60 - 120 |
| Benzene | 0.97 | 26.57 | -1.56×10^{-2} | 40 - 120 |
| Dichloromethane | 0.96 | 1.58 | -7.47×10^{-3} | 40 - 100 |
| Chloroform | 0.99 | 2.81 | -6.94×10^{-3} | 80 - 160 |

APPENDIX 8

PARAMETERS FOR GASCHROM COLUMN

50% Compound Removal

| | R | A | -Bi | Temperature Range °C |
|---------------------|------|------|------------------------|----------------------|
| 1-Chloronaphthalene | 0.97 | 5.98 | -1.54×10^{-2} | 160 - 220 |
| Toluene | 0.96 | 0.87 | -9.39×10^{-3} | 60 - 120 |
| Benzene | 0.98 | 0.61 | -6.89×10^{-3} | 40 - 120 |
| Dichloromethane | 0.99 | 0.56 | -3.18×10^{-3} | 40 - 140 |
| Chloroform | 0.99 | 0.56 | -1.72×10^{-3} | 40 - 100 |

90% Compound Removal

| | R | A | -Bi | Temperature Range °C |
|---------------------|------|-------|------------------------|----------------------|
| 1-Chloronaphthalene | 0.98 | 1492 | -1.71×10^{-2} | 160 - 220 |
| Toluene | 0.99 | 346.7 | -1.59×10^{-2} | 60 - 120 |
| Benzene | 0.94 | 32.67 | -1.34×10^{-2} | 40 - 120 |
| Dichloromethane | 0.99 | 1.78 | -4.24×10^{-3} | 40 - 140 |
| Chloroform | 0.94 | 2.46 | -8.30×10^{-3} | 40 - 100 |

APPENDIX 9

PARAMETERS FOR POROPAK COLUMN

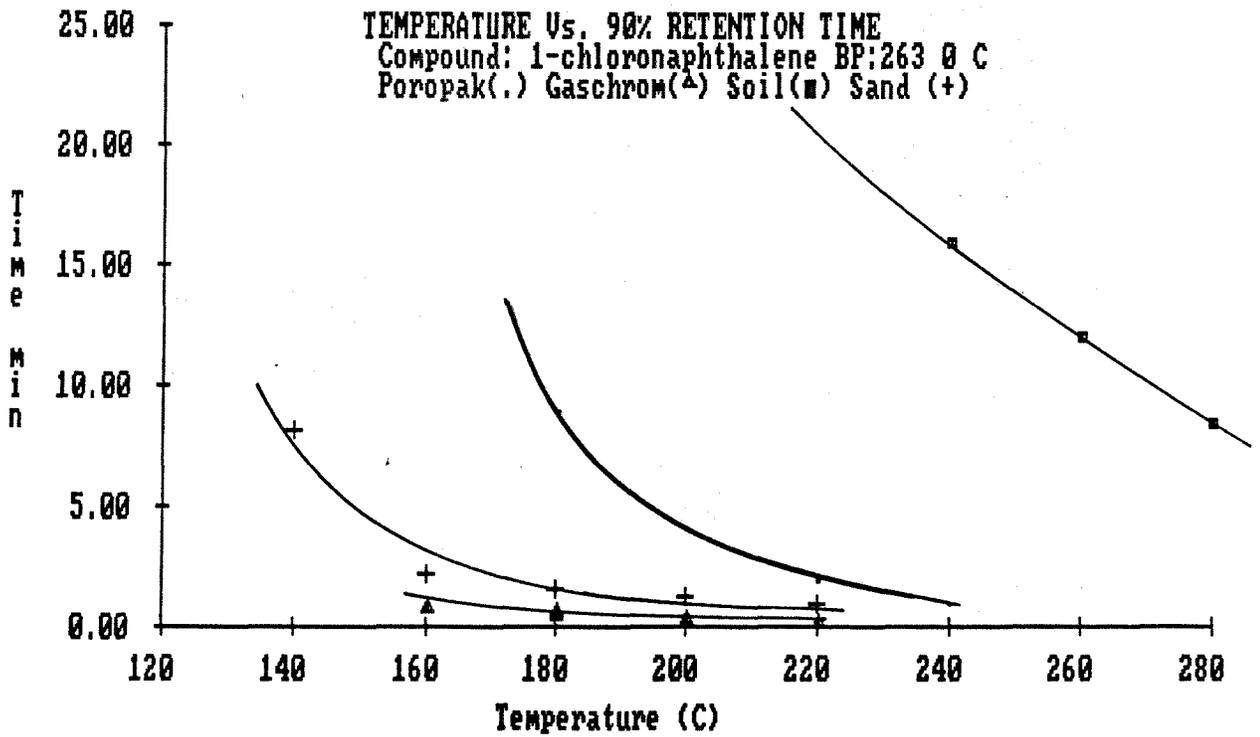
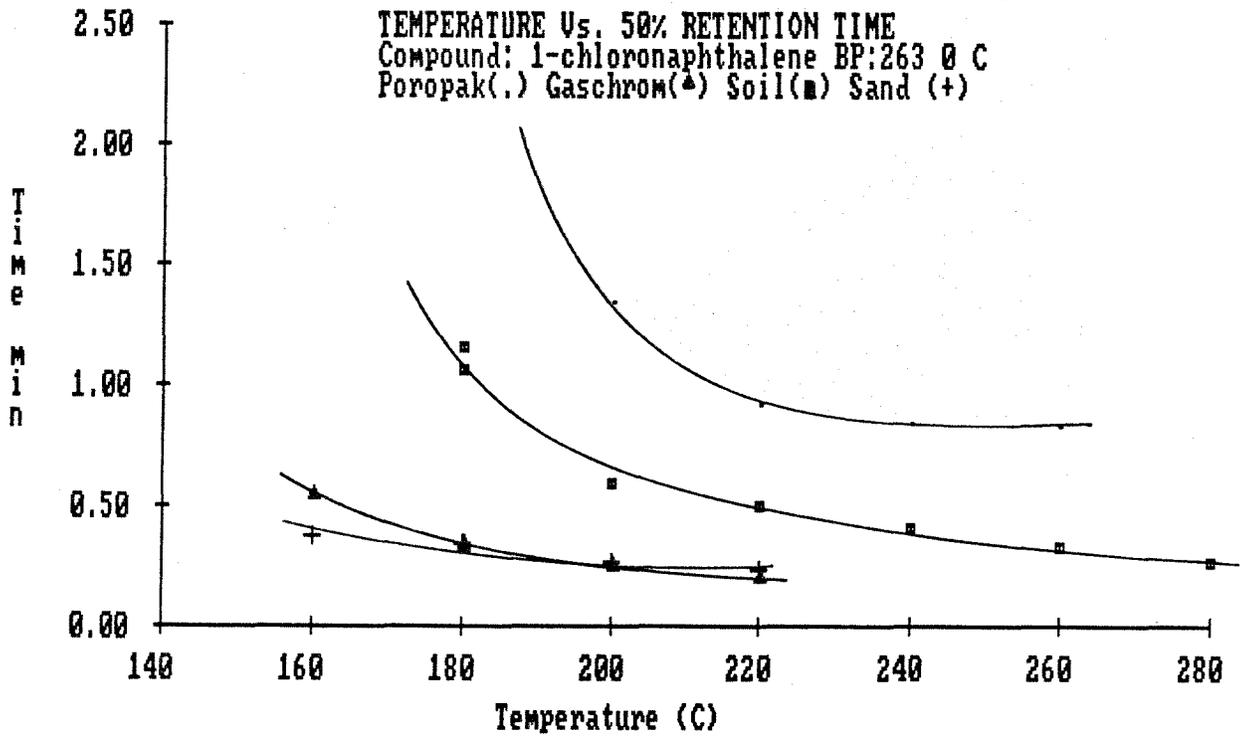
50% Compound Removal

| | R | A | -Bi | Temperature Range °C |
|---------------------|------|-------|------------------------|-------------------------|
| 1-Chloronaphthalene | 0.96 | 41.69 | -1.67×10^{-2} | 180 - 220 |
| Toluene | 0.97 | 14.24 | -2.24×10^{-2} | 120 - 180 |
| benzene | 0.99 | 10.89 | -2.58×10^{-2} | 80 - 140 |
| Dichloromethane | 0.99 | 27.0 | -2.39×10^{-2} | 40 - 100 |
| Chloroform | 0.99 | 28.4 | -2.18×10^{-2} | 80 - 160 |

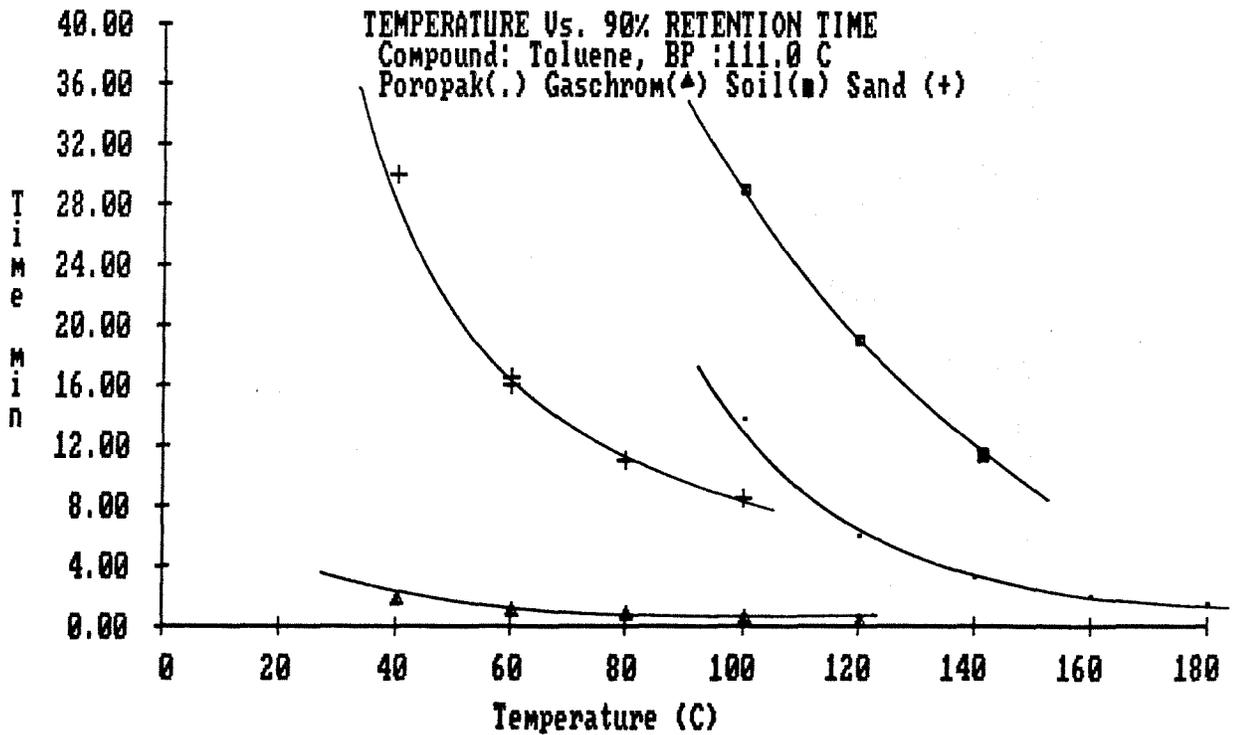
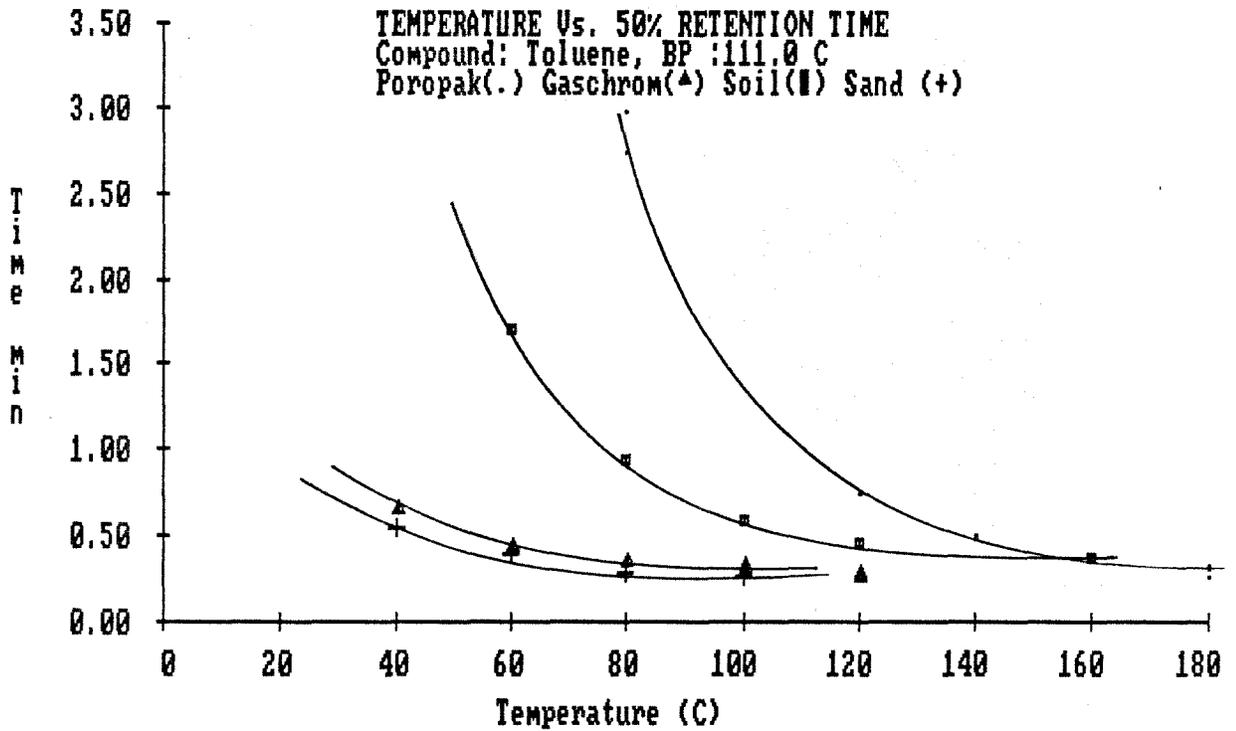
90% Compound Removal

| | R | A | -Bi | Temperature Range °C |
|---------------------|------|-------|------------------------|-------------------------|
| 1-Chloronaphthalene | 0.99 | 9881 | -3.89×10^{-2} | 180 - 220 |
| Toluene | 0.99 | 162.7 | -2.68×10^{-2} | 120 - 180 |
| Benzene | 0.99 | 170.2 | -3.29×10^{-2} | 80 - 140 |
| Dichloromethane | 0.99 | 164.6 | -3.10×10^{-2} | 40 - 100 |
| Chloroform | 0.99 | 56.42 | -2.06×10^{-2} | 80 - 160 |

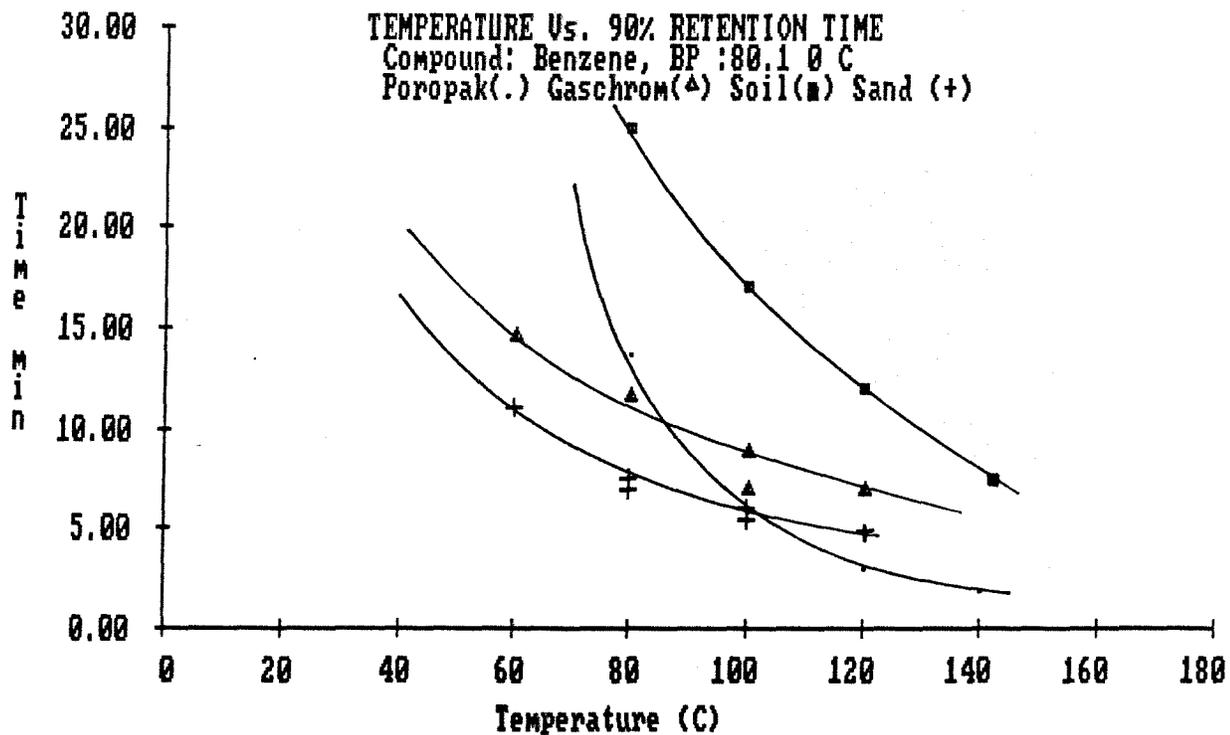
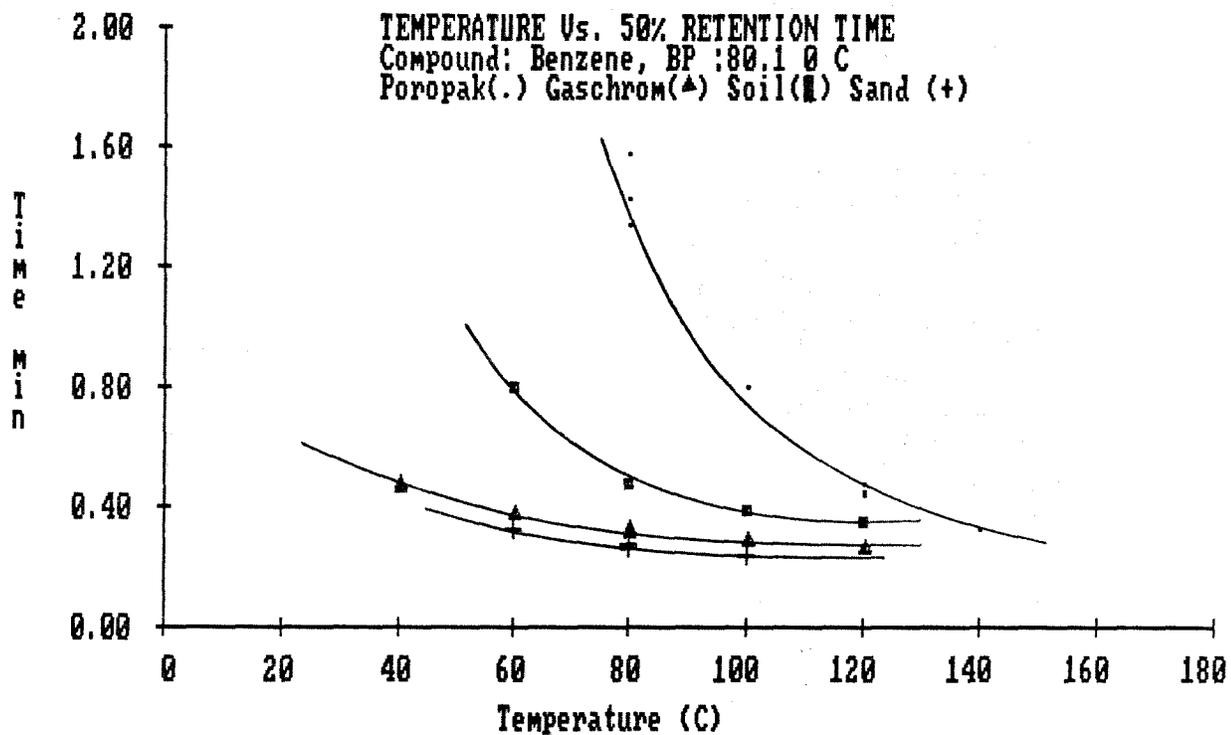
APPENDIX 10
1-chloronaphthalene



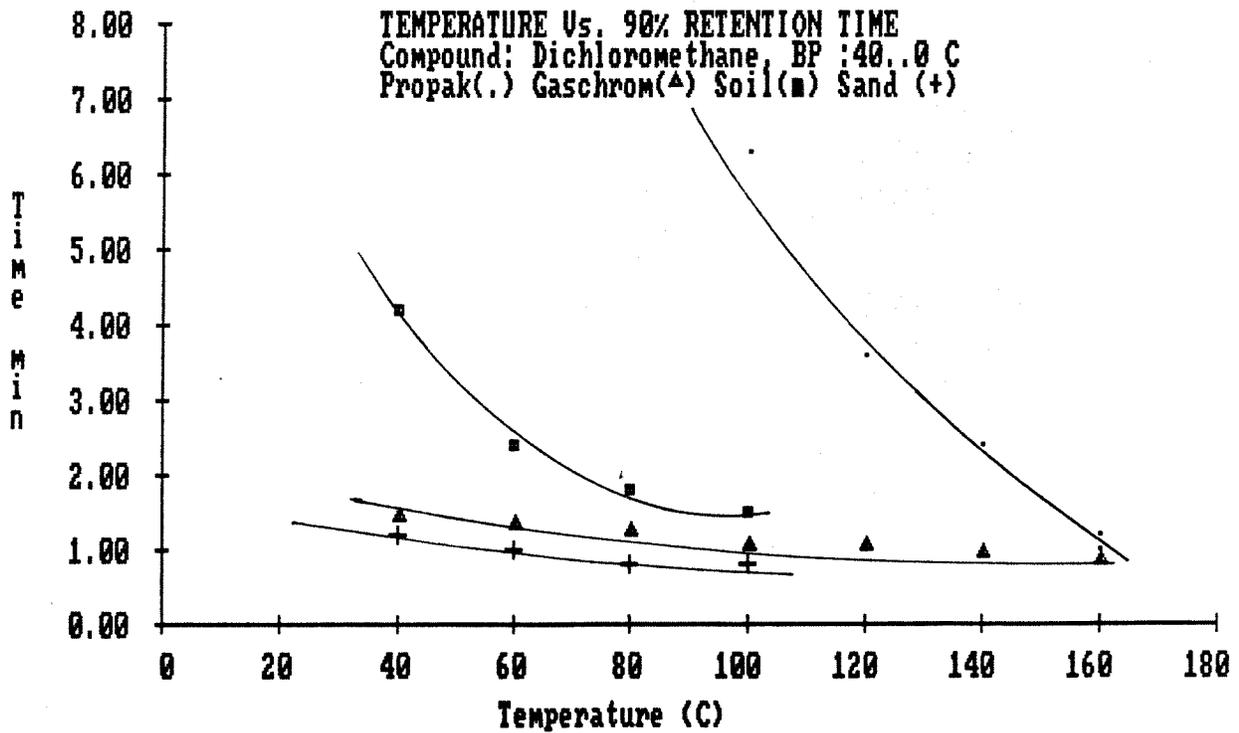
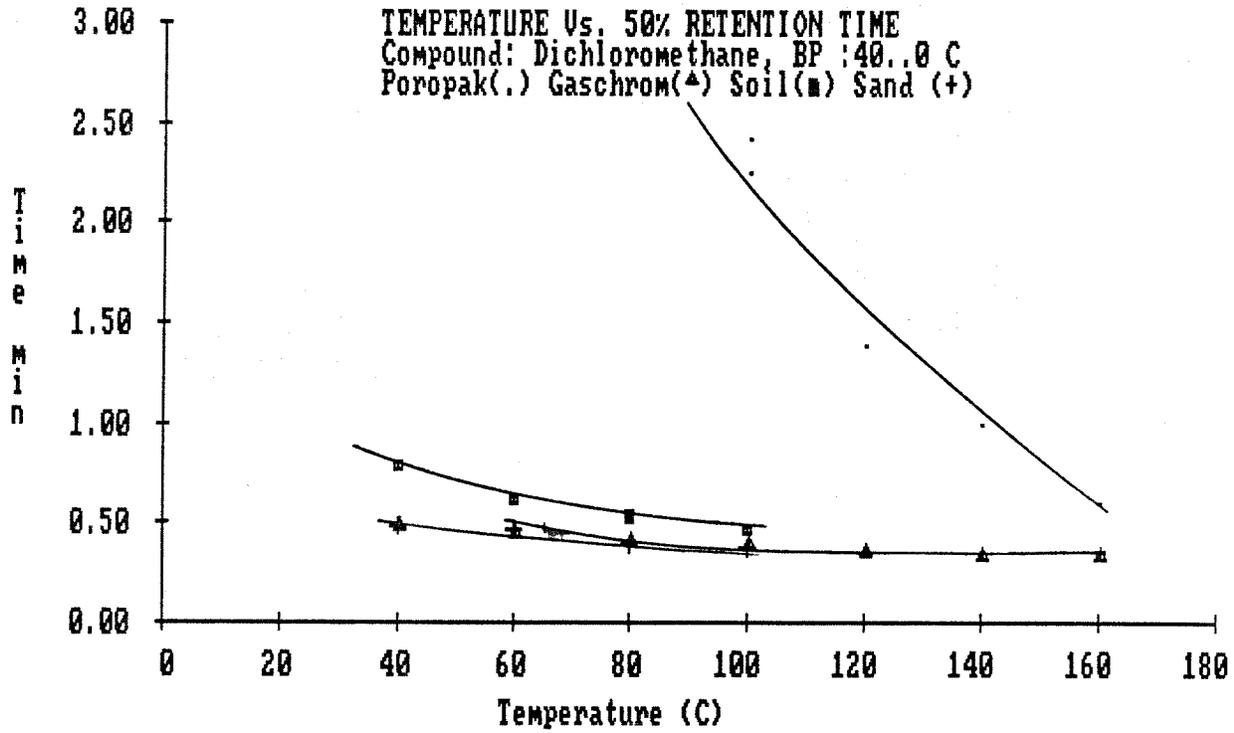
APPENDIX 11
Toluene



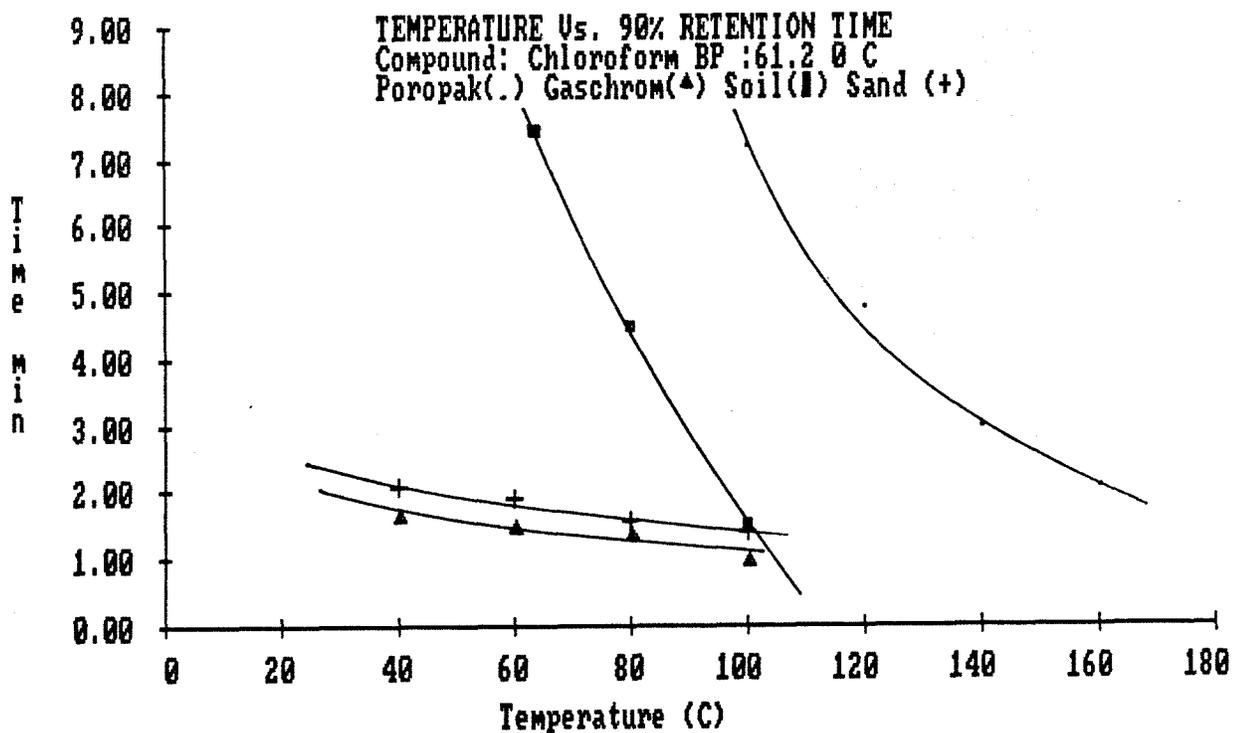
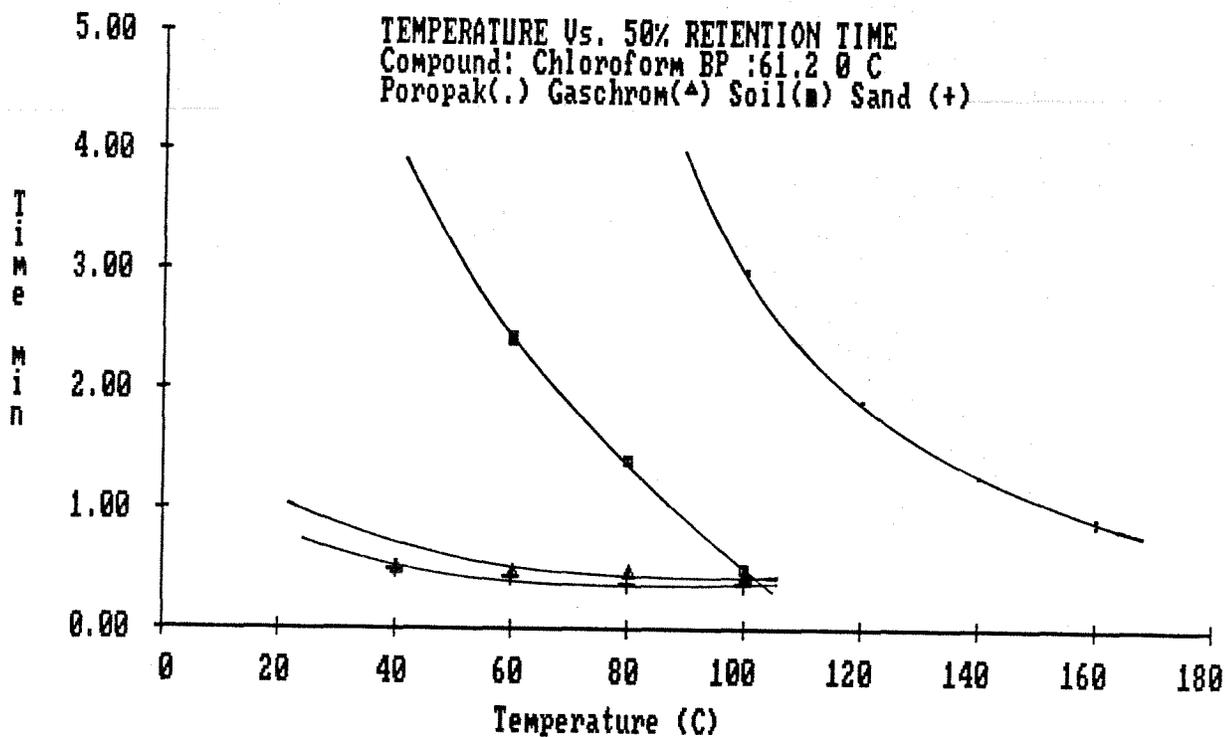
APPENDIX 12
Benzene



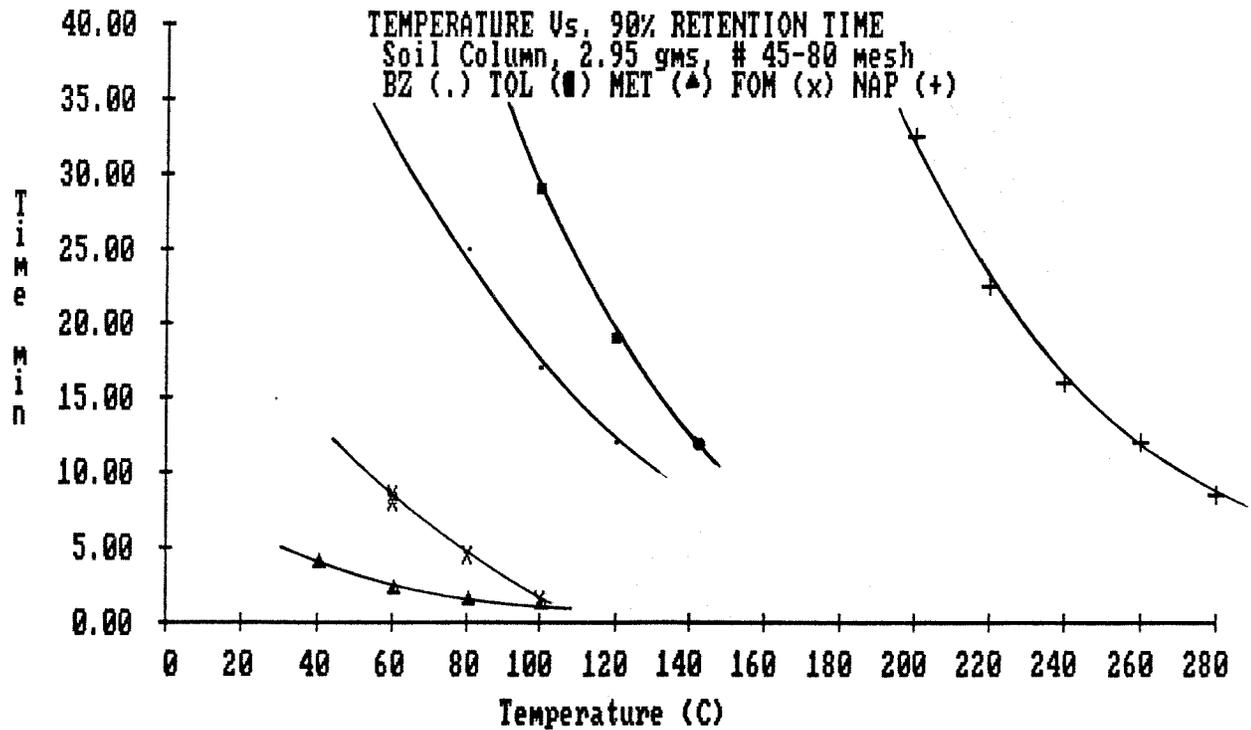
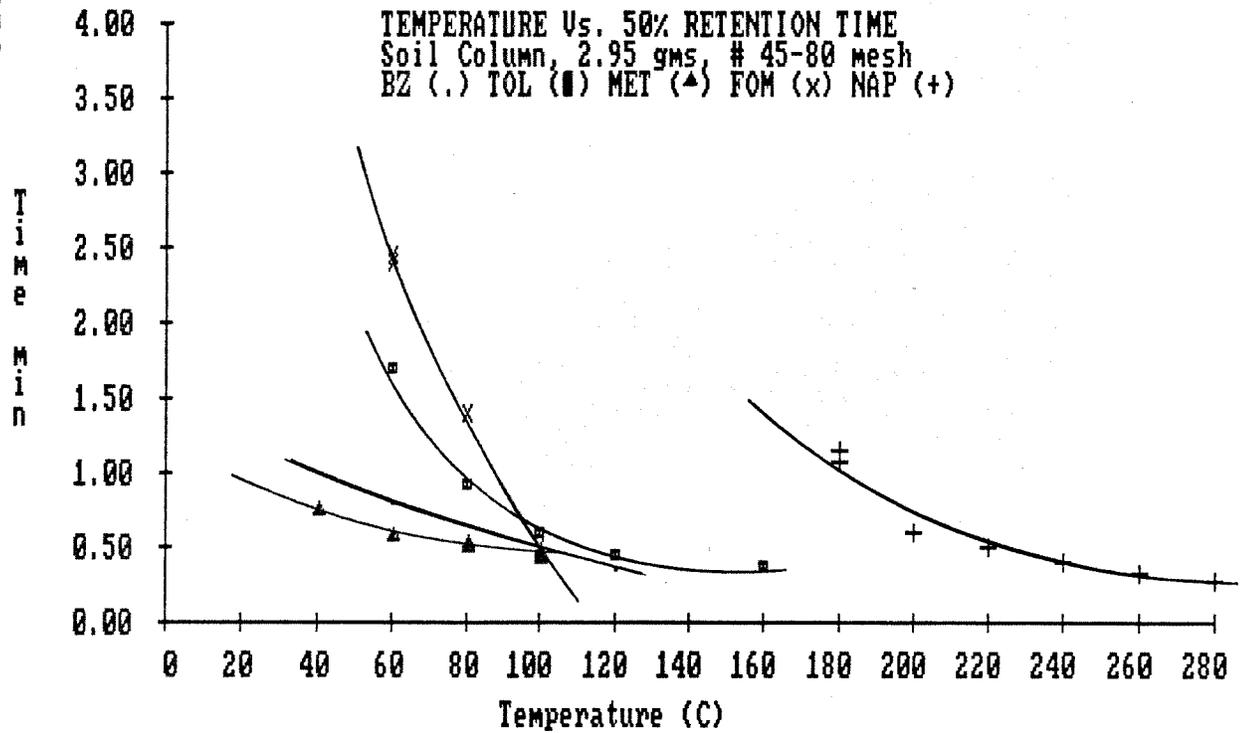
APPENDIX 13
Dichloromethane



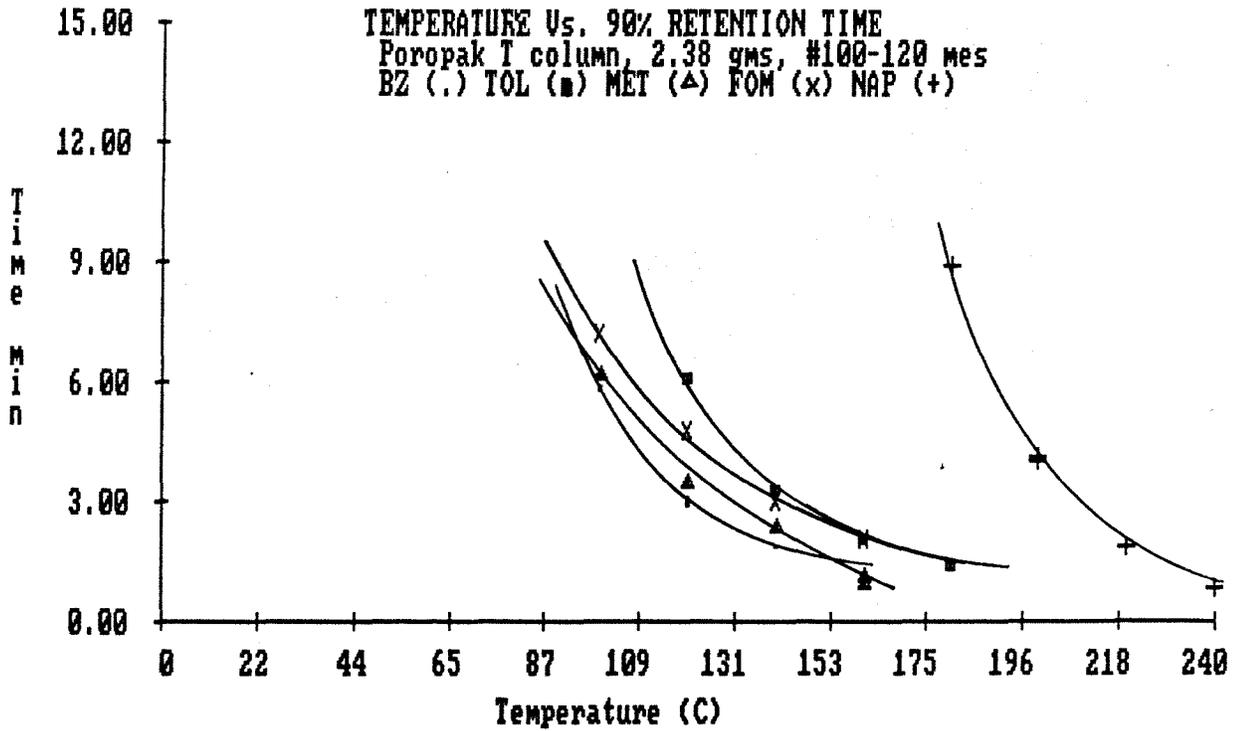
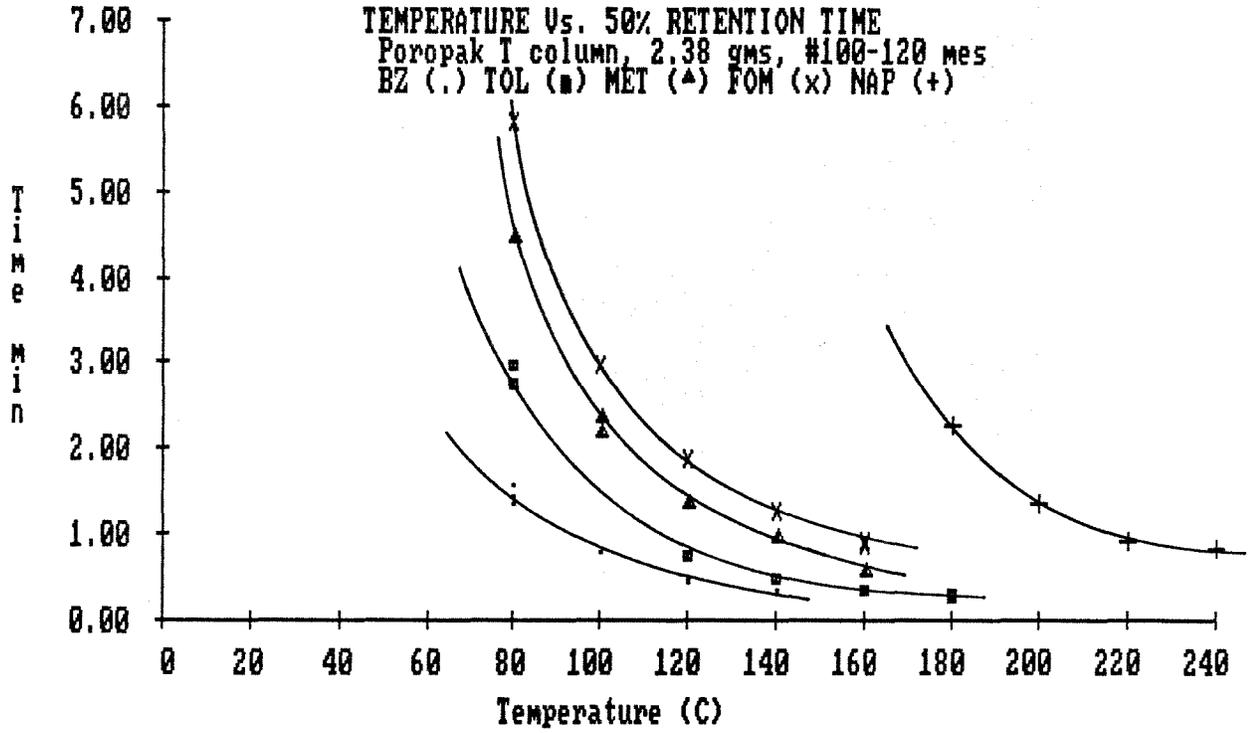
APPENDIX 14
Chloroform



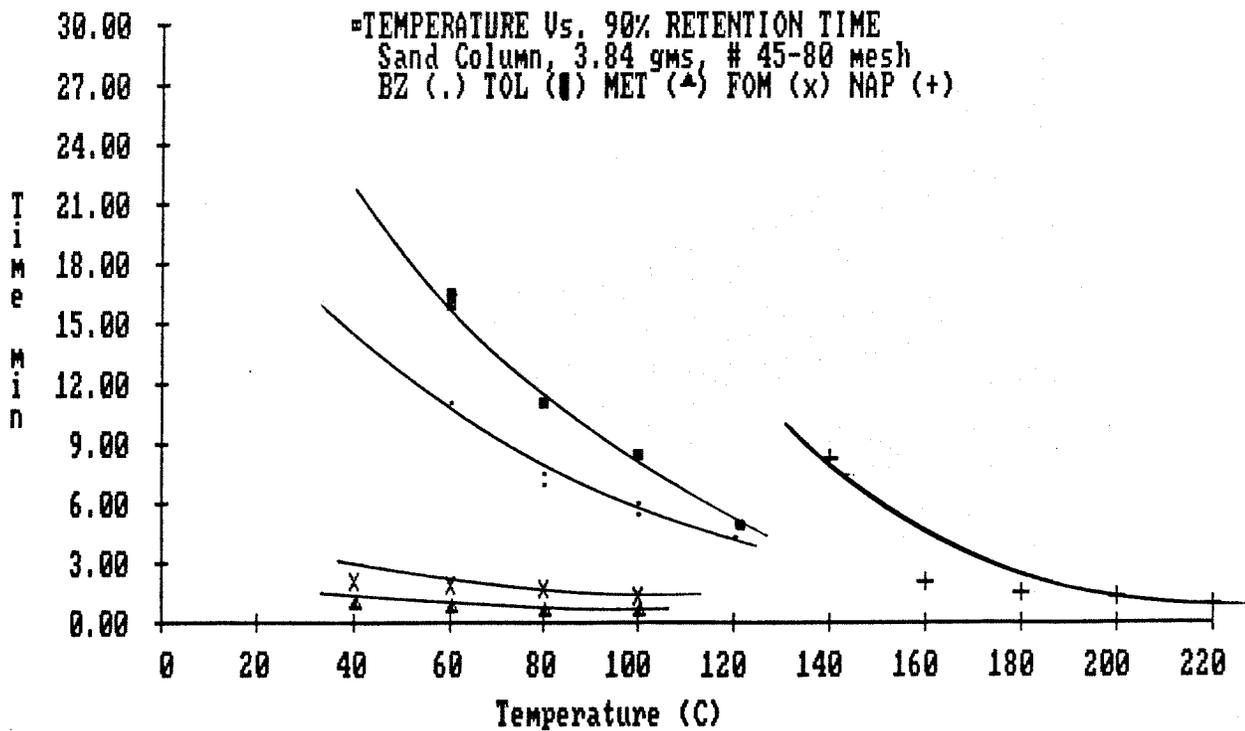
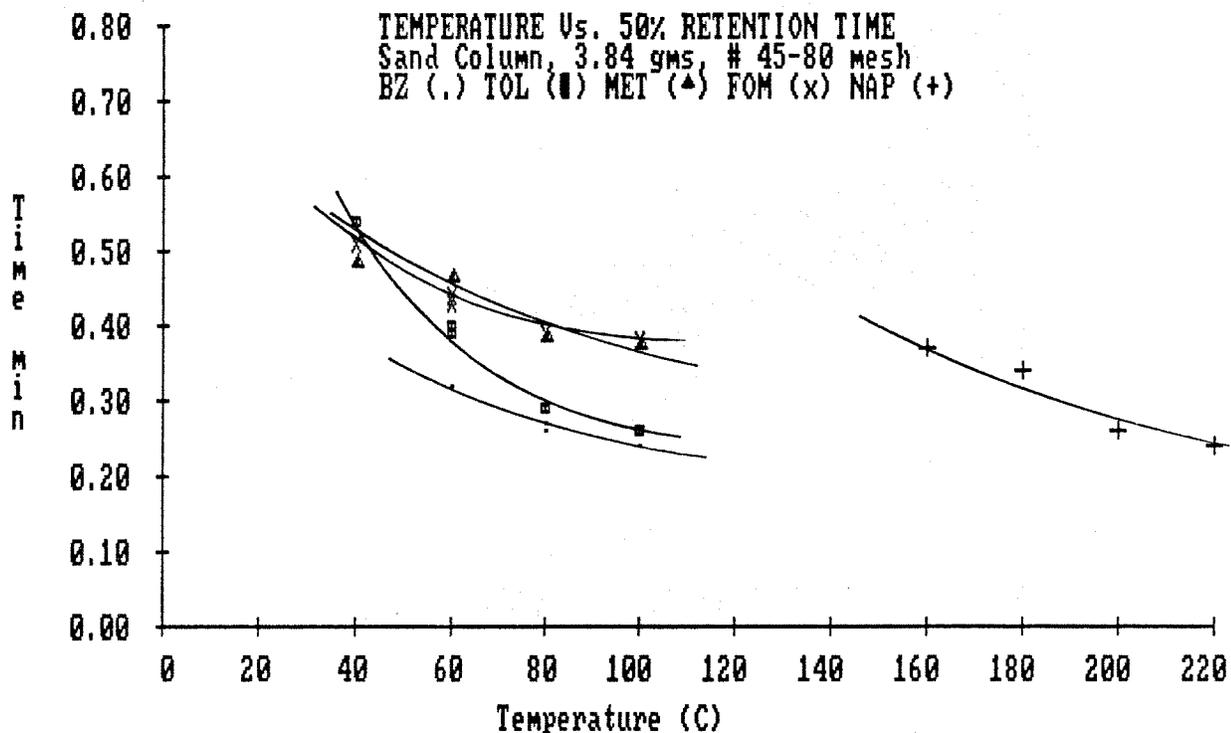
APPENDIX 15
Soil Column Result Summary



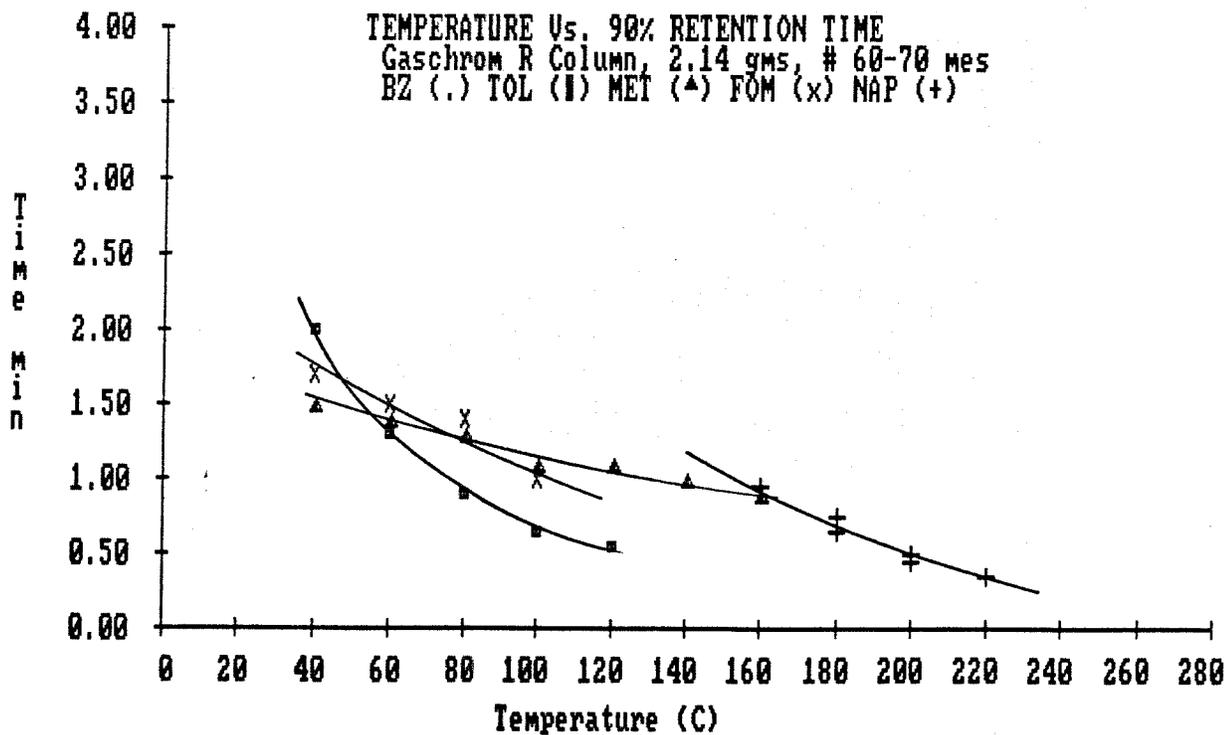
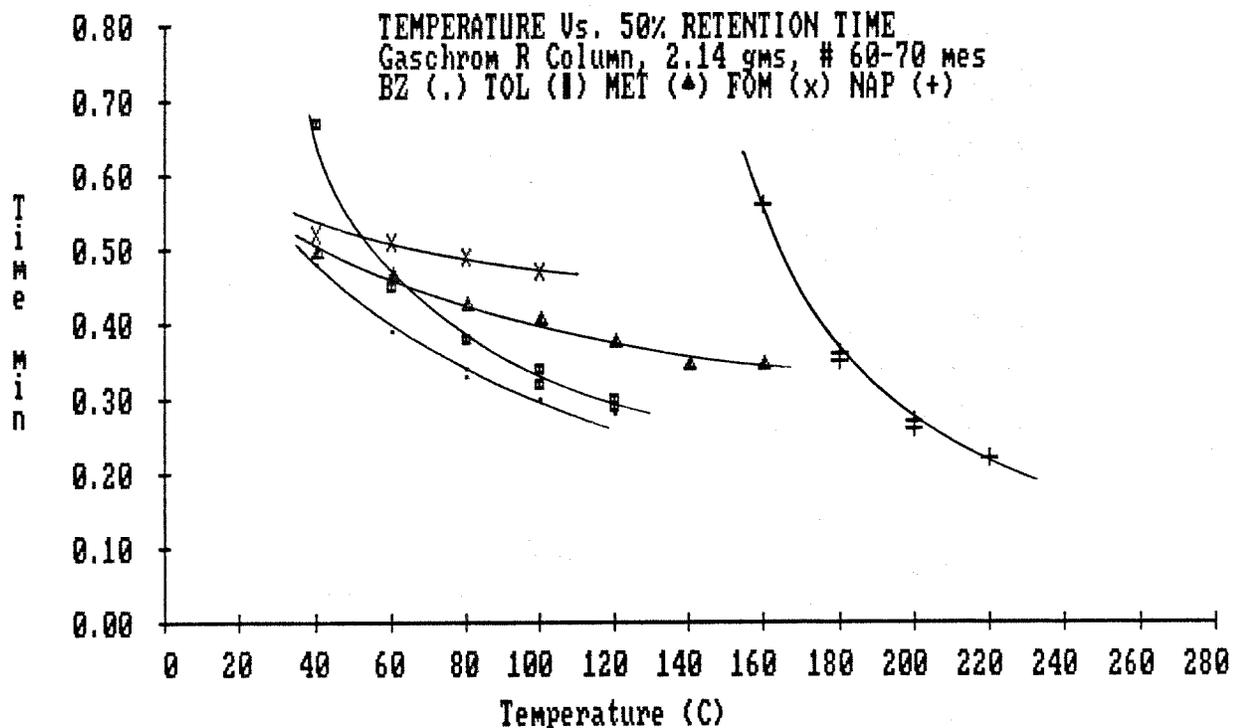
APPENDIX 16
 Poropak T column Result Summary



APPENDIX 17
Sand Column Result Summary



APPENDIX 18
 Gaschrom R Column Result Summary



APPENDIX 19

SOIL PARTICLE SIZE DISTRIBUTION

| Particle Diameter (inches) | Mesh Size | Mass Grams | % Mass Fraction |
|----------------------------------|--------------|---------------|--------------------|
| - | 7100 | 2000 | 6.9 |
| - | 100 | 2910 | 10.0 |
| 0.0086 | 70 | 480 | 1.7 |
| 0.0098 | 60 | 3200 | 11 |
| 0.0165 | 40 | 7060 | 24.3 |
| - | <40 | 13,400 | 46.1 |
| | | | ----- |
| | | | 100% |

Total Mass 29,050 grams

Bulk Density 1.0 gm/cc

Actual Density 0.8 gm/cc

(by water displacement)

APPENDIX 20

EMISSION SPECTROGRAPHIC ANALYSIS REPORT

| SAMPLE | MASS FRACTION |
|--------|---------------|
| Al | > 10% |
| B | 0.005 |
| Ba | 0.05 |
| Ca | 7.0 |
| Cr | 0.005 |
| Cu | 0.005 |
| Fe | 5.0 |
| K | 5.0 |
| Mg | 0.5 |
| Mn | 0.8 |
| X | 8.0 |
| Na | 5.0 |
| Ni | 0.005 |
| Si | > 10% |
| Sr | 0.005 |
| Ti | 0.5 |
| V | 0.005 |
| Zn | 0.05 |
| Zr | 0.005 |

Note : Results are semiquantitative. Accuracy and sensitivity are element and matrix dependent.

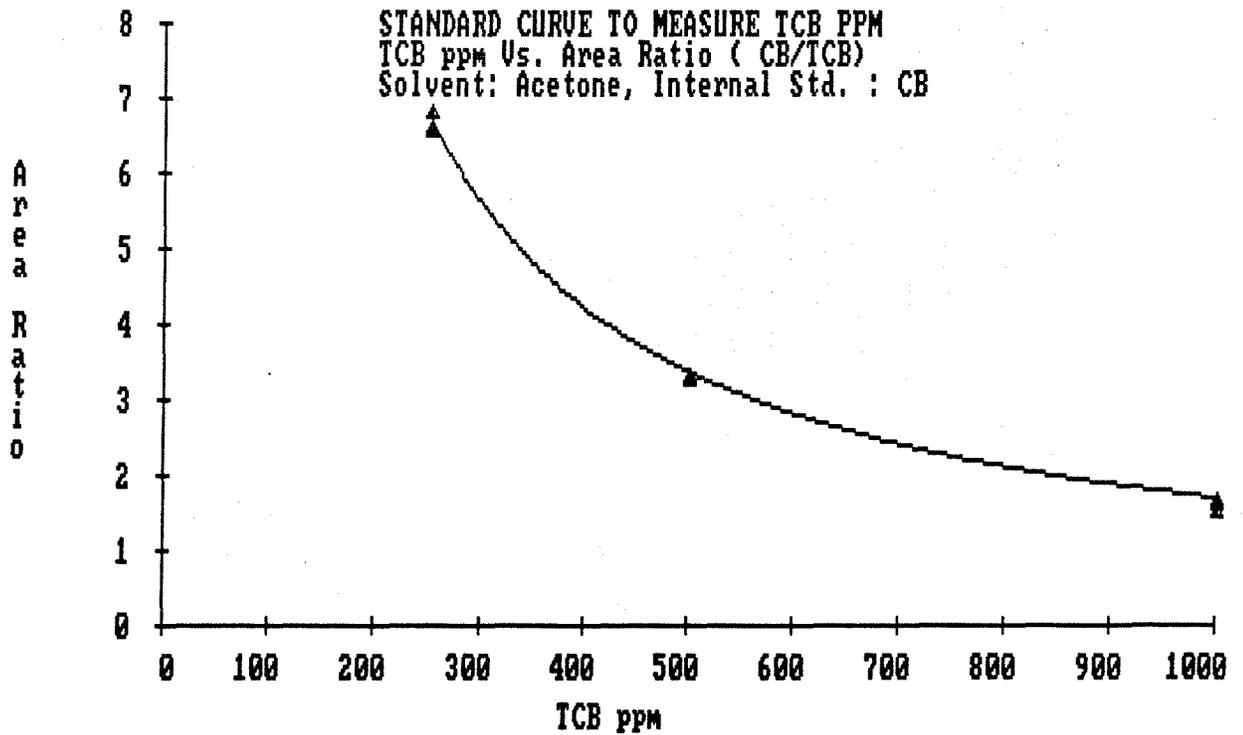
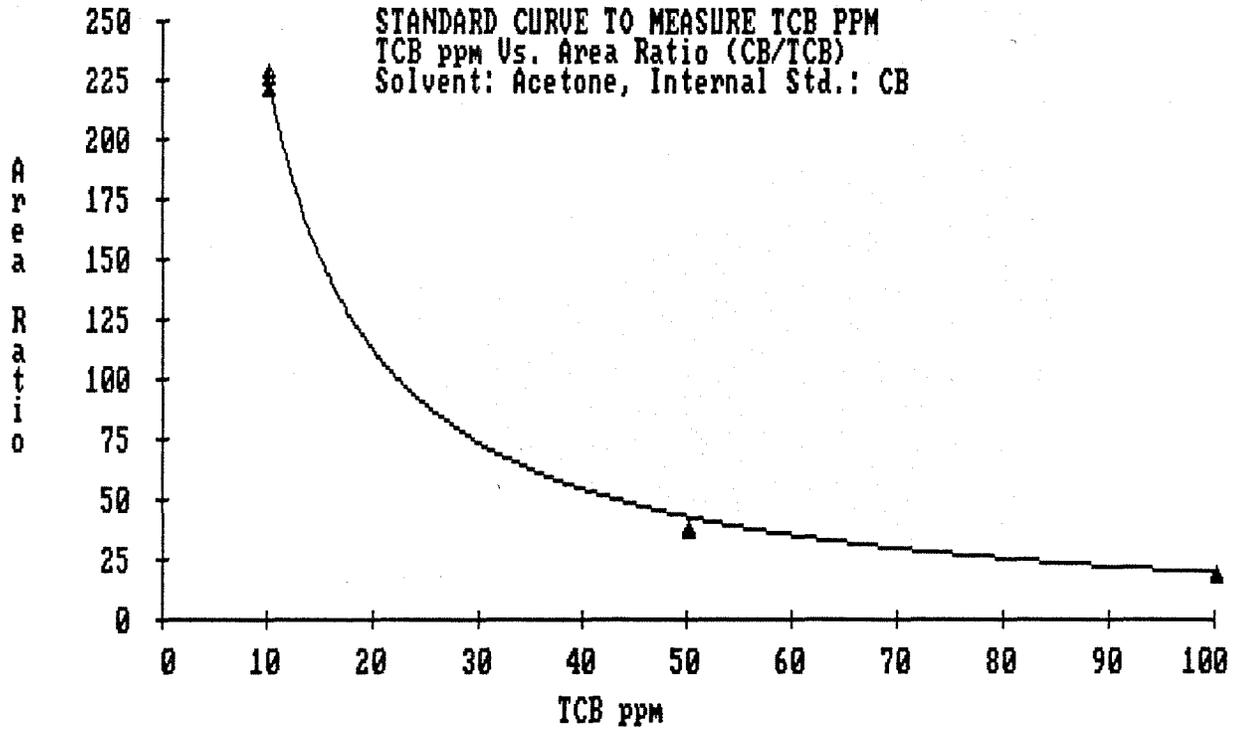
APPENDIX 21

X-RAY DIFFRACTION RESULTS

The x-ray diffraction analysis was made on the sample after grinding to less than 270 mesh. It showed the major compound is silicone dioxide with some feldspar, and possibly some iron oxides. The feldspars albite, andesine, anorthite, anorthoclase, and labradorite all have similar diffraction patterns and any one of them or all are possible in the soil sample. These are sodium aluminium silicates or calcium aluminium silicates (some of them are potassium rich) or the mixture of the two.

The Philips xx-ray diffraction unit used for the work is calibrated every three months with a silicone standard obtained from Philips. The particle size of the standard is 1 micron or less.

APPENDIX 22
STANDARD CURVE FOR TCB



APPENDIX 23
STANDARD CURVE FOR CNAP

