A COMPARISON OF TWO TECHNIQUES FOR THE DETECTION AND ANALYSIS OF LOW CONCENTRATIONS OF HAZARDOUS ORGANIC EMISSION FROM SOIL

by

Stephen A. Erickson

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Golden, Colorado
Date 4/17/89

Signed: Stephen A. Erickson
Stephen A. Erickson

Approved: Kent J. Voorhees
Dr. Kent J. Voorhees
Advisor

Golden, Colorado
Date 4/17/89

Dr. Stephen R. Daniel
Head of Department
Chemistry-Geochemistry
Department

ABSTRACT

Chemical spills on the land follow the second law of thermodynamics; they disperse through the environment to achieve maximum entropy. Chemical constituents rapidly become mobile through several mechanisms of environmental transport. A legitimate public concern is the water pollution problems that arise from the groundwater transport of hazardous materials.

This thesis presents the results of a study comparing two direct sampling methods for measuring volatile organic emission from organic solvent contaminated soil surfaces. The methods are compared on their ability to estimate the extent of groundwater contamination. Both methods quantify air emission of volatile organic compounds from contaminated soil surfaces. The first sampling method uses an Emission Isolation Flux Chamber (EIFC). The EIFC is a dynamic sampling method that encloses a defined surface to isolate the surface emission. Data from the EIFC sampling show that soil properties are an important factor in achieving reproducible emission measurements. The results of the EIFC data at two field sites are presented.

The second sampling method uses a Ferromagnetic Carbon Coated (FCC) wire sampler and is considered a static

sampling technique. The wire sampler is placed in a culture tube and buried 25 to 35 cm deep in the soil. After equilibrating with the volatile constituents in the soil for a specific period, the FCC wires are removed and analyzed.

The emission sampling techniques were tested at sites where large spills of trichloroethene, 1,1,1-trichloroethane (1,1,1-TCA), and tetrachloroethane (PCA) infiltrated through the soil and contaminated a groundwater source. Predictions on the severity of contamination can be made using the sampling methods if enough is known about the soil, the chemical spill, the geology, and the meteorological site conditions. Unfortunately, site conditions are often variable, so good comparisons of the concentrations of contaminant in groundwater to surface fluxes cannot always be made.

A mathematical expression was developed to relate the groundwater concentrations to the surface emission concentrations for both surface methods. Trichloroethene (TCE) and 1,1,1-trichloroethane emission was high in clay soils and steady state emission for the EIFC was difficult to achieve. Sandy soils exhibited low emission of these compounds and steady state emission for the EIFC was achieved almost instantaneously.

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INTRODUCTION

1.1 The Necessity for Surface Emission Methods

Studies of the ambient air next to the Love Canal chemical landfill site(1) and at the Capilto PCB dump site in New York State showed that the air contained significant concentrations of hazardous material. At the Hudson River Basin(2) concentrations of volatile PCB emission from uncapped landfills and dredge spoil sites were significant compared to transport of PCB via the aqueous route. Few studies have been undertaken to make semi-quantitative approximations on the extent of organic ground water contamination by measuring the emission of volatile organic compounds at the soil surface.

In 1984, Section 201 of the Resource, Conservation, and Recovery Act (RCRA) Amendments prohibited land disposal of certain halogenated and non-halogenated solvents(3). This stemmed from studies that demonstrated the large potential for volatile organic emission from hazardous waste treatment, storage and disposal facilities (TSDF). Subsequently, the Environmental Protection Agency (EPA) funded studies of methods that measure volatile organic emission from surface impoundments. Some of the common methods used are: measurement of ambient air concentrations at downwind locations and use of meteorological data along with dispersion modeling to estimate the emission rate; measurement of liquid phase concentrations and use of mass transfer theories and emission rate models to estimate the emission rate; and measurement of the emission using static or dynamic emission sampling techniques(4).

1.2 Mechanisms of Volatile Organic Transport

The transport mechanism of volatile organic contaminants through the soil is dependent on the following variables(5):

1. Vapor pressure of the contaminant.
2. Water solubility of the contaminant.
3. Henry's Law constant of the contaminant.
4. Concentration of the contaminant at the source.
5. Organic carbon distribution coefficient (K_{oc}) of the soil.
6. Dielectric constant of the soil.

Compounds with high vapor pressure will be present in the vapor phase in the soil's pore space. These compounds are generally water insoluble. The transport path of highly soluble compounds will be greatly aided by the infiltrating water. In comparison, compounds with low water solubility, such as trichloroethene (TCE), take longer to move down in the soil.

Two constants are vital in characterizing the transport process of volatile contaminants. The Henry's Law constant (K_h) is the ratio of the partial pressure in the vapor to the concentration in the liquid. Compounds with high vapor pressure and low water solubility favor the vapor phase. The soil organic carbon distribution coefficient (K_{oc}) relates the partitioning between the air and total organic carbon present. It reflects the potential for an organic compound to exsolve out of solution onto soil organic material.

The dielectric constant relates the force of attraction between two charged particles. Water, with its large dielectric constant, will cause clay soils to expand. This, in turn, reduces the soils' porosity. TCE, which has a small dielectric constant, shrinks clay soils and increases the soils' porosity(6). This increases the rate at which TCE vapor migrates from the aquifer to the soil surface.

<u>1.2.1 Properties of the Alluvium.</u> The air-filled porosity of a soil is defined as the ratio of the volume of air in the pore spaces of a soil to the total volume occupied by the soil. The volumetric water content is the ratio of the volume of water in the soil to the total volume occupied by the soil. Sandy soils tend to have a smaller volumetric water content than clay soils. As the volumetric

water content increases, the air filled porosity of a soil decreases. Thus, the rate of volatile organic transport upward through soils decreases as the water content increases.

Changes in soil temperatures also affect the transport of volatiles. Because of the inverse relationship between gas volume and temperature, volatiles tend to move from warm areas to cooler areas. On warm day, volatiles move from the warm upper soil boundary layer to the cool lower boundary layer. By the same reasoning, on cool days or at night when the upper soil boundary layer becomes cooler than the lower boundary layer, vapors may migrate vertically towards the top soil.

Electrolytes are more concentrated in the top few inches of most soils, primarily due to evaporation. Electrolytes can lower the partial pressure of the water present in the soil pores. This mineral fraction will be a strong adsorbent of organic vapors at lower water vapor pressures and may restrict volatile migration to the soil surface.

<u>1.2.2 Organic Phases in the Soil.</u> After a water-immiscible organic compound encounters the soil, it may undergo several phase changes. The phases that will be present are dependent on the properties and condition of the

soil. The phases are: immiscible liquid, dissolved component of the soil-water solution, and vapor. Adsorbed to stationary particles, immiscible organic compounds become immobilized. In nonadsorbing media, immiscible organic compounds can move freely. The rate and path of transport is dependent on how permeable the soil is to water and to the immiscible liquid. The transport rate is also dependent on the amount of water and immiscible liquid.

As immiscible liquids infiltrate through pore voids in soil, air voids are displaced while water voids are largely unaffected. Depending on the type of soil and immiscible organic liquid, immiscible liquids leave behind a residual immobilized concentration of insoluble organic material in about 5 to 20 percent of the void pore space(7). If the total volume of the soil's pore space between the surface and the groundwater aquifer is less than the volume of immiscible liquid that infiltrates the soil, it is probable that groundwater contamination will follow. This effect may be somewhat diminished by immiscible liquids with high vapor pressures because a small fraction of these liquids will evaporate when exposed to soil air and then migrate to the soil surface by vapor diffusion.

<u>1.2.3 Movement of Immiscible liquids.</u> Immiscible liquids migrate both laterally and vertically after

introduction into the soil. The soil's heterogeneity, permeability, and moisture content determine the transport path(8). Vertical transport is the favored path for both homogeneous fine-textured and coarse-textured soil. A cone shaped plume will be developed for both soil textures(9). The vertical extent of the plume will be greatest for the coarse-textured soils. As the soil's permeability decreases or geologic barriers are encountered, lateral flow may become the favored flow path.

1.2.4 The Soil's Retention of Contaminants. The volume of contaminant that reaches the groundwater after a spill can be estimated. After a contaminant infiltrates into the soil, as much as 20 percent of the total void pore space in the soil can become occupied(10). Trichloroethene, a volatile compound of low viscosity compound, could occupy a total void pore space of only about 5 to 10 percent because of evaporation and the ease of infiltration for low viscosity compounds. A rough calculation can be made of the spatial volume occupied by a spill by using the following equation(11)

$$V_s = V_o / p\ S_o - f(V_o)$$

where

V_s = Soil volume occupied by immiscible liquid.

V_o = Volume of spill that penetrates the soil.

p = Total soil porosity.

S_o = Total residual void fraction.

$f(V_o)$= The fraction of spill that evaporates.

This equation can be used to make theoretical estimates of the volume of immiscible fluid that would be required to infiltrate to a certain depth in the soil. Without any other external factors such as evaporation, a sample calculation for the volume of TCE required to infiltrate into the water aquifer 30 meters below the ground surface is given below.

For simplicity, assume a cylindrical soil volume above the groundwater aquifer that is 30 meters deep and has a surface spill area of 10 m^2. The volume of soil occupied is given by:

$$V_v = AL = (10\ m^2)(30\ m) = 300\ m^3$$

The volume of TCE required to fill the residual pore spaces is:

$$V_o = V_s\ p\ S_o$$

$$V_o = (300\ m^3)(.4)(.1) = 12\ m^3 \text{ or } 3170 \text{ gallons.}$$

From this calculation, a spill of TCE in excess of 3170 gallons would infiltrate into a ground water aquifer to a depth of 30 meters below the ground surface.

As dissolved organic chemicals move through the soil pores, they are continually being adsorbed and desorbed. This is termed reversible adsorption(10). The extent of reversible adsorption is dependent on the stationary soil organic matter and the number of clay mineral surfaces.

Chemicals that have a density larger than water are termed "chemicals that sink." The two chemicals, TCE (d = 1.47 g/ml) and 1,1,1-trichloroethane (d = 1.34 g/ml), sink when they reach the upper aquifer boundary. When the chemicals sink and are immiscible, they will be found in the lower phase of the water/immiscible organic boundary. Immiscible organic chemicals, by definition, have low water solubility. 1,1,1-trichloroethane (1,1,1-TCA) has 0.44 percent by weight solubility in water and TCE has a low 0.11 percent by weight solubility in water(12). For this reason, it does not require a significant relative volume of these immiscible chemicals to saturate the groundwater aquifer.

<u>1.2.5 Diffusion of Vapor Through the Soil.</u> Once the chemical is dissolved in the groundwater, it becomes mobile with the groundwater movement. The vapor concentration of the organic above the moving water flow is largely

controlled by Henry's Law. The vapor that diffuses vertically to the soil surface is a function of the soil's resistance to vapor flow, of the amount that is redissolved in the moisture of the soil, and by the amount adsorbed and/or degraded in the soil. A mathematical description of the transport process combines a mass balance equation with the Fick's law equation to describe the vapor movement(8).

$$C_T = p_b\ C_a + t\ C_l + a\ C_v$$

where

C_T (ug/cm^{-3}) is total concentration in the soil

p_b (g cm^{-3}) is soil dry bulk density

C_a (ug g^{-1}) is the mass adsorbed per mass of soil

t (cm^3 cm^{-3}) is soil volumetric water content

C_l (ug cm^{-3}) is the mass dissolved per volume of solution

a (cm^3 cm^{-3}) is soil volumetric air content

C_v (ug cm^{-3}) is the mass in vapor per volume of soil air

The vapor phase concentrations can be used to make quantitative estimates of the concentrations of the contaminant in the groundwater aquifer. Likewise, the concentrations of contaminant found in the groundwater aquifer can be used to estimate the extent of surface flux given the necessary geologic and meteorological site conditions.

1.3 Industrial Sampling Site History

1.3.1 Site Characteristics

Emission data were collected from two sites to test several volatile organic emission sampling methods. These locations were previously characterized to determine their chemical and geological nature. The sampling sites were located at the base of the Front Range. The location was on the extreme West Flank of the Denver Basin and located on the Pennsylvanian-age Fountain Formation. The two sites selected were both downgradient from known contamination sources. Site A was about 500 yards downgradient from two unlined ponds. Site B was downgradient from a PVC-lined evaporation pond and upgradient from paint and chemical storage facilities. Unknown quantities of liquid chemical waste had been disposed in the ponds. Records indicating the exact amount of liquid solvents disposed in these ponds are nonexistent. It is known that the dumping began sometime in the late Fifties and continued through the Seventies. The disposal process at the two sites resulted in significant groundwater contamination.

Alluvial and bedrock wells were installed in the years between 1985 and 1987 to investigate the extent of groundwater contamination. The depth of the alluvial water at Site A is 30 feet and at Site B is 27 feet. Bedrock wells at Site A range from 104 to 204 feet deep and Site B from 103 to 327 feet deep. The surficial geology consists of reddish-brown sandstone with minor shale Quaternary alluvium 15 to 30 feet thick. This is mostly continuous over large areas of the valley bottom. Ridges and spires of the Fountain Formation interrupt the alluvial water in some areas.

Groundwater was present in the alluvial overburden. Drilling in the area showed that the groundwater was more often present in the valley bottoms than in the inter-valley areas. This phenomenon is probably due to thicker overburden near the center of the valleys. The well data collected indicate the soil permeability of the overburden is higher than that of the Fountain Formation(10).

The alluvial and bedrock wells at the two selected sampling Sites have been monitored for volatile contaminants since 1985. Well data show that trichloroethene was the only appreciable volatile contaminant at Site A (see Table I.). The average TCE concentration in the wells at Site A between 1985 and 1988 was 4550 ug/L in the alluvium. The average TCE concentrations in the shallow, medium, and deep bedrock wells were 16983 ug/L, 97 ug/L, and 119 ug/L, respectively. 1,1,1-Trichloroethane was the only appreciable volatile contaminant in the groundwater at Site B (see Table II.). The average 1,1,1-TCA concentrations in the wells at Site B were 3367 ug/L in the alluvium, 443 ug/L in the shallow bedrock, and below detection limits in the deep bedrock. Higher concentrations of contaminant were found in the wells nearest to the dumping ponds. Contaminant concentrations in the alluvial aquifer are diluted downgradient from the contaminated ponds. Lower concentration of contaminant in the downgradient wells showed this dilution affect. Groundwater contamination upgradient from the dumping ponds was negligible.

Table I. TCE Concentrations in Well Water at Site A

Well Type	Date	Value ug/L
Alluvial	11/15/85	2600
Alluvial	03/04/86	7000
Alluvial	07/24/86	4750
Alluvial	12/16/87	4080
Alluvial	09/15/88	4320
Shallow Bedrock	07/25/86	15600
Shallow Bedrock	11/19/86	197
Shallow Bedrock	12/08/87	18200
Shallow Bedrock	12/17/87	31700
Shallow Bedrock	01/20/88	19600
Shallow Bedrock	09/15/88	16600
Medium Bedrock	12/07/87	153
Medium Bedrock	01/20/88	102
Medium Bedrock	09/15/88	36
Deep Bedrock	12/08/87	156
Deep Bedrock	01/21/88	182
Deep Bedrock	09/15/88	19

Table II. 1,1,1-TCA Concentrations in Well Water at Site B

Well Type	Date	Value ug/L
Alluvial	03/04/87	6700
Alluvial	05/05/87	4700
Alluvial	09/19/87	1400
Alluvial	12/02/87	1600
Alluvial	02/21/88	3300
Alluvial	04/13/88	2500
Shallow Bedrock	03/02/87	210
Shallow Bedrock	05/13/87	420
Shallow Bedrock	09/19/87	590
Shallow Bedrock	12/02/87	600
Shallow Bedrock	02/22/88	470
Shallow Bedrock	04/13/88	370
Deep Bedrock	03/03/87	< 5.0
Deep Bedrock	05/15/87	< 5.0
Deep Bedrock	09/20/87	< 5.0
Deep Bedrock	12/03/87	< 5.0
Deep Bedrock	02/22/88	< 5.0
Deep Bedrock	04/15/88	< 5.0

1.3.2 Site Geology Investigations at Site A have shown that the groundwater flow in the Fountain Formation is not enhanced due to fracturing(10). Textural and matrix permeability are the primary geologic factors affecting the groundwater flow velocities and directions.

The Fountain Formation is made up of approximately 62 percent arkosic sandstones, 21 percent conglomerates, 13 percent sandy and silty claystones and 4 percent feldspathic sandstones. These particles are poorly sorted and have a large variance in grain size. The claystones are often pebble size. The sandstones and conglomerates are more finely grained. Gamma-gamma neutron data and geophysical log data were used to determine the porosity. Slug and core test were used to determine hydraulic conductivity (groundwater velocity). Low porosities and low hydraulic conductivities were measured in the Fountain Formation. This is probably caused by the high percentage of silt and clay in the formation's matrix and pore spaces. Open fractures and poor sorting of the conglomerate also leads to low porosities and low hydraulic conductivities. The percent pore space at Site A between 181 and 201 feet below the land surface is in the range of 8 percent to 27 percent. Porosity data indicate that the soil's porosity decreases with depth. The measured hydraulic conductivity at Site A is 0.023 feet/day for the saturated alluvium.

The monitoring wells at Site A have maximum yields of about one to two gallons/minute. The low porosity and low hydraulic conductivity are probably the reason for the low well output.

The dumping ponds acted as a contamination recharge area for the groundwater (see Figure 1.1). This was due to the groundwater elevations, the underlying alluvium, and the shallow bedrock. The bedrock might have been recharged directly by leakage from the ponds or indirectly from the saturated alluvium underlying the ponds.

At Site A groundwater levels in the alluvial and bedrock wells are below the alluvium/bedrock contact. The alluvium in this area is saturated and leads to unconfined water flow conditions.

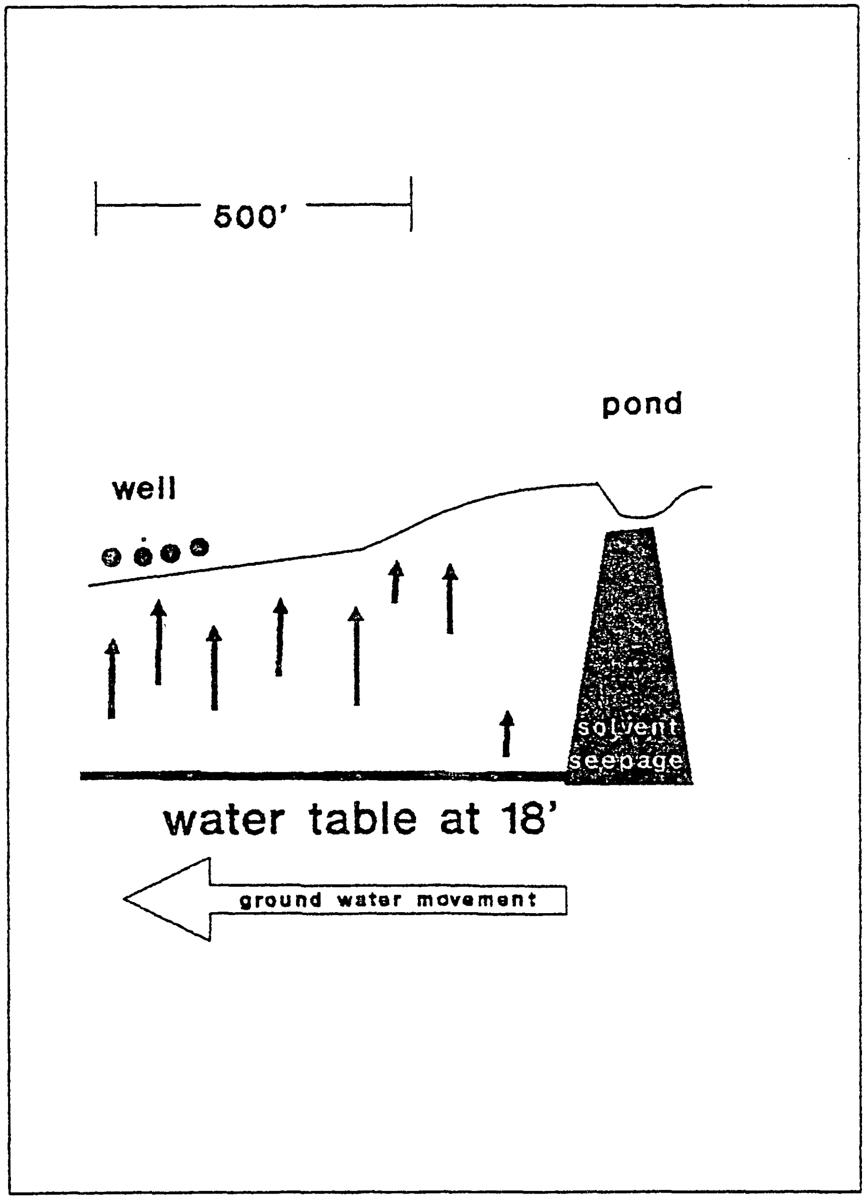

Figure 1.1 Source of Contamination Recharge.

1.3.3 Site Contamination Movement. Analytical data collected by other workers from 1985 to 1986 show that TCE and cis-1,2-dichloroethene are the only volatile organic compounds consistently collected. TCE accounts for about 95 percent by mass of the volatile organic compounds present in the groundwater at Site A. The presence of small amounts of cis-1,2-dichloroethene in the water is probably the result of anaerobic biodegradation of TCE. There is no record that cis-1,2-dichloroethene has ever been used at the industrial area.

Data collected by other workers from 1985 to 1987 show that TCE primarily migrates through the alluvium. Low horizontal flow velocities and high concentrations of TCE in the alluvium are found at Site A. This shows TCE migration is through the alluvium rather than through the underlying bedrock. Infiltration of TCE from the alluvium into the shallow bedrock gives rise to the high concentrations of TCE found in the bedrock.

1.4 Emission Monitoring Methods

Two methods for assessing soil gas emission due to a contaminated groundwater aquifer include flux chamber measurements and measurements with passive ferromagnetic carbon coated (FCC) wire sorbent samplers. Both techniques adequately provide qualitative information for the type of contaminant present. However, the techniques do not provide the same quantitative data due to their different design. The flux chamber measures the rate of emission over a short, specific time. The passive samplers measure the integrative emission from the soil for a greater length of time.

Both techniques are dependent on the movement of volatilized species through the underlying soil. The overall soil characteristics (moisture, total organic carbon, etc.) may affect the transport of the volatile species more strongly for the flux chamber than for the FCC wire samplers.

1.4.1 Surface Flux Chamber. Previous workers have conducted studies using an emission isolation flux chamber (EIFC) to investigate volatile hazardous emission from land treatment facilities(13). The chamber encloses a defined head space above a known soil surface area to allow the collection and concentration of volatile organics emitted from a contaminated surface. A purge gas of high purity air (Ultra-pure Carrier grade, Air Products Inc.) is introduced into the chamber at a known controlled rate to sweep volatile contaminants from the chamber for collection and concentration by carbon sorbent tubes. A schematic of the flux chamber developed by the Radian Corporation is shown in Figure 1.2(14).

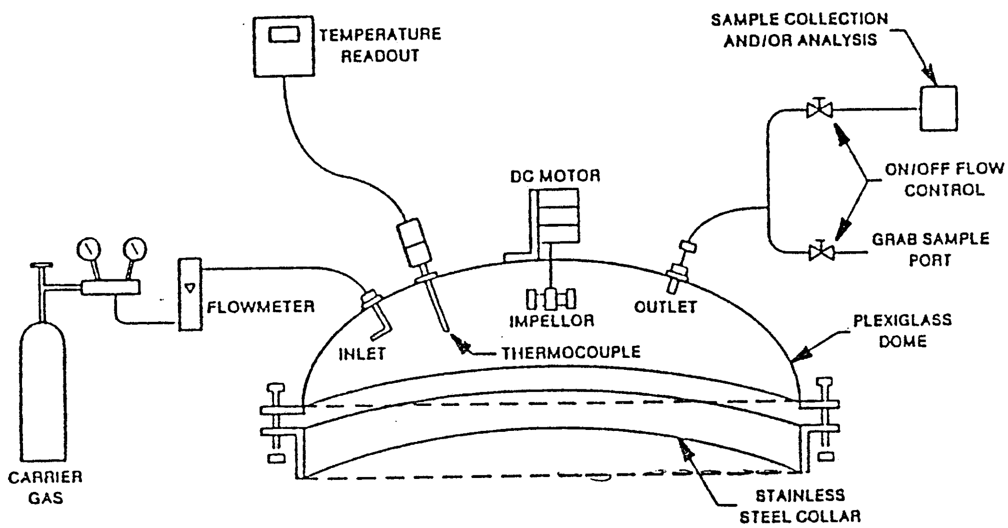

Figure 1.2 Radian Emission Isolation Flux Chamber.

The EIFC collects gaseous emission at the surface level and is suited for most soil types. The sampling time is adjusted to provide an adequate concentration of volatile species for analysis. The Radian Corporation found that recoveries ranging from 88.5 to 124 percent could be achieved with the EIFC(15) for a standard containing 36 volatile compounds introduced into the inlet of the chamber. Accuracies relative to the standards for their flux chamber data were better than +/- 10 percent and analytical variabilities within +/- 20 percent.

The major limitations of the flux chamber are(16).

1. It is not suited for sites with caliche or other semi-impermeable soils.

2. It is not well suited for soil surfaces saturated with water.

3. It measures gases at the surface, rather than at the subsurface.

The sample collection with the flux chamber may also disturb the soil. The flux chamber covers the soil and therefore, will alter the natural environmental conditions such as rain, sun, and relative humidity. These factors, along with the inlet and outlet air streams to the chamber, could potentially disturb the equilibrium between the soil gas and the gas sorbed on the soil particles.

1.4.2 FCC Samplers. The FCC wire sampler was developed at the Colorado School of Mines and is considered a static collection device (see Figure 1.3). It consists of a ferromagnetic wire to which charcoal has been glued with an inorganic cement(17). The FCC wires, supported in culture tubes (see Figure 1.4), are placed in 25-35 cm deep holes in the soil. The holes are then backfilled. After equilibrating with the volatiles in the soil for five to ten days, the wires are removed. They are then transported to a laboratory for analysis by Curie-point pyrolysis/mass spectrometry (Py-MS).

Ferromagnetic wires, used as the support for the charcoal on FCC wire samplers, also serve as the heat source to desorb the absorbed compounds. Compound desorption occurs at a reproducible temperature (358 °C) when a FCC wire is placed in the high frequency field of a Curie-point pyrolyzer.

The FCC wire samplers have the following disadvantages:

1. Long sampling time.
2. The sampling site is disturbed.
3. The efficiency of the collection process is generally not known and may vary depending upon soil type.

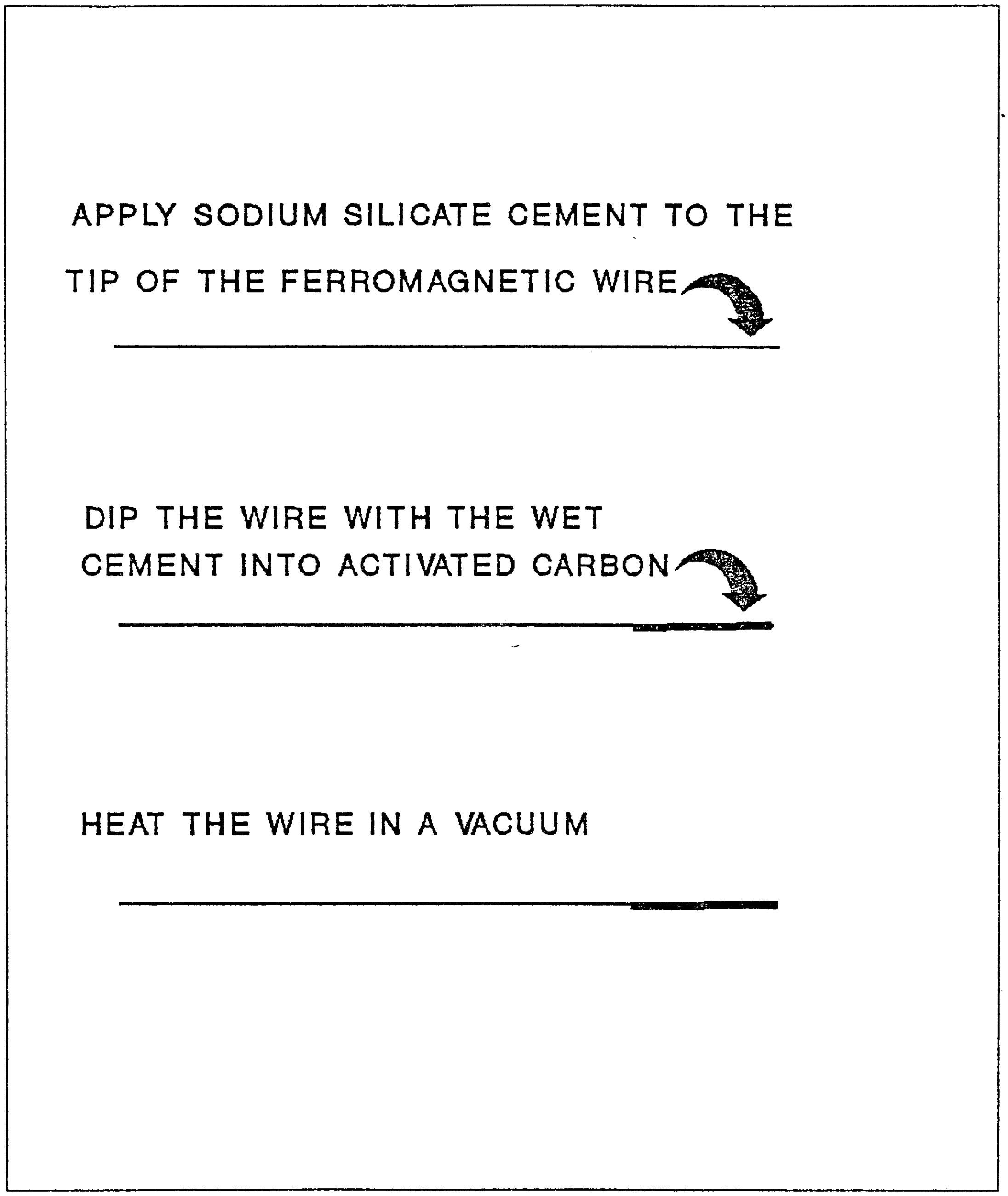

Figure 1.3 FCC Wire Sampler.

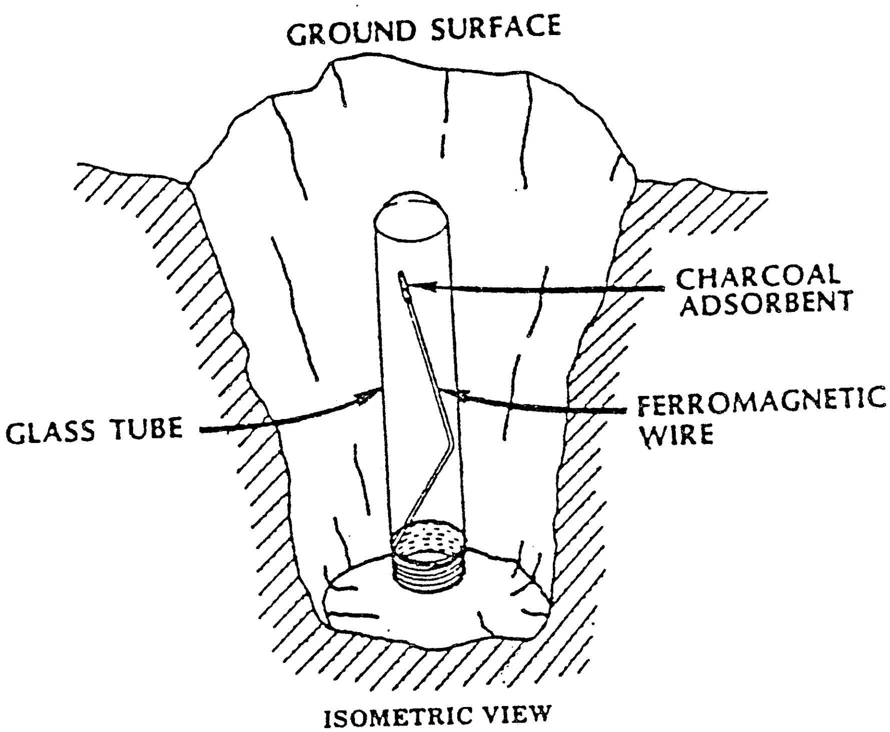

Figure 1.4 Buried FCC Wire Sampler.

The efficiency of the FCC wire samplers cannot be determined since the sample enters the culture tube by passive diffusion; therefore, the volume of the gas that enters the tube cannot be directly measured.

1.5 Objectives.

The aim of this study was to analyze the volatile organic emission at an industrial site using both the EIFC and the FCC wires. The emission data were to be compared to the contaminant concentrations found in water samples collected at the sites investigated.

This thesis was designed to answer the following questions:

1. What analytical procedures must be designed to obtain quantitative data from both the flux chamber and the ferromagnetic carbon coated wire samplers?

2. What is the relationship between the concentration of volatile organic species in the groundwater and the flux of the volatilized species at the soil surface?

3. How is the migration of the contaminant through the soil to the surface influenced by the soil type?

4. What effect does the flux chamber have on the emission from the soil surface that is enclosed by the chamber?

5. What comparison can be made on the rate of emission

detected by the flux chamber to the soil gas diffusion detected by the passive FCC wire samplers?

EXPERIMENTAL METHODS

2.1 Pyrolysis - Mass Spectrometry Analysis

The FCC wire samplers used in this study were analyzed by pyrolysis-mass spectrometry. A schematic (see Figure 2.1) illustrates the Py-MS used for the analysis. A sample was thermally desorbed from the FCC wire to gaseous components by absorption of high frequency energy. The gaseous components then entered an expansion chamber where they diffused into the ion source region. A cold screen was present in the source region to condense any sample which was not ionized. The component molecules that entered the source of the mass spectrometer were ionized by low energy electron ionization (EI).

Electron ionization fragments molecules into several positively charged ions that vary in molecular weight. The extent of fragmentation is governed by the voltage supplied to the electron ionization source. Low voltage (15 eV) was used to avoid extensive fragmentation, thus maximizing the intensity of the molecular ion for target compounds. The positively charged fragments were then accelerated through a ramping RF/DC field of a quadrupole mass filter. At any given instant, only ions with a specific mass/charge ratio are allowed to pass through the quadrupole mass filter, followed by detection using an electron multiplier.

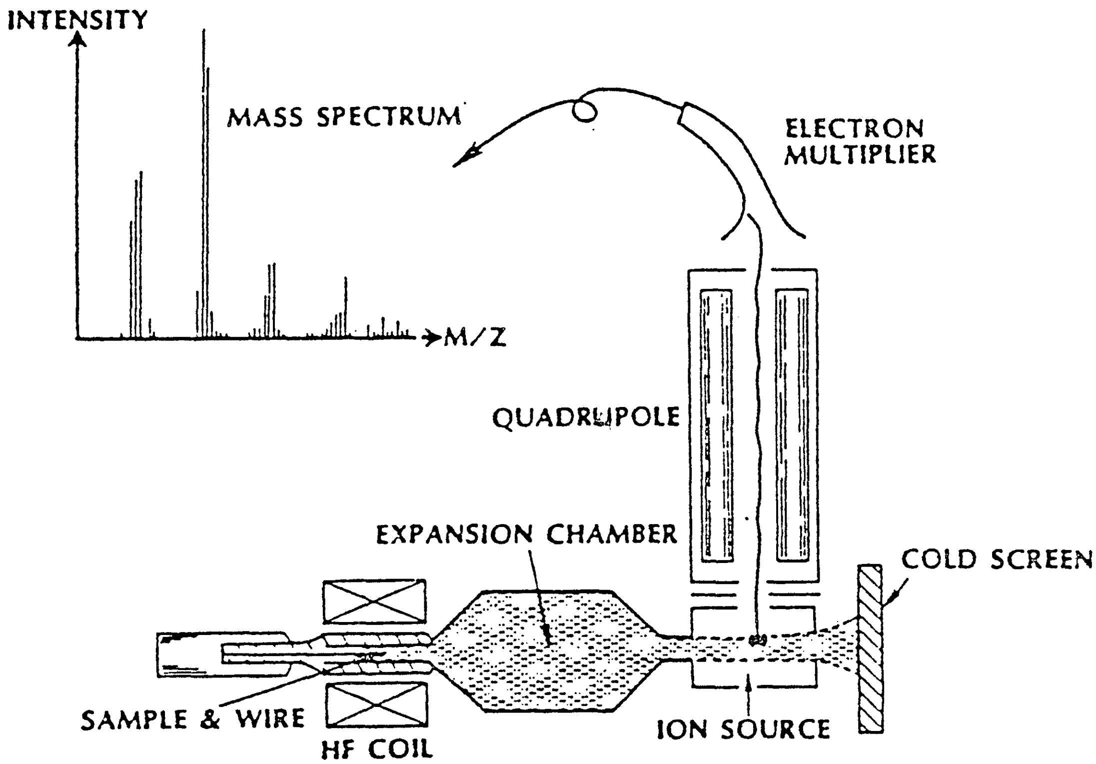

Figure 2.1 Schematic of the Py-MS.

As the field is ramped, a spectrum of mass/charge ratios is produced. The resulting mass spectrum is a fingerprint of a molecule's ionization fragments and their relative intensities. This spectrum usually provides sufficient information to identify a particular molecule. Table III lists the instrumental parameters that were set before tuning and calibrating the Py-MS instrument.

Table III. MS - Electronic Settings

Parameter	Setting
Ionization energy	15-17 eV
Emission	15-25 uamps
Electron multiplier	2.8-3.2 kV

Perfluorotributylamine (PFTBA) vapor introduced into the mass spectrometer by opening a needle was used as a standard for tuning the instrument. Table IV lists target ranges for the mass intensities of PFTBA that were attained before sample analysis.

Table IV. Mass Intensities Obtained for PFTBA.

Mass	Intensity (%)
69	100
131	28-40
219	30-40
414	3-4
502	1-2

2.2 FCC Wire Sample Preparation and Analysis

The Petrex Group provided the FCC wire samplers for this study. Low temperature (358 °C) Curie-point wires were used in the construction of the FCC wire passive samplers. Glass pyrolysis tubes were used as a support for the FCC wires during sample analysis. The pyrolysis tubes were cleaned prior to use by placing them in a 150 ml beaker with Chromerge (Fisher Scientific, A.C.S Grade). The beaker was then heated at 80 °C over a hot plate for approximately 2 hours. The Chromerge was removed and the pyrolysis tubes were rinsed with deionized water not less than ten times. The tubes were then sonicated in methanol for 10 minutes and heated in a drying oven at 250 °C for 1 hour.

A blank FCC wire was analyzed in a clean pyrolysis tube to test the efficiency of the cleaning process. If no interfering background peaks were apparent in the blank, exposed FCC wire samples were prepared for analysis.

The best quantitative results for the FCC wire analysis were obtained by minimizing changes in the Py-MS operating conditions. Vacuum level was found to have the most significant influence on the precision of each analysis. The Py-MS is a high vacuum instrument. During the analysis of a sample, the vacuum is disturbed during the sample insertion and subsequent thermal desorption. The vacuum disturbance during each analysis was monitored using the instrument's ion gauge for each analysis. Following sample insertion, the samples were analyzed at the same vacuum reading, 3×10^{-6} Torr. A further vacuum change resulted after thermal desorption of the samples which varied with different concentrations of adsorbate. FCC wires saturated with water caused a larger vacuum change than FCC wires without water present. Similarly, samples with large amounts of analyte adsorbed caused a greater vacuum change than small amounts adsorbed on FCC wires. This vacuum disturbance was only a problem when wires were analyzed that had been exposed to high moisture conditions or very different analytes. Samples compared in this study were generally collected at sample sites that had similar moisture and analyte concentrations.

2.2.1 Laboratory Reproducibility Study. Four lots of FCC wires were exposed to TCE in a 5 liter desiccator for different time intervals. Nine wires each of two groups labeled Lot 1 and Lot 2 were exposed for 2.5 hours to a 5.00 ppmv atmosphere of TCE. Nine wires in another group, Lot 3, were similarly exposed for 1.83 hours. Another 10 wires in Lot 4 were exposed for 1.47 hours to the 5.00 ppmv atmosphere of TCE.

The standard deviation was calculated for the intensity of the characteristic 130 amu signal obtained from the TCE mass spectra. To compare the variation in the sets of data, the coefficient of variation (CV) was used.

$$CV = \frac{\text{Standard Deviation}}{\text{Mean}} * 100$$

This gives the standard deviation as a percentage of the mean, and is independent of the scale of the measurement.

2.2.2 Field Reproducibility Study. Four sets of FCC wires were field tested in October and November, 1987 to test the field reproducibility of the FCC wire samplers. Culture tubes containing two wires each were buried for varying time periods to test the loading level with time and the subsequent reproducibility. The exposure time for Set 1 was 7 days; Sets 2 and 3 were 4 days; and Set 4 was 1 day. The Sand Creek area in Adams County near the Colorado Chemical Specialties facility was chosen as the test site. This area had been previously surveyed using FCC wires by Petrex of Lakewood, Colorado and was known to have extremely high concentrations of tetrachloroethylene (PCE) in the soil and groundwater(18). The meteorological conditions during exposure were similar for the four sets of samples. The weather during the exposure of Sets 1 and 4 was clear with daytime temperatures reaching the mid 60's for Set 1 and 50's for Set 4. The weather for Set 2 and Set 3 was partly cloudy, with temperatures in the 40's and 50's .

2.2.3 Reproducibility with an External Standard. An external standard containing all of the target analytes expected in field samples was used to quantitate the data collected from the FCC wire sample analyses. In this analysis, the external standard was directly injected onto the tip of an FCC wire sampler.

Following instrumental calibration of the mass spectrometer, a FCC wire that had been exposed in the field, was prepared and analyzed. The sample was then desorbed a second time to ensure that all the volatile analytes were desorbed by the first thermal desorption. The FCC wire was removed, still bearing the activated carbon, and 1 uL of an external standard was injected uniformly on the carbon tip of the FCC wire (see Figure 2.2). The wire was reinserted into the instrument and reanalyzed.

The method of standard addition was used to calculate the relative mass of analyte adsorbed on the sample wires. The characteristic ion signal, unique to each compound, was used in the calculation. A sample calculation is given below.

1 uL of standard contains 10 ug each of TCE, 111-TCA, and 1,1,2-TCA in methanol.

m/e = 130

$$\text{TCE (ug)} = \frac{(10\ \text{ug})(\text{ion counts unknown})}{(\text{ion counts standard})}$$

m/e = 117

$$\text{1,1,1-TCA (ug)} = \frac{(10\ \text{ug})(\text{ion counts unknown})}{(\text{ion counts standard})}$$

m/e = 83

$$\text{1,1,2-TCA (ug)} = \frac{(10\ \text{ug})(\text{ion counts unknown})}{(\text{ion counts standard})}$$

The reason for the second thermal desorption was to ensure that all analytes were desorbed from the FCC wire samplers. This concern stemmed from an earlier attempt to find an appropriate external standard for quantitative Py-MS studies. Dibenzothiophene was chosen because its mass

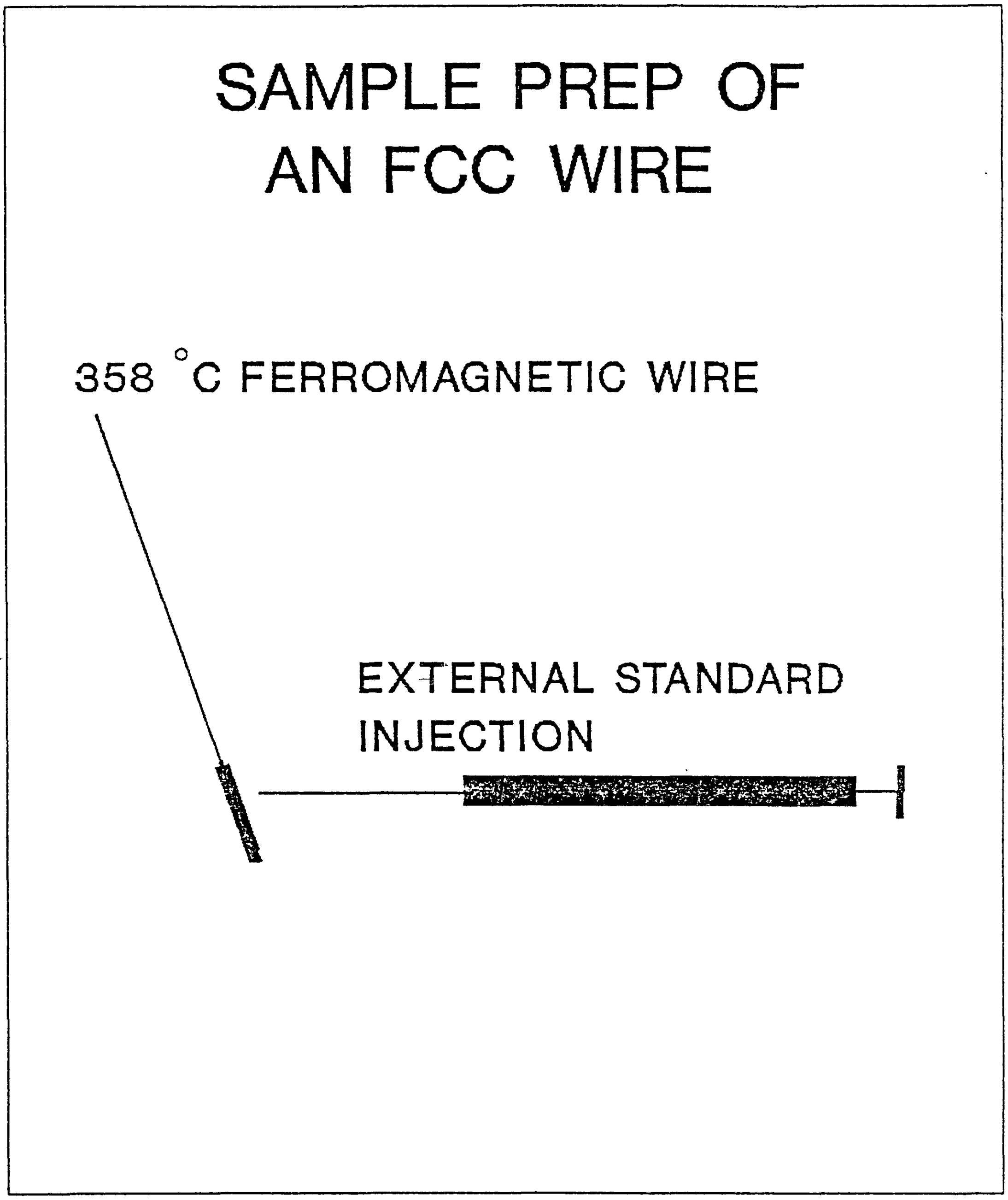

Figure 2.2 External Standard Injection Method.

spectrum has a small number of peaks in the range bracketed by 40 and 170 atomic mass units (amu).

Dibenzothiophene vapors were adsorbed onto a FCC wire. Repeated thermal desorption at 358 °C showed that only fractional quantities of the dibenzothiophene were desorbed by each thermal desorption. To alleviate the problem, FCC wires were constructed using 710 °C ferromagnetic wires. More of the dibenzothiophene was desorbed at 710 °C, but the compound was not totally desorbed. Later, the use of the 710 °C ferromagnetic wires was abandoned because of the possibility of thermal degradation of the analyte.

A laboratory experiment was performed to determine the linearity and accuracy with which an external standard could be used to quantitatively calculate the absorbance of TCE onto the FCC wires. Four lots of five wires each were exposed in a desiccator to a atmosphere of 5.00 ppm trichloroethylene and water vapor for intervals of 30, 50, 70, and 90 minutes. An external standard, m-xylene, was injected directly onto the carbon tip of the wire.

More precision may be gained for quantitative Py-MS by using an external standard because of the uncertainties due to sample introduction into the Py-MS, changes in instrumental conditions, and variability of the amount of carbon on each FCC wire. In this procedure, 1 uL of a 500 ng/uL m-xylene standard was introduced onto each sample via direct injection, and the ratio of TCE to external standard peak area served as the analytical parameter. For this method to be successful, it was necessary that the external standard's ion fragments used for quantitation be different from those for TCE or other components of the sample. For the ion fragments 130 and 132 of TCE the difference relative to the 106 ion of m-xylene is 26 and 28 amu, respectively (130-106 amu and 132-106 amu).

2.3 Flux Chamber Construction

A 30 liter stainless steel mixing bowl was used to construct the flux chamber. It enclosed a ground surface area of 993 cm^2. The chamber had an inlet for introduction of zero grade air and an outlet to trap the volatile constituents once they were purged from the chamber (see Figure 2.3). A collection pump at the outlet of the flux chamber withdrew air from the flux chamber at the same rate (3 L/min.) in which the air entered. A carbon tube (see Figure 2.4) between the pump and the outlet was used to trap the volatiles purged from chamber. The chamber was also equipped with temperature and pressure gauges to monitor these parameters during analysis. The smooth dome top construction of the flux chamber, along with moderate inlet and outlet air flow rates facilitated mixing within the vessel. The base of the flux chamber was buried

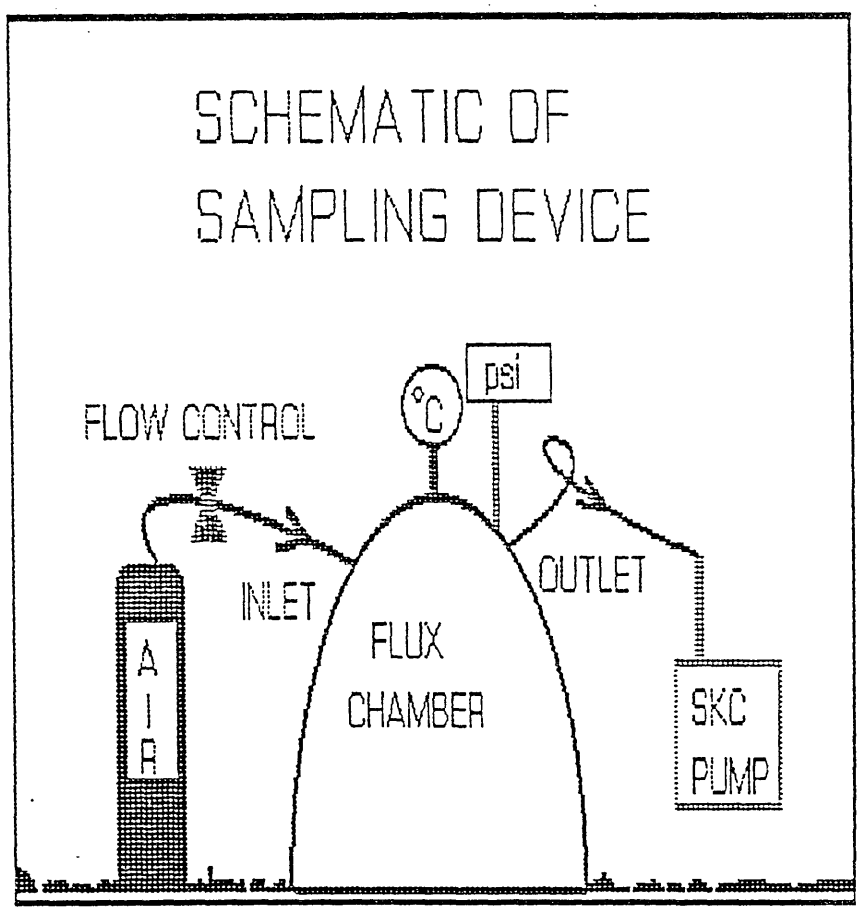

Figure 2.3 Flux Chamber.

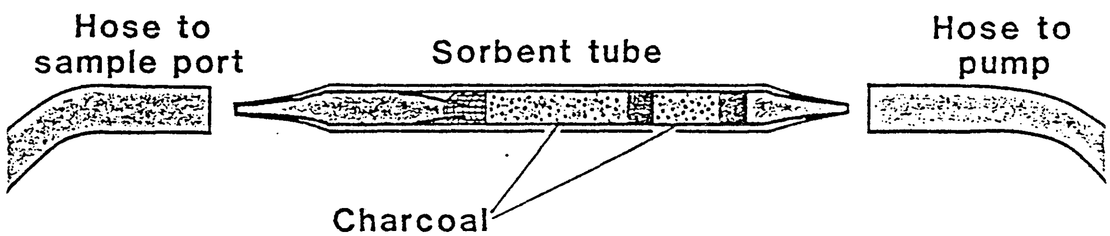

Figure 2.4 Carbon Sorbent Tube.

approximately four inches in the soil when the site conditions permitted (i.e. soft clay soil or sand). The chamber was shaded by a tent to avoid excessive chamber heating due to surface irradiation. When the site consisted of bedrock or shale, the flux chamber was buried approximately one inch. The sampling time was chosen to assure collection of soil emission that was above detection limits. At the same time, the collection time did not allow the capacity of the carbon tube to be exceeded.

The flux chamber built for this study met the following specifications:

DESIGN PARAMETERS	SPECIFICATIONS
Depth of penetration	2 to 12 cm
Sweep air flow rate	3 L/min.
Sampling duration	5 to 30 min.
Sample line length	30 to 90 cm
Construction Material	Stainless Steel
Inlet Gas	High Grade Air

2.4 Flux Chamber Sample Preparation and Analysis

The carbon tube samples collected using the flux chamber were analyzed at the Colorado School of Mines. Also collected was a carbon sorbent tube blank which was opened to the atmosphere for the same time required to connect and disconnect the sampling tubes from the sampling system. The carbon sorbent tubes were extracted by removing and weighing the activated carbon from the carbon tube and sonicating for 15 minutes in a solvent of 5 percent acetone and 95 percent hexane by volume(19). A 5 ul syringe was used to withdraw 0.5 ul of the extract for GC analysis. When the carbon settled following the sonication, 0.50 mL of the extract was removed and a 0.10 ppm internal standard was added to the extract.

The carbon tube extracts were analyzed using a Hewlett Packard 5890 gas chromatograph equipped with an electron capture detector (GC/ECD). A 15 meter capillary column (DB-1701) with a polyphenylmethylsiloxane stationary phase was used to separate compounds. The oven temperature was maintained at 38 ^{o}C isothermal, the electron capture detector temperature 300 ^{o}C, and the injector temperature at 220 ^{o}C. Typical run times for an analysis were 20 minutes. An HP integrator was interfaced to the GC/ECD to record peak areas and retention times for target compounds and standards. The relative peak areas of the target compounds to an internal standard (1,1-dibromoethane) was used for quantitation.

The concentration of the analytes was determined by standard addition, taking into account the carbon extraction efficiencies and blank corrections. A sample calculation is given below.

$$\text{ug analyte} = \frac{(10\ \text{ppm})(\text{area unknown sample})}{(\text{area internal standard})(\text{extraction efficiency})}$$

ug of analyte in sample = ug sample - ug blank

Analytes adsorbed onto the carbon tubes have traditionally been desorbed with carbon disulfide prior to analysis(20). However, when this solvent is used with an electron capture (EC) detector, an excessive solvent response of the detector results. An appreciable solvent tailing on the GC column is also a problem. In addition, the highest grade of carbon disulfide, Baker Instra-Analyzed reagent, contains appreciable impurities that are detected by ECD. Methanol is not appreciably detected by EC and can be obtained in high purity grade (Baker Resi-Analyzed). When methanol was used for desorbing TCE, 1,1,1-TCA, and 1,1,2-TCA from activated carbon, extraction efficiencies of 10 percent were obtained. Acetone has been shown to desorb TCE from activated carbon more efficiently than CS_2(15), but also has a large response by an EC detector. Samples collected in this study were extracted with a reagent consisting of 5 percent (V/V) acetone in HPLC grade hexane. Hexane was used instead of methanol because it had a shorter retention time than methanol for the column used in this study. Hexane also has a smaller EC detector response than methanol.

The extraction efficiencies for the activated carbon were determined by weighing out 100 mg of activated carbon from the same lot as the carbon contained in the SKC sorbent tubes. The carbon (100 mg) was placed in five 1 dram vials and spiked with 500 ng each of TCE, 1,1,1-TCA, and 1,1,2-TCA. The vials were then allowed to sit overnight. The extract (0.5 ml) was removed from the carbon and 5 ul of 6.6 ug/ml internal standard (1,1-dibromoethane) was added to the extract. Five 1 dram vials containing 0.5 ml of the same TCE, 1,1,1-TCA, and 1,1,2-TCA standard without any carbon were used as a standard reference. Comparison of the analysis data for the SKC carbon extract with those from the reference solution then gave the desorption efficiencies at each concentration level tested.

2.5 Industrial Site Field Study

The sample collections at the industrial field site included seven sets of flux chamber samples taken at Site A and four sets of flux chamber samples taken at Site B (see Tables V - VIII). The sample collections for the FCC wires included five sets of samples taken at Site A and two sets taken at Site B (see Tables (IX - XII).

Samples were collected from two different soil surfaces at Site A. One surface consisted of primarily low porosity clay type soil which was soft enough that the bottom of the flux chamber could be buried about four inches underground. The uncovered surface appeared saturated with water and had a soil temperature of 20 °C. Samples were collected on three different days at Site A. Another surface at this site consisted of coarse sand and pebbles. The sandy soil was firmly packed about one inch below a top layer of loose sand which resulted in burying the bottom of the flux chamber only one inch at this site. The coarse surface had no apparent moisture and the soil temperature was 29 °C.

Table V. Flux Chamber Sample Collection Scheme at Site A from Clay Soil

Sample Set	Date	Total Collected Air Volume (L)
1	9/2/88	100
2	9/6/88	81
3	9/15/88	108

Table VI. Flux Chamber Sample Collection Scheme at Site A from Sand Soil

Sample Set	Date	Total Collected Air Volume (L)
1	9/6/88	108
2	9/15/88	54

Table VII. Flux Chamber Sample Collection Scheme at Site B from Sand-Clay Soil

Sample Set	Date	Total Collected Air Volume (L)
1	9/15/88	108
2	9/23/88	135

Table VIII. Flux Chamber Sample Collection Scheme at Site B from Conglomerate Soil

Sample Set	Date	Total Collected Air Volume (L)
1	9/15/88	135
2	9/23/88	135

Table IX. FCC Wire Sample Collection Scheme at Site A from Clay Soil

Sample Set	Date	Number of FCC Wires Collected
1	9/6/88	3
2	9/15/88	3

Table X. FCC Wire Sample Collection Scheme at Site A from Sand Soil

Sample Set	Date	Number of FCC Wires Collected
1	9/6/88	2
2	9/15/88	3

Table XI. FCC Wire Sample Collection Scheme at Site B from Sand-Clay Soil

Sample Set	Date	Number of FCC Wires Collected
1	9/23/88	4

Table XII. FCC Wire Sample Collection Scheme at Site B from Large Conglomerate Soil

Sample Set	Date	Number of FCC Wires Collected
1	9/23/88	3

The higher soil temperature was due to the sun's irradiation and the lack of soil moisture. Samples were collected on two different days from the sandy area.

Flux chamber samples were also collected from two different soil surfaces at Site B. One surface was a mixture of coarse sand and clay and contained appreciable moisture. The flux chamber was buried two inches at the sandy clay site. The soil temperature was 22 °C one inch below the surface. The other surface at Site B consisted of coarse conglomerate and sand. The bottom of the flux chamber could only be buried to a depth of one inch. The soil temperature was 26 °C one inch below the surface.

The FCC wire sampling was conducted over a total sampling period of twenty three days. All of the FCC wires were planted at a depth of eight inches and within 1 yard of the flux chamber sampling sites. Three lots of FCC samplers were collected after five days. The second and third lots were collected after eight and ten days, respectively.

RESULTS

3.1 Laboratory Reproducibility Study

The raw data for the laboratory FCC wire exposure in a desiccator are listed in Appendix A. The mean, standard deviation, and the coefficient of variation (CV) for the exposure data are shown in Table XIII.

Table XIII. Means and Standard Deviations for FCC Wire Laboratory Exposure

m/e = 130

SET	MEAN (counts)	STD. DEV. (counts)	CV	
1	33304	5885	18	n*=9
2	35744	5572	16	n=10
3	53289	6634	12	n=8
4	39027	4344	11	n=10

* n= the number of samples analyzed under the same instrumental conditions.

The largest CV existed for the longer wire exposure times (data Sets 1 and 2) to the TCE atmosphere, while shorter wire exposure times (data Sets 3 and 4) show less deviation in the data.

3.2 Field Reproducibility Study

Appendix B contains the raw data for all the FCC wire analyses of samples collected at the Sand Creek area near the Colorado Chemical Specialties facility site. The duplicates in the culture tubes are listed consecutively such that A and B were from one tube and C and D were in another, etc.

The means, standard deviations, and coefficient of variation for the four data sets are shown in Table XIV.

Table XIV. Means and Standard Deviations for Sand Creek Field Exposure

m/e = 166

SET	MEAN (counts)	STD. DEV. (counts)	CV	
1	43751	11104	25	n*=6
2	37736	5374	14	n=10
3	35532	4208	12	n=3
4	19740	3251	16	n=10

* n= the number of samples analyzed under the same instrumental conditions.

The wires in Set 1 were very heavily loaded and probably were close to saturation. Based on the coefficient of variation for the different data sets, it appears that the best reproducibility is achieved when the wire's loading occurs well below saturation. The ratio of mean to standard deviation for the field samples are nearly identical to the values obtained for the laboratory exposures (see Appendix A).

The comparison of the reproducibility of duplicate FCC wires to the remainder of the set shows that the major scatter in the data results from wire manufacturing differences rather than from exposure differences. This may be due to varying amounts of carbon loaded on to the wires during manufacturing.

3.3 Reproducibility with an External Standard

An external standard was used to quantitate the FCC wire analysis data. The standard was implemented to correct for differences in FCC wire manufacturing and Py-MS instrumental conditions. The external standard was directly injected onto the tip of each FCC wire. The precision of the relative peak area of the target peak to the external standard peak is represented graphically (see Figure 2.5). Note that the deviations or residuals (Sr) represent the vertical displacements of experimental data from the least-squares line.

The calibration curve in Figure 2.5 represents first order loading when the FCC wires were exposed to a constant 5 ppm TCE standard at varied time intervals. The data are plotted to give the calibration curves using the characteristic 130 and 132 ion fragments of TCE. The plots approximate a straight line with more indeterminate error for the process associated with the wires exposed for 70 minutes than the wires exposed for 30, 50, and 90 minutes. A "best" straight line was derived from the points using least squares regression analysis. In applying the method of least squares to the derivation of the calibration curve, two assumptions were made. The first was that a linear relationship existed between the time of FCC wire exposure to TCE and the intensities of the ion fragments. This is a valid assumption if the amount of analyte adsorbed onto the carbon is well below the absorption capacity of the passive carbon samplers. Previous work has shown that second and third order loading may typify the absorption process with time as the capacity of a passive carbon sorption device is approached(21). Second, it was assumed that no significant change occurred in the concentration of the 5 ppm TCE and water vapor atmosphere for the length of the experiment (90 min.). This is a valid assumption since there was less than 0.1 percent evaporation of the standard for the length of

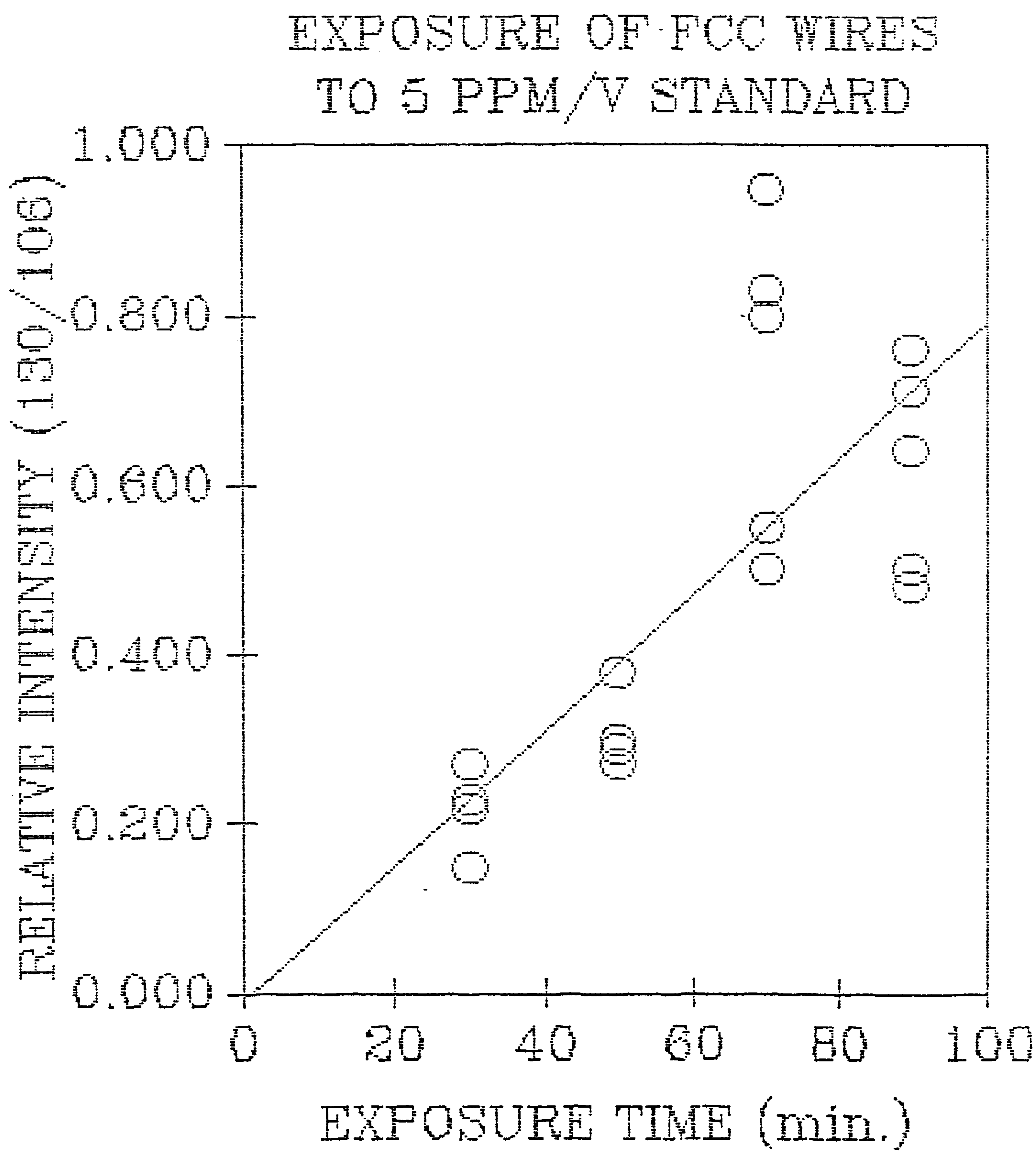

Figure 2.5 Linearity of Adsorption.

the exposure experiment. The deviations of the points from the straight line (see Figure 2.5) are a consequence of theindeterminate error in the area of the characteristic ion fragment.

The ratio of the residuals to the mean (Sr_x/Mean x) can be used to compare the precision of the data sets to one another. Appendix C contains the intensity data, mean, and standard deviation for TCE (130 and 132 ions) and for the external standard m-xylene (106 ion). Appendix C also contains the relative intensity data, mean, and standard deviation (130/106 and 132/106 ratios) for the same data. Table XV contains the calculated ratio of the residuals over the mean for the two data sets.

Table XV. Precision of Relative Intensity Data

Exposure=30, 50, 70, and 90 min.
Electron multiplier= 3.2

Sr/Mean 130/106	Sr/Mean 132/106
0.34	0.33

* Sr=residuals

3.4 Flux Chamber Sample Extraction Efficiencies

The flux chamber carbon tube samples were extracted with 5.0 percent by volume acetone in hexane. Extraction efficiencies for desorption of 330 to 10000 ng/(g of carbon) were 95.8 percent for 1,1,1-TCA, 74.6 percent for TCE, and 88.7 percent for 1,1,2-TCA (see Figure 2.6).

3.5 Field Sampling Results

The flux chamber sample and the FCC wire sample results at both Site A and B are represented graphically in Figures 3.1 - 3.4. The data for the flux chamber and FCC wire samples are listed in Appendix D. The flux chamber emission data are plotted as a function of the total volume of air flushed through the chamber. The emission data on the ordinate axis are in units of ng/m^2-Hr. An average emission value, also in units of ng/m^2-Hr, for the FCC wire data is drawn as a horizontal line on the flux chart to compare the flux for both methods. All FCC mean data are multiplied by a constant in order to fit both the flux chamber data and the FCC wire data on the same plot. A constant k=1/36 was chosen to decrease the FCC wire data so that the mean approximates the steady state value of the flux chamber data over time.

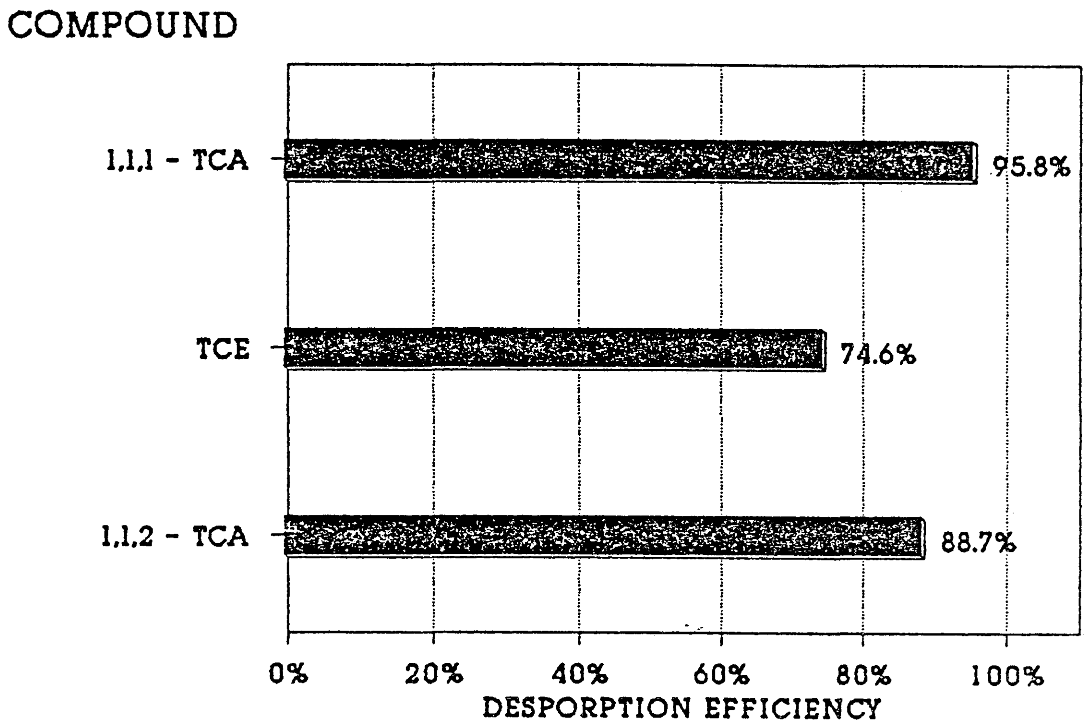

Figure 2.6 Desorption Efficiencies for Activated Carbon.

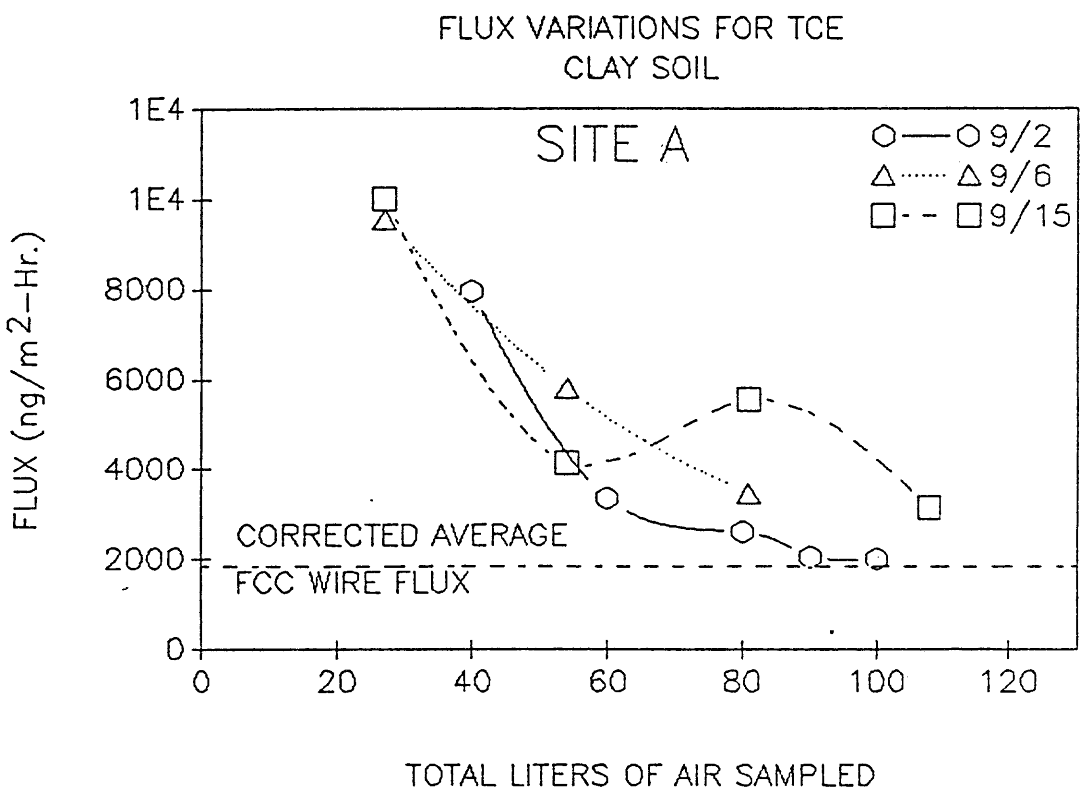

Figure 3.1. Flux Variations for TCE (Clay)

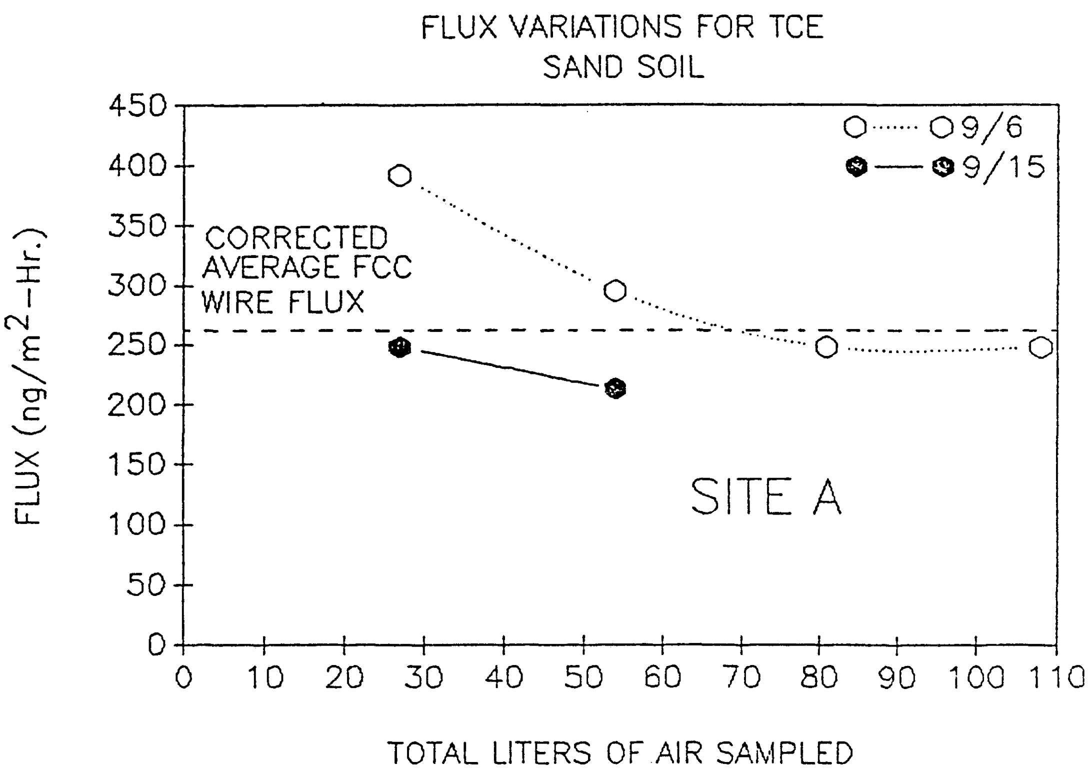

Figure 3.2. Flux Variations for TCE (Sand)

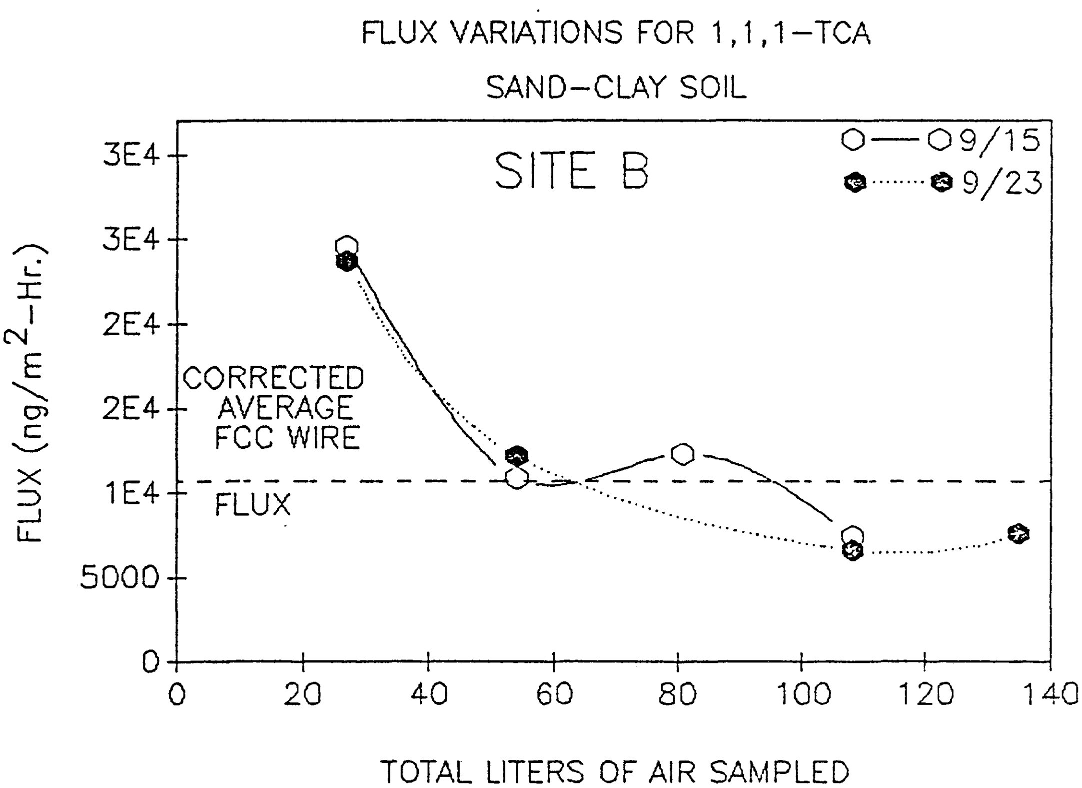

Figure 3.3. Flux Variations for TCE (Sandy Clay)

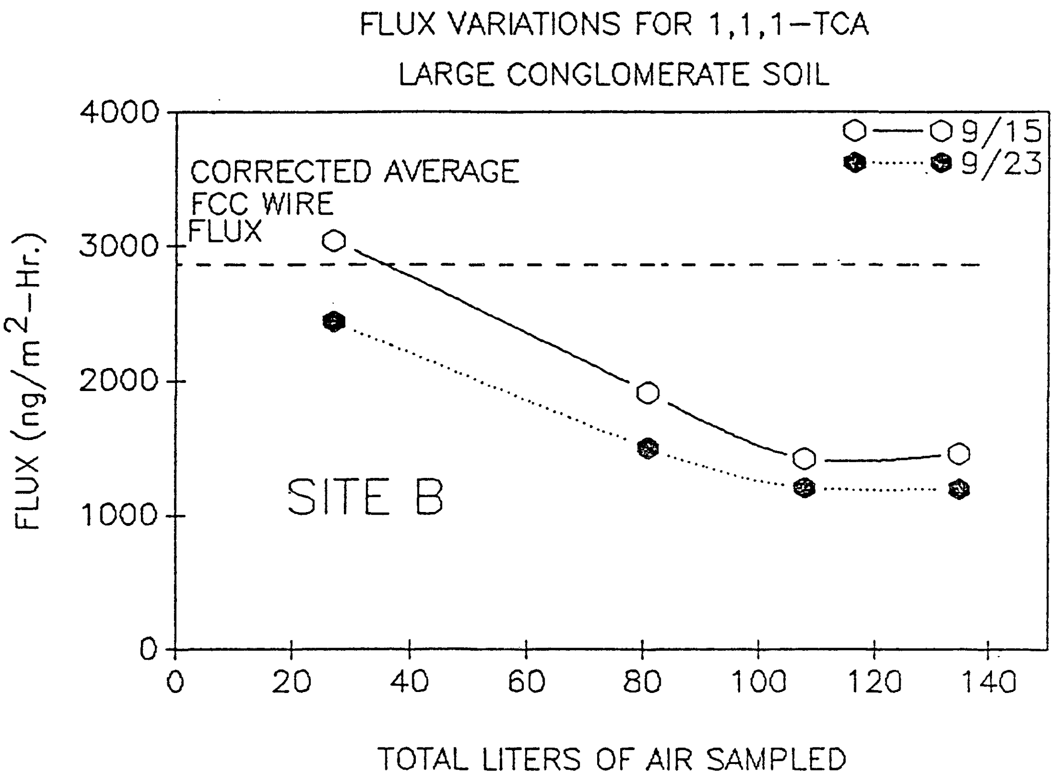

Figure 3.4. Flux Variations for TCE (Conglomerate)

DISCUSSION OF RESULTS

4.1 Comparison of the Flux Chamber and FCC Wire Data.

Samples in this study were collected using both passive and active type samplers. The FCC wire samplers are considered a passive sampler and were used to collect TCE and 1,1,1-TCA vapors over a period of approximately one week. The sampling period allowed sufficient quantity of TCE and 1,1,1-TCA to be collected for analysis. The FCC wire samplers gave an integrated sample that compensated for the changes in meteorological condition. On the other hand, the flux chamber is an active sampling technique. The chamber enclosed a known soil surface area to sample TCE and 1,1,1-TCA emission. Air was introduced at the inlet of the chamber to sweep soil emission from the chamber through a carbon tube for trapping at the exit of the chamber. The soil emission was calculated by measuring the flow rate of air through the chamber and the concentration of the gas at the exit.

The flux chamber samples collected at the beginning of the sampling period showed the highest concentrations of volatile organic emission. The concentration of emission decreased exponentially with increased sampling time. Eventually, the emission leveled off to a constant concentration flux which should represent a steady state value. The sandy soils showed less decline of emission with time for the sampling period than did the clay soils.

Table XVI lists the maximum (initial) value, steady state value, and the ratio of the steady state value to the initial value obtained with the flux chamber at the different sampling sites.

Table XVI. Flux Chamber Steady State Emission.

Soil Type	Initial Emission (ng/m^2-Hr.)	Steady State Emission (ng/m^2-Hr.)	Steady State/Initial Emission
SITE A			
Clay	10000	2000	.20
Sand	400	250	.60
SITE B			
Sandy clay	30000	7500	.25
Conglomerate	3000	1000	.33

The steady state emission for the clay and the sand soils at Site A were 20 and 60 percent of the initial sampling emission, respectively. The steady state values were 25 and 33 percent of the initial emission for the sandy clay and the large conglomerate soils, respectively at Site B. Emission concentrations from the soils that contained clay are higher than the emission concentrations for the sand and large conglomerate type soils. Figure 3.1 and 3.3

are plots of the flux emission as a function of the total liters of air sampled with the flux chamber for the soils that contained clay. The clay and the sandy clay soils exhibited a more rapid exponential decline in emission than the sand and coarse conglomerate soils (see Figure 3.2 and 3.4). It is possible that the clay may be acting as a concentrating medium for TCE and 1,1,1-TCA vapors through chemical and physical adsorption processes. A previous study(22) examined ethylene dibromide sorption on 20 different soils. The data were expressed as sorption coefficients. Surface area, organic matter content, moisture content, and clay content were correlated to these coefficients. Clay content and specific surface area were the principal factors regulating sorptive capacity of dry soils, whereas organic matter was critical for soils containing high moisture.

In this study, the soils that contained clay were very moist, causing droplets of condensation to form on the interior wall of the flux chamber during sampling runs. The sand and conglomerate soils contained very little moisture, and exhibited no precipitation on the interior wall of the flux chamber during a sampling run. The sorption of nonionic organic chemicals is more complete in dry soils than in wet soils(23). Immiscible organic compounds that are nonionic cannot compete with water for the surface of

clay minerals. The water is preferentially adsorbed compared to organic compounds, which accounts for observations in which immiscible organic compounds adsorbed by dry soils or clays are rapidly released upon the addition of water(22). This phenomenon may explain the sharp exponential decline in the flux chamber emission with increased sampling time. The air purge stream introduced into the flux chamber
(3 L/min.) may have drawn water from the soil, thus freeing absorption sites on clay particles. Trichloroethene and 1,1,1 - TCA would bind to the exposed clay surfaces and a new soil's equilibrium would be established. Another factor, probably more significant, is the soil's equilibration with the flux chamber placed on the soil's surface. At the beginning of the flux chamber sampling, organic vapors residing in the top 1 or 2 inches of the soil were purged from the soil's pore spaces by the air introduced at the chamber inlet. The vapors collected during this initial stage were not representative of the soils equilibrium with the flux chamber cover. Eventually, the organic vapors were purged from the soil's pore space and a new soil equilibrium that represented the steady state flux emission was achieved.

The emission data (Appendix D) for both the flux chamber and the FCC wires can be plotted on the same graph by normalizing the average FCC wire emission value with a normalization factor. The value obtained from this calculation is the normalized average FCC wire value with respect to the steady state flux chamber emission for the clay soil at Site A. The following equation is used for the normalization:

Normalized Average FCC Value = Average FCC Value * k

where k (normalization factor) = 1/36

The average FCC value for a sampling site is the mean of all the FCC wire emission data collected at a particular site. The normalization factor (k) was chosen by using a value that would raise the FCC wire data to approximately the steady state emission concentration determined with the flux chamber for the clay soil at Site A. The same normalization factor (k=1/36) was used for the remaining soil types in order to compare the average FCC wire emission concentrations to the steady state emission concentrations obtained with the flux chamber.

Figure 3.4 shows that the normalized average value for the FCC wires buried in the large conglomerate soil at Site B is slightly higher than the flux chamber emission values. After 100 liters of air were sampled with the flux chamber, the volatile emission detected by the flux chamber was assumed to have reached a steady state value. Porous soils such as sand, with high diffusion coefficients, have emission rates which change very little throughout the sampling period. In this case, the steady state emission was nearly 60 percent of the initial value. The sites that contained clay soils approached steady state with a rapid exponential decline. Soils containing high moisture and clay may not be well suited for emission monitoring with the flux chamber due to drastically changing gas diffusion rates due to high water evaporation and low soil diffusion coefficients.

4.2 Comparison of the Emission Data to Water Contamination.

A constant (k) has already been introduced to compare the FCC wire data to the data collected with the flux chamber. A correlation of the two emission sampling methods to the concentrations of a particular analyte in the groundwater has not been previously demonstrated. A correlation can be shown between the concentration of contaminants in the water and a surface collection by introducing the unitless form of the Henry's law constant (K_h) and the soil properties constant (Y_{soil}). The following equations are given for both the flux chamber and FCC wire sampling methods to make semi-quantitative comparisons of the groundwater concentrations to measured fluxes.

Water Concentration (ug/L) = $F_x * Y_{soil} / K_h$

where

F_x (ng/m^2-Hr.) is the steady state value obtained with the flux chamber and K_h (unitless) is the dimensionless form of the Henry's constant that describes the partitioning between the vapor and liquid concentrations. It is used to adjust the flux chamber data to the water aquifer concentration data for a specific soil type. Table XVII lists the Henry's constants for various volatile organic compounds. Y_{soil}(m^2-Hr./L) is a diffusion constant that corrects for soil properties which impede the transport of volatile constituents (i.e. moisture, total organic carbon content, porosity, etc.) relative to the standard soil type. It also accounts for the surface area that the flux chamber covered, the length of sampling time, and the volume of air sampled.

Table XVII. Henry's Constant for Various Organic Chemicals(24).

Chemical	Henry's Constant
Benzene	.22
Carbon Tetrachloride	.94
Chlorobenzene	.15
Ethylene Dichloride	.04
TCE	.44
1,1,1 - TCA	1.5
Toluene	.3
Vinyl Chloride	97

Water Concentration (ug/L) = F_{cc} * Z_{soil} / K_h

where

F_{cc} (ng/m^2-Hr.) is the average value obtained with the FCC wire samplers and K_h (unitless) is the same dimensionless form of the Henry's constant previously described. It is used to adjust the FCC wire flux data to the water aquifer concentration data for a standard soil type.

Z_{soil}(m^2-Hr./L) is the previously described diffusion constant that corrects for soil properties which impede the transport of volatile constituents (i.e. moisture, total organic carbon content, porosity, etc.) relative to the standard soil type. It also accounts for surface area that the FCC wire support covered and the length of sampling time.

4.3 Comparison of Groundwater Contamination to Soil Emission

Tables XVIII-XIX contain the values for the steady state flux data and the average FCC wire data obtained at each sampling location. The average water concentrations are taken from Tables I-II and the dimensionless Henry's constant taken from Table XVII. The soil constant for both the flux chamber (Y_{soil}) and the FCC wires (Z_{soil}) can be calculated with these variables. Tables XVIII-XIX contain the values obtained for the four soils monitored by the two sampling methods.

To make practical use of the soil diffusion constants, the flux chamber would be calibrated at a site that had a groundwater monitoring well and soil types representative of the geologic region. The calibration would be accomplished using the following procedure. Flux chamber and FCC wire samples are taken in the general proximity of the monitoring well over the different soil types present. Soil constants are calculated for each type of soil. The soil constants are then tabulated and coupled with emission results at different sampling locations to make semi-quantitative estimates of the levels of groundwater contamination by a particular volatile organic compound. These two methods could be used as cost-effective ways to map contamination plumes and also to determine where groundwater monitoring wells should be installed.

Table XVIII contains the data for the flux chamber calibration for TCE and 1,1,1-TCA at Site A and Site B, respectively. The flux chamber was used to sample the emission at various locations in proximity to Site A and Site B to establish estimates of the extent of groundwater contamination. Similarly, Table XIX contains the calibration for TCE and 1,1,1-TCA at Site B for the FCC wire data. The FCC wire sampling method was used to sample the soil types in this area to estimate the extent of TCE and 1,1,1-TCA groundwater contamination. Limited access to the industrial sites, in addition to an early snowfall, prevented the collection of data from more sites. Additional sampling would have allowed the determination of the boundaries of a contamination plume.

Table XVIII. Chamber and Water Data Comparisons.

Site A (TCE)		Water Conc. (ug/L)	Average Flux Chamber Emission (ng/m^2-Hr.)	Henry's Constant	Soil Constant Y_{Soil}
n*=6	Clay Soil	4320	2874	0.44	0.66
n=5	Sand Soil	4320	231	0.44	8.23
Site B (1,1,1-TCA)					
n=4	Clay-Sand Soil	2500	7500	1.5	0.50
n=4	Conglomerate Soil	2500	1331	1.5	2.82

* n = The number of samples used to calculate Y_{Soil}.

Table XIX. FCC Wire and Water Data Comparisons.

Site A (TCE)		Water Conc. (ug/L)	Average FCC Wire Emission (ng/m^2-Hr.)	Henry's Constant	Soil Constant Z_{Soil}
n*=6	Clay Soil	4320	82400	0.44	0.023
n=5	Sand Soil	4320	11630	0.44	0.163
Site B (1,1,1-TCA)					
n=4	Clay-Sand Soil	2500	476800	1.5	0.008
n=3	Conglomerate Soil	2500	127300	1.5	0.029

* n = The number of samples used to calculate Z_{Soil}.

The Henry's Law constants give an estimate of the relative volatility of organic compounds. As expected from the values of the Henry's Law constants for the two compounds studied, the emission of 1,1,1-TCA was higher, relative to the water concentration, than the TCE emission. These results are shown in Table XIX for both the flux chamber data and the FCC wire data. Soil diffusion constants were calculated to determine if a consistent relationship could be observed, based on the type of soil, between the 1,1,1-TCA data and the TCE data. The Henry's Law constants were used to normalize the two sets of data based on the water aquifer concentration. The diffusion constants normalize the data taking into account the soils' resistance to vapor flow. The two types of soil which contain clay had comparable soil diffusion constants for the flux chamber of 0.66 and 0.50 for the clay and the sandy clay, respectively. The values obtained for the two porous soil types, sand and conglomerate, are 8.23 and 2.82 using the flux chamber, respectively. The values obtained in the porous soils are not as close to each other as the values for the clay soils. Comparing soil diffusion constants for soils which contain clay to those which do not, the values for clay soils are approximately an order of magnitude higher.

Using the FCC wire samplers, the soil diffusion constants obtained are 0.023 and 0.008 for the clay and the sandy clay, respectively. The values obtained for the two porous soil types, sand and conglomerate, are 0.163 and 0.029 for the FCC wire samplers, respectively. The values for the clay soils are a factor of three to five times higher than the values obtained for the porous soils. This is probably due to the low vapor diffusion observed for the porous soils.

The mean, standard deviation, and the coefficient of variation (CV) for the field sampling data are shown in Table XX for both sampling methods. The mean and standard deviation for the flux chamber data were calculated by using the flux chamber emission data once steady state was achieved.

Table XX. Field Sampling Data Precision.

Flux Chamber

SET	MEAN	STD. DEVS.	CV	n
Clay	2670	751	28	6
Sand	239	18	7.5	5
Sandy Clay	8484	2602	31	4
Conglomerate	1324	140	11	4

FCC Wire Samples

SET	MEAN	STD. DEVS.	CV	n
Clay	7.183E4	2.974E4	42	6
Sand	1.392E4	4802	35	5
Sandy Clay	4.690E5	1.580E5	34	4
Conglomerate	1.273E5	3.724E4	29	3

The flux chamber CV indicates that the data is more precise for the samples collected from porous soils (sand and conglomerate) than from the soils which contained clay. The FCC wire precision was relatively consistent, with the highest CV for the clay soil.

4.4 Limitations of Surface Emission Monitoring

The flux chamber and the FCC wire sampling methods may have introduced inaccuracy due to disturbance of the soil matrix. The elimination of environmental elements (i.e. wind and surface irradiation by the sun) introduced errors with the flux chamber method. The effect the flux chamber had on the surface moisture content must also be considered. By decreasing the soil's moisture, the porosity of the soil should increase. This should increase the emission through the soil. On the other hand, decreasing the soil's moisture gives the soil particles more surface area which increase the medium for binding and trapping volatile emission. This would decrease the emission through the soil and may have taken place for the clay soils sampled in this study. No work was done to quantify the effect of these two competing factors.

Another problem resulted from inserting the chamber and the FCC wire samplers in the soil at various sampling sites. The insertion of the chamber 4-inches and the FCC wire samplers 8-inches into the ground at the sampling sites may have resulted in a higher measured emission than would have been measured were the samplers placed on the soil surface without disturbances. It is not expected that insertion of the FCC wire samplers or the chamber into the ground would change the emission, but the disturbance could have loosened the soil next to the samplers. The increased air content may have allowed better diffusion of the gas through the soil.

The basic assumptions made during the investigation were:

1. The transport of volatile emission from the groundwater aquifer to the soil surface during the sampling occurred by gaseous diffusion only. The barometric pressure fluctuations near the surface were ignored. Sudden changes in barometric pressure may produce some transport of volatiles by mass flow, but this method of transport was considered negligible and was ignored.

2. The concentrations of volatiles were low in the flux chamber at the beginning of the sampling due to the 15 minute chamber purge in the sampling protocol. Furthermore, it was assumed that no concentration of volatiles built up inside the chamber during the sampling (Steady state assumption: In=Out).

3. The rate of surface emission detected by the flux chamber was assumed to be proportional to the emission detected by the FCC wires buried 8 inches in the soil.

Devices placed at the soil surface to monitor surface emission of volatiles measure an instantaneous surface flux. For soil with high diffusion coefficients (volumetric air content (cm^3 voids/cm^3 soil)) corresponding to air contents of .1, .15, and .2, steady state soil emission is essentially achieved within a short period of time after the soil is disturbed. For soils with small diffusion coefficients corresponding to an air content of .05, steady state soil emission is not reached within 24 hours(24). Depending on the extent of the surface disturbance, the time necessary to attain a steady state flux can vary from less than 1 hour to more than 50 hours.

The soil was very wet at the clay site and the steady state emission at the surface may not have been achieved over the length of the sampling period. This was primarily due to the slow diffusion rate caused by the presence of the water. Under dry conditions and high soil porosity, exhibited by the sand soil at site A, a high diffusion coefficient allowed steady state flux relative to the subsurface flux to be achieved in approximately one hour. In cases where soil water content was high for appreciable time periods, the monitoring may have required several days to achieve steady state flux. The FCC wire samplers are a better sampling method for this condition.

CONCLUSIONS

Ferromagnetic Carbon Coated (FCC) wires and an Environmental Isolation Flux Chamber (EIFC) were tested in similar environments. The FCC wire sampler is a static sampling technique and measures the average soil organic vapor concentration. The EIFC is a dynamic sampling technique and measures the rate of emission of volatile organic compounds. The average sampling time for the EIFC was 1 hour while the average FCC wire sampling time was about 1 week.

The FCC wire sampler is a more sensitive technique since it can be left in the field for several days and adsorb low levels of volatile compound until suitable loading is achieved. The flux chamber is not as sensitive since sample run times are limited by the quantity of the high purity air supply at the chamber inlet and by the life of the batteries in the collection pump at the chamber outlet. The EIFC surface sampler does provide data on the rate of emission of soil vapors. The FCC sampler cannot since sample is adsorbed by passive diffusion.

Analytical procedures (Objective 1) were developed for both the EIFC and the FCC wires. The carbon tube samples collected with the EIFC were desorbed with 5 percent acetone in hexane by volume and analyzed by GC/ECD. The acetone reagent used was effective for desorbing sample from activated carbon without causing an excessive response of the EC detector during sample analysis. The FCC wires were desorbed and analyzed by Py-MS. Maintaining a steady instrument vacuum was found to be the most significant factor in order to achieve reproducible results for sample analysis. An external standard was also implemented in sample analysis to correct for minor changes in instrumental conditions.

These methods were evaluated on their ability for making semi-quantitative approximations on the extent of groundwater contamination by a volatile organic solvent. Trichloroethene and 1,1,1-trichloroethane were the compounds detected by both the surface methods and by the analysis of the groundwater. Both methods showed similar behavior for their preference to adsorb TCE and 1,1,1-TCA in clay soils. This demonstrates the tendency for these compounds to adsorb onto clays and organic constituents of the soil.

A comparison was made on the rate of emission detected by the flux chamber to the soil gas diffusion detected by the passive FCC wire samplers (Objective 5). This was done by using a proportionality constant to relate the FCC wire data to the EIFC data. Using the proportionality constant, the FCC wire data correlated well with the flux chamber data for the clay, sand, sand-clay, and the coarse conglomerate type soils studied.

A relationship between the concentration of volatile organic species in the groundwater and the flux of the volatilized species at the soil surface was suggested (Objective 2). A mathematical expression containing the unitless Henrys' Law Constant and a constant to describe the rate of migration due to the soils' properties (ie. resistance to vapor flow, to the amount adsorbed to soil particles, the amount redissolved into the liquid phase, etc.) was developed to relate the groundwater concentrations to the surface emission concentrations for both methods.

From the data and above discussion, two emission monitoring methods have been suggested to quantify groundwater contamination based on measured surface flux. A necessary condition for a quantitative relationship between groundwater concentration and surface flux is that steady state be reached in the entire soil atmosphere. The steady state migration of the contaminant through the soil to the surface was influenced by soil type (Objective 3). For clay soil conditions, this time period is likely to be long with the flux chamber (Objective 4). For higher porosity soils like sand and drier conditions, steady state is reached rapidly enough that the emission out of the soil surface might be compared to the concentration in the groundwater. In this case, a flux chamber and the FCC wire samplers may be fast, reliable methods for estimating the concentration of volatiles present in the groundwater.

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APPENDIX A: FCC WIRE REPRODUCIBILITY DATA

9-23-87

Intensities of characteristic mass ion fragments.
Exposure=5.00 ppmv TCE standard (2.5 Hr.).
Electron multiplier= 3.00 eV.
LOT 1.

	94.00	130.00	132.00
	21356.00	23745.00	23790.00
	33668.00	29600.00	28977.00
	26491.00	28711.00	25864.00
	32747.00	34048.00	32771.00
	27235.00	34466.00	32484.00
	32687.00	30962.00	28399.00
	35859.00	40570.00	39483.00
	31162.00	34953.00	30373.00
	27179.00	42682.00	39607.00
Mean	29820.00	33304.00	32416.00
Std. Dev.	4558.00	5885.00	5819.00

9-23-87

Intensities of characteristic mass ion fragments.
Exposure=5.00 ppmv TCE standard (2.5 Hr.).
Electron multiplier= 3.00 eV.
LOT 2.

	96.00	130.00	132.00
	32392.00	37422.00	37413.00
	22887.00	32585.00	31173.00
	31252.00	31784.00	32216.00
	37030.00	40795.00	37941.00
	30265.00	25763.00	25121.00
	30844.00	44309.00	40911.00
	35625.00	32334.00	31250.00
	36766.00	42068.00	40530.00
	28255.00	34864.00	33973.00
	32658.00	35521.00	33135.00
Mean	31797.00	35744.00	34366.00
Std. Dev.	4260.00	5572.00	4883.00

9-25-87

Intensities of characteristic mass ion fragments.
Exposure=7.3 ppm TCE standard (1 HR AND 50 MIN.).
Electron multiplier= 3.00 eV.
LOT 3.

	94.00	130.00	132.00
	48425.00	47517.00	44783.00
	34933.00	44273.00	42715.00
	52976.00	59431.00	57865.00
	44978.00	50590.00	48648.00
	36322.00	55495.00	52978.00
	57621.00	47836.00	59672.00
	59634.00	48654.00	60046.00
	54469.00	62515.00	62136.00
Mean	48670.00	53289.00	53605.00
Std. Dev.	9315.00	6634.00	7470.00

10-2-87

Intensities of characteristic mass ion fragments.
Exposure=7.3 ppm TCE standard (1 HR AND 28 MIN.).
Electron multiplier= 3.00 eV.
LOT 4.

	94.00	130.00	132.00
	30860.00	39459.00	37192.00
	13348.00	37243.00	36049.00
	25702.00	38903.00	36241.00
	24178.00	43744.00	40336.00
	19300.00	39134.00	26698.00
	14549.00	44990.00	43516.00
	27159.00	38419.00	35266.00
	37973.00	39164.00	34625.00
	15029.00	37406.00	36875.00
	27718.00	41815.00	39719.00
Mean.	23582.00	39027.00	36662.00
Std.Dev.	7977.00	4344.00	4420.00

APPENDIX B: ADAMS COUNTY DATA

10-08-87

Intensities of characteristic mass ion fragments.
Exposure=7 Days buried in Adams County.
Electron multiplier= Decreased to 2.6 after 4th run.
FILE=SE18.01

	129.00	164.00	166.00	Em
A			46994.00	3.20
B			31027.00	3.00
C			25968.00	2.80
D			25352.00	2.80
E			42715.00	2.60 }
F			56441.00	2.60 }
G			55158.00	2.60 }
H			44023.00	2.60 }
I			26984.00	2.60 }
J			37186.00	2.60 }
MEAN			39184.80	
STD.DEV.			11113.99	

11-20-87

Intensities of characteristic mass ion fragments.
Exposure=4 Days buried in Adams County.
Electron multiplier= Decreased to 2.6 after 5th run.
FILE=SE20.01

	129.00	164.00	166.00	Em
A			29880.00	3.00
B			55731.00	3.00
C			32296.00	3.00
D			51260.00	2.80
E			49305.00	2.80
F			31803.00	2.60 }
G			38508.00	2.60 }
H			32557.00	2.60 }
MEAN			40167.50	
STD.DEV.			9664.31	

11-23-87

Intensities of characteristic mass ion fragments.
Exposure=4 Days buried in Adams County.
Electron multiplier= Constant at 2.6.
FILE=SE21.01

	129.00	164.00	166.00	Em
A			49388.00	2.60
B			37852.00	2.60
C			36654.00	2.60
D			34813.00	2.60
E			31991.00	2.60
F			40135.00	2.60
G			40858.00	2.60
H			28109.00	2.60
I			38865.00	2.60
J			38701.00	2.60
MEAN			37736.60	
STD.DEV.			5374.84	

11-23-87

Intensities of characteristic mass ion fragments.
Exposure=1 Days buried in Adams County.
Electron multiplier= Constant at 2.6.
File=SE22.01

	129.00	164.00	166.00	Em
A			25085.00	2.60
B			19077.00	2.60
C			23347.00	2.60
D			19482.00	2.60
E			21180.00	2.60
F			17662.00	2.60
G			17485.00	2.60
H			17864.00	2.60
I			13457.00	2.60
J			22759.00	2.60
MEAN			19739.80	
STD.DEV.			3250.73	

APPENDIX C: FCC WIRE EXPOSURE DATA

Intensities of Characteristic Mass Ion Fragments
Exposure=30, 50, 70, and 90 min.
Electron multiplier= 3.2

Intensity 106.00	130.00	132.00	Exposure Time (min.)
31473.00	8436.00	8279.00	30.00
32904.00	5080.00	4688.00	30.00
32558.00	7142.00	6720.00	30.00
33857.00	7852.00	7387.00	30.00
35619.00	9540.00	9079.00	30.00
28270.00	7605.00	6901.00	50.00
25617.00	7419.00	6999.00	50.00
32589.00	9819.00	9169.00	50.00
28108.00	10556.00	9966.00	50.00
26800.00	8131.00	7752.00	50.00
36239.00	18089.00	16967.00	70.00
29622.00	16270.00	15302.00	70.00
14362.00	13642.00	12684.00	70.00
24812.00	19786.00	19187.00	70.00
27975.00	23193.00	21659.00	70.00
39734.00	18914.00	18244.00	90.00
29589.00	19029.00	18576.00	90.00
28820.00	20460.00	19639.00	90.00
27471.00	20897.00	20198.00	90.00
35511.00	17892.00	17613.00	90.00

Relative Intensities of Mass Ion Fragments
Exposure=30, 50, 70, and 90 min.
Electron multiplier= 3.2

130/106	132/106	Exposure Time (min.)
0.27	0.26	30.00
0.15	0.14	30.00
0.22	0.21	30.00
0.23	0.22	30.00
0.27	0.25	30.00
0.27	0.24	50.00
0.29	0.27	50.00
0.30	0.28	50.00
0.38	0.35	50.00
0.30	0.29	50.00
0.50	0.47	70.00
0.55	0.52	70.00
0.95	0.88	70.00
0.80	0.77	70.00
0.83	0.77	70.00
0.48	0.46	90.00
0.64	0.63	90.00
0.71	0.68	90.00
0.76	0.74	90.00
0.50	0.50	90.00

APPENDIX D: FCC WIRE AND EIFC DATA

FCC WIRE DATA

	ION INTENSITIES				CONC. (ng)		FLUX (ng/m^2-Hr.)	
DESCRIPTION	111TCA	STD.TCA	TCE	STD.TCE	111TCA	TCE	111TCA	TCE
10 UG STD							HRS	DAYS
						EXPOSURE=	120.00	5.00
CLAY SITE A			5822	19243	ND	3026	ND	99237
CLAY SITE A			4946	19243	ND	2570	ND	84305
SAND SITE A			547	19243	ND	284	ND	9324
SAND SITE A			414	19243	ND	215	ND	7057
CLAY SITE A			5600	19243	ND	2910	ND	95453

	ION INTENSITIES				CONC. (ng)		FLUX (ng/m^2-Hr.)	
DESCRIPTION	111TCA	STD.TCA	TCE	STD.TCE	111TCA	TCE	111TCA	TCE
10 UG STD							HRS	DAYS
						EXPOSURE=	192.00	8.00
CLAY SITE A			8391	17742	ND	4729	ND	96954
CLAY SITE A			6883	17742	ND	3879	ND	79530
CLAY SITE A			3375	17742	ND	1902	ND	38996
SAND SITE A			867	17742	ND	489	ND	10018
SAND SITE A			1669	17742	ND	941	ND	19284
SAND SITE A			1079	17742	ND	608	ND	12467

	ION INTENSITIES				CONC. (ng)		FLUX (ng/m^2-Hr.)	
DESCRIPTION	111TCA	STD.TCA	TCE	STD.TCE	111TCA	TCE	111TCA	TCE
10 UG STD							HRS	DAYS
						EXPOSURE=	240.00	10.00
SAND/CLAY SITE B	3020	969			31166	ND	511125	ND
SAND/CLAY SITE B	2690	969			27761	ND	455273	ND
SAND/CLAY SITE B	1650	969			17028	ND	279257	ND
SAND/CLAY SITE B	3910	969			40351	ND	661754	ND
CONGL. SITE B	970	969			10010	ND	164169	ND
CONGL. SITE B	530	969			5470	ND	89701	ND
CONGL. SITE B	756	969			7802	ND	127950	ND

FLUX CHAMBER DATA

DESCRIPTION	CONCENTRATION (PPM)							
DESCRIPTION	111TCA	TCE	11DBE	112TCA	111TCA	TCE	11DBE	112TCA
.10 PPM STD	RECOVERY EFFICIENCY				ABSOLUTE FLUX			
	95.8 %	74.6 %		88.7 %			(ng/m^2·Hr.)	
						40 L		
BLANK	0.0068	0.0090	0.1000	0.0000	21	36	315	0
STD	0.0932	0.0910	0.1000	0.1000	294	369	315	460
SITE A CLAY	0.0605	1.9653	0.1000	0.0000	0	7959	315	0
SITE A CLAY	0.0102	0.4142	0.1000	0.0000	0	3355	315	0
SITE A CLAY	0.0074	0.3232	0.1000	0.0000	0	2618	315	0
SITE A CLAY	0.0023	0.1271	0.1000	0.0000	0	2059	315	0
SITE A CLAY	0.0030	0.1235	0.1000	0.0000	0	2001	315	0

DESCRIPTION	111TCA	TCE	11DBE	112TCA	111TCA	TCE	11DBE	112TCA
.10 PPM STD	RECOVERY EFFICIENCY					ABSOLUTE FLUX		
	95.8 %	74.6 %		88.7 %			(ng/m^2-Hr.)	
						27	L	
BLANK	0.0032	0.0059	0.1000	0.0000	20	48	631	0
STD	0.0968	0.0941	0.1000	0.1000	610	762	631	681
SITE A CLAY	0.0492	1.1812	0.1000	0.0286	0	9567	631	0
SITE A CLAY	0.0299	0.7180	0.1000	0.0351	0	5816	631	0
SITE A CLAY	0.0203	0.4285	0.1000	0.0259	0	3471	631	0
SITE A SAND	0.0173	0.0484	0.1000	0.0000	0	392	631	0
SITE A SAND	0.0200	0.0364	0.1000	0.0000	0	295	631	0
SITE A SAND	0.0138	0.0307	0.1000	0.0000	0	248	631	0
SITE A SAND	0.0147	0.0306	0.1000	0.0000	0	248	631	0

DESCRIPTION	111TCA	TCE	11DBE	112TCA	111TCA	TCE	11DBE	112TCA
.10 PPM STD	RECOVERY EFFICIENCY				ABSOLUTE FLUX			
	95.8 %	74.6 %		88.7 %			(ng/m^2-Hr.)	
						27 L		
HEXANE BLANK	0.0035	0.0068	0.1000	0.0000	22	55	631	0
STD	0.0965	0.0932	0.1000	0.1000	609	755	631	681
SITE A CLAY	0.6911	1.2367	0.1000	0.1337	0	10016	631	0
SITE A CLAY	0.1921	0.5115	0.1000	0.0491	0	4143	631	0
SITE A CLAY	0.4289	0.6871	0.1000	0.0704	0	5565	631	0
SITE A CLAY	0.3360	0.3889	0.1000	0.0360	0	3150	631	0
SITE A SAND	0.0100	0.0306	0.1000	0.0000	0	248	631	0
SITE A SAND	0.0138	0.0262	0.1000	0.0000	0	213	631	0

CONCENTRATION (ug/L)

DESCRIPTION	111TCA	TCE	11DBE	112TCA	111TCA	TCE	11DBE	112TCA
.10 PPM STD	RECOVERY EFFICIENCY				ABSOLUTE FLUX			
	95.8 %	74.6 %		88.7 %			(ng/m^2-Hr.)	
							27 L	
BLANK	0.0088	0.0081	0.0000	0.0000	55	66	0	0
STD	0.0912	0.0919	0.1000	0.1000	575	744	631	681
SITE B CLAY/SAND	3.9034	0.0447	0.1000	0.0000	24619	0	631	0
SITE B CLAY/SAND	1.7270	0.0068	0.1000	0.0000	10893	0	631	0
SITE B CLAY/SAND	1.9554	0.0145	0.1000	0.0000	12333	0	631	0
SITE B CLAY/SAND	1.1787	0.0134	0.1000	0.0000	7434	0	631	0
SITE B CONGL.	0.4827	0.0088	0.1000	0.0000	3045	0	631	0
SITE B CONGL.	0.6063	0.0134	0.1000	0.0000	1912	0	631	0
SITE B CONGL.	0.2259	0.0043	0.1000	0.0000	1425	0	631	0
SITE B CONGL.	0.2320	0.0042	0.1000	0.0000	1463	0	631	0

CONCENTRATION (ug/L)

DESCRIPTION	111TCA	TCE	11DBE	112TCA	111TCA	TCE	11DBE	112TCA
.10 PPM STD	RECOVERY EFFICIENCY				ABSOLUTE FLUX			
	95.8 %	74.6 %		88.7 %			(ng/m^2-Hr.)	
							27 L	
BLANK	0.0036	0.0076	0.1000	0.0000	22	61	631	0
STD	0.0964	0.0924	0.1000	0.1000	608	749	631	681
SITE B CLAY/SAND	3.7604	0.0000	0.1000	0.0000	23718	0	631	0
SITE B CLAY/SAND	1.9316	0.0000	0.1000	0.0000	12183	0	631	0
SITE B CLAY/SAND	2.0932	0.0000	0.1000	0.0000	6601	0	631	0
SITE B CLAY/SAND	1.1997	0.0000	0.1000	0.0000	7566	0	631	0
SITE B CONGL.	0.3862	0.0084	0.1000	0.0342	2436	0	631	0
SITE B CONGL.	0.4768	0.0138	0.1000	0.0191	1504	0	631	0
SITE B CONGL.	0.1917	0.0071	0.1000	0.0000	1209	0	631	0
SITE B CONGL.	0.1899	0.0090	0.1000	0.0000	1198	0	631	0