Soil Gas Analysis as a Predictor of VOC Concentrations in Groundwater and Stream Inflow

by

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Abstract

The spatial and temporal variability associated with soil gas sampling was investigated. Samples taken with a fixed point technique were found to have no short term variability. Spatial variability, due to probe installation, appears to be dependent on soil type. Soil gas measurements from replicate sampler installations in a homogeneous loam had a maximum variability of 22 percent, while in a sandy loam with pebbles and cobbles strewn throughout it the maximum variability was 260 percent. A seasonal decrease in mean soil vapor concentration of 1,1,1-TCA, from September to December, was noted. The concentration decrease followed the same trend as soil temperature, but could not be explained solely on the basis of decreases in the temperature dependent Henry's constant, indicating that other variables may be important. Repeated sampling at three sites on the Aberjona watershed indicated that the trend in barometric pressure during the previous 24 hours may be inversely correlated with changes in soil gas concentration.

The correlation between VOC composition in soil gas and stream inflow was also determined. Only 40 percent of the VOCs present in stream inflow were detected in the soil gas of adjacent sites. Differences in soil gas and stream inflow composition may be due to several factors including bio-mediated chemical transformations and the passage of time between stream inflow and soil gas surveys. In all areas where stream inflow of anthropogenic VOCs occurred, however, VOC contamination was noted in soil gas.

Thesis Advisor: Harold Hemond
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“Come, wash the night-time clean.
Come, grow the scorched ground green.”

Bob Weir and John Barlow, *Cassidy*

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Chapter 1. Introduction

1.1 Watershed Background

In May of 1979 two municipal wells (wells G and H) supplying drinking water to the town of Woburn, Massachusetts were tested and found to contain elevated concentrations of several volatile organic compounds (VOCs) which appear on the U. S. Environmental Protection Agency's (EPA) list of priority pollutants. A series of studies in 1980-81 by the Massachusetts Department of Public Health revealed an elevated level of childhood leukemia in Woburn as compared to the national average (Parker and Rosen 1981). A subsequent study by Lagakos et al. (1986) found a significant correlation between exposure to water from the wells and the occurrence of childhood leukemia, lung/respiratory tract and kidney/urinary tract disorders.

The Aberjona watershed (figure 1.1) encompasses most of the town of Woburn as well as parts of Stoneham, Winchester, Wilmington, Burlington, Lexington and Reading. The watershed, located approximately 12 miles north of Boston, has been the site of industrial activity since the mid-nineteenth century. Major industries which were situated on the watershed include tanneries, chemical plants and textile and paper manufacturers (Lagakos et al. 1986). Many of these companies have been responsible for widespread pollution on the watershed.

1.2 Stream Inflow

Several sites on the Aberjona watershed, other than wells G and H, have been found to contain elevated levels of several species of VOCs. Although they

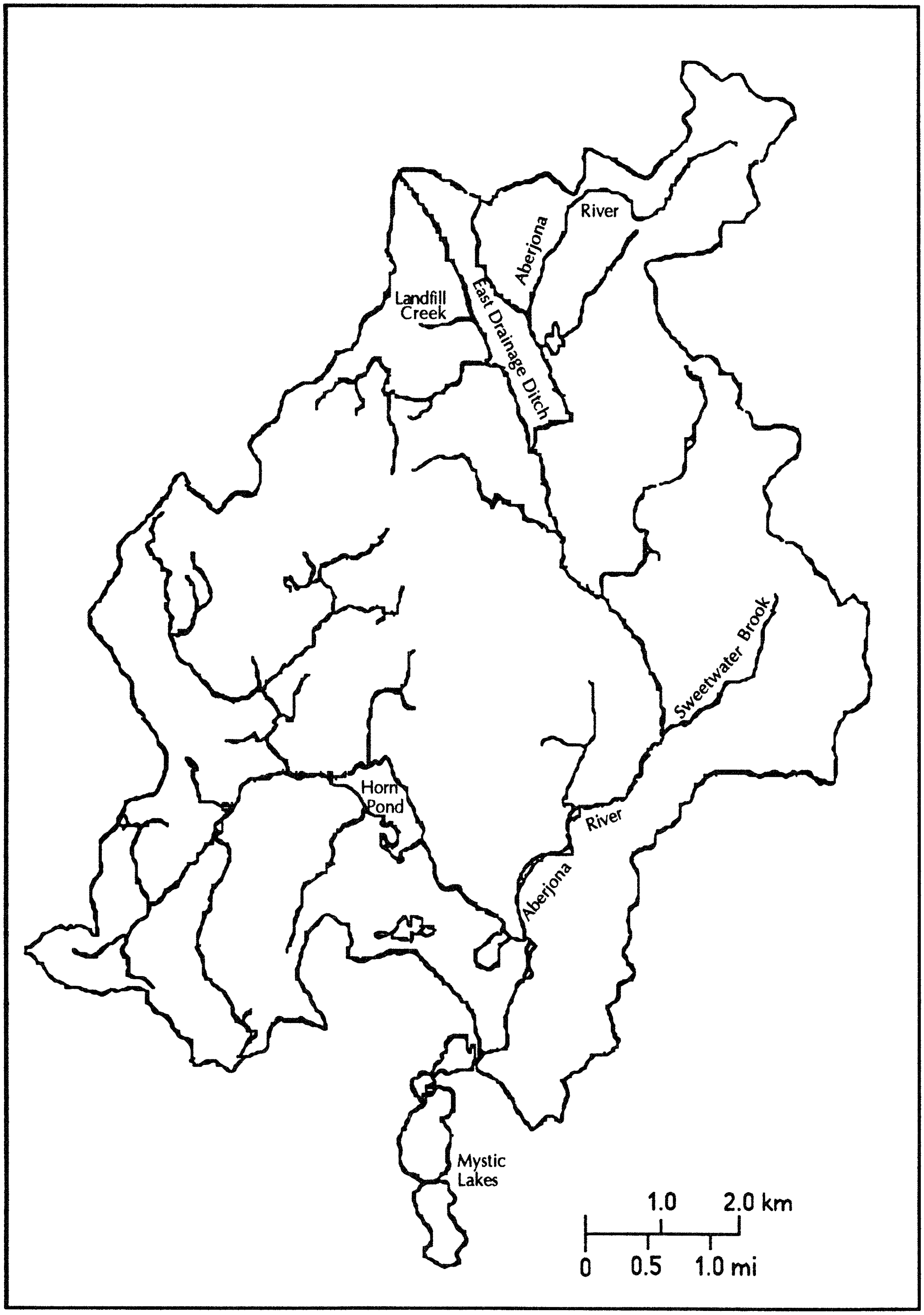

Figure 1.1: Aberjona Watershed

may no longer be influencing drinking water supplies there are still many questions that can be asked concerning their sources and paths of migration. A number of these areas of VOC contamination have been found to be flowing though the ground into adjacent surface waters of the watershed (Kim 1992). This raises the question of possible human exposures through contact with these surface waters. In addition there have been some indications that adverse health effects can be caused by outgassing of VOCs from the ground (Moseley and Meyer 1992, Michael et al., 1990).

1.3 Soil Gas Monitoring

Soil gas monitoring is a technology which was first developed in the early 1980s (Spittler 1980, Marrin and Thompson 1984, Voorhees, Hickey and Klusman 1984, Spittler, Clifford and Fitch 1986) and has since gained widespread acceptance as an extremely useful tool in the determination of VOC contamination in the subsurface. Since this time active soil gas sampling has gained widespread acceptance over passive, sorptive equilibrium sampling because of its ability to give real time results that can immediately be interpreted and used as a basis for further sampling.

By carefully and thoughtfully employing gas surveying techniques it is possible to delineate one or more distinct areas of contamination by a host of volatile pollutants (Tillman et al. 1989). In addition soil gas sampling is useful for identifying multiple point sources and the extent of plume migration (Crockett and Taddeo 1988). C_1 and C_2 halogenated hydrocarbons are the most easily detectable VOCs in soil gas over a wide range of conditions, due to high Henry's constants, high diffusion coefficients and resistance to degradation (Marrin 1987).

1.3.1 Soil Gas / Groundwater Correlation

Theoretically soil gas concentrations of VOCs, in a homogenous material at steady state, will decrease linearly with depth above the water table as shown in the analogous situation of steady state heat flow through a solid (Thibodeaux 1979, Carslaw and Jaeger 1959). In theory then, by knowing the gas concentration at a certain depth above the water table it should be possible, using Henry's Law, to predict the concentration of VOCs in the groundwater. It has been noted in several studies that the best correlation between soil gas and groundwater distribution of VOCs is found when soil gas samples are taken as close to the water table as possible or in homogeneous soils above shallow water tables (Kerfoot 1990, Tolman and Thompson 1989, Marrin 1987, Marrin and Thompson 1987, Kerfoot 1987).

Marrin and Thompson (1987) found a linear correlation (correlation coefficient of 0.90) between shallow soil gas concentration of TCE (< 2 meter depth) and ground water concentration above a 35 meter deep water table. Kerfoot (1987) found a linear correlation of chloroform concentration with depth ($r = 0.99$). Groundwater was present at a depth of 3 - 5 meters below the ground surface and was overlain by a soil described as "gravelly sandy loam with a clay content of 2 - 8 % that decreases with depth." Kerfoot (1990) found a linear correlation ($r = 0.88$) between TCA concentration in soil gas and in ground water.

Unfortunately in most field situations homogeneous soil conditions do not exist and the depth to the water table is often more than just a few meters. In these cases it is often impossible to obtain an accurate correlation between soil gas and groundwater VOC concentrations. For example, Kerfoot (1987) found anomalous data points in areas where perched water was encountered. The need to consider unsaturated zone stratigraphy when planning or interpreting the results of a soil gas survey was noted in this study. Tolman and Thompson (1989) also observed that groundwater contaminant plumes may be inaccurately depicted due geological obstructions in the vadose zone. Marrin and Thompson (1984) found a logarithmic "correlation" between TCE concentration in shallow soil gas and in groundwater at 110 to 125 feet. Variations from a linear profile of soil gas concentration with depth appear to be explainable by changes in soil stratigraphy. For example, a higher porosity gravel layer appears to be a gas conduit giving higher than expected concentrations in some areas and lower than expected concentrations in others.

In addition to stratagraphic concerns, problems may be encountered when monitoring compounds other than C_1 and C_2 halocarbons. Halogenated propanes, propenes and benzenes and C_9 to C_{12} petroleum hydrocarbons tend to remain near the water table once they have partitioned into the soil gas due to their low vapor pressures and gas diffusion coefficients (Marrin 1987). C_1 to C_8 petroleum hydrocarbons may undergo oxidation once they have partitioned into the soil gas. For accurate detection of both of these sets of compounds it is necessary to sample as close as possible to the water table (Marrin 1987, Tolman and Thompson 1989). For BTX compounds Kerfoot and Soderberg (1988) found a logarithmic distribution of concentrations with depth.

1.4 Goals and Hypothesis

1.4.1 Development of Soil Gas Monitoring Stragedy

The initial goal of this research was to develop a soil gas monitoring system that would provide the precision necessary to usefully analyze of the data that I was collecting. The system of gas collection and analysis was developed during the initial groundwater plume mapping studies. A complete description is contained in chapter 2.

1.4.2 Temporal and Spatial Variability of VOCs in Soil Gas

An attempt was made to understand the temporal and spatial variables that may control the distribution of VOCs in soil gas. It was initially believed that changes in atmospheric pressure, soil moisture and soil temperature would control the subsurface gas concentrations of VOCs. It was expected that spatial differences in soil gas profiles would be noted due to large scale variations in soil structure. In order to come up with any statistically significant correlations of spatial and temporal variables with changes in soil gas composition it was necessary to understand the extent of the variability due to the act of sampling soil vapor.

1.4.3 Contaminant Distribution and Correlation with Stream Inflow Data

The applicability of stream inflow monitoring as a predictor of VOC contamination in adjacent soil gas was tested. It was initially expected that there would be good correlation between stream inflow data obtained by Kim (1992) and soil gas monitoring. A correlation of these two studies would indicate that stream inflow could accurately predict groundwater VOC contamination. The results of these studies are presented in Chapter 3.

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Chapter 2 - Variability in Soil Gas Sampling

2.1 Introduction

2.1.1 Soil Gas Sampling

In order to determine the factors which affect soil gas distributions it is first necessary to gain an understanding of the precision of the sampling method that is being used. A major goal of this work was to gain an understanding of the magnitude of variations in the concentration of volatiles, in soil vapor, that occurred due purely to the sampling technique. Only once this is done can the data obtained be used to indicate anything other than gross presence of VOCs. Only a few previous studies have even postulated about the effects that the sampling itself may have on the results which are obtained. Many authors have all but ignored this question, merely assuming that by using an accepted sampling method they could insure that sampling induced variability was sufficiently small, and did not affect their results.

The sampling method which was investigated was based on the type active soil monitoring setup which has gained widespread acceptance in the detection of VOCs in soil gas in areas of contaminated soil and groundwater. It was hoped that the results would provide a much needed error budget for an accepted methodology which has long been lacking one.

2.1.2 Temporal and Spatial Soil Gas Variability

Soil gas measurements may show large variations from one sampling time to another due to apparent temporal changes which may alter a soil's physical and chemical properties. Factors such as changes in barometric pressure, soil moisture and rainfall have all been invoked to qualitatively explain variability in soil gas composition in the case of VOCs (Spencer 1970, Tinsley 1979, Swallow 1983, Reisinger et al. 1987, Tolman and Thompson 1989, Culver et al. 1991, and Davis et al. 1991), CO_2 (Reardon et al. 1979) and radon (Kraner et al. 1964, Schery et al. 1984). None of these studies however, has attempted to account for the variability of the sampling process when interpreting their results, leading to great uncertainty about some of the correlations which are presented.

In addition to temporal changes in soil gas composition there are spatial variations in soil gas signals. It is important when sampling soil gas for VOCs to understand differences in signals between sampling points due to soil composition and sampling depth. In shallow aquifers it has been noted that slight variations in distance to the water table may result in significant changes in soil gas concentrations (Marrin 1987). It has been claimed that differences in soil organic content between sampling points may also have a noticeable effect on the concentrations of VOCs in pore air (Spencer 1970). Soil porosity may also affect signals determined by soil gas monitoring, as the diffusivity of a gas through a porous solid is proportional to the air filled porosity (Buckingham 1904, Penman 1940, Reisinger et al. 1987).

Previous studies of soil gas variability have not looked at the differences in soil gas signals due to sampling methods. Among studies which have mentioned the resolution of gas sampling only gross qualitative statements have been made. Marrin (1987) advises that soil gas sampling should be done on intervals no less than fifty feet apart because "the resolution of the technique is exceeded." Tillman et al. (1989), on the other hand, suggest that VOCs in the ground will most accurately detected when fine grids are used. The fact that these two authors disagree on the resolution of soil vapor surveys that and neither attempts to quantitatively support their assertions gives an impetus to quantitatively address variability in soil gas measurements due purely to the act of sampling.

The goal of this research was to attempt to provide an error budget which can predict sampling variability. It was first necessary to accurately determine and account for the analytical uncertainty associated with the equipment used. A sampling methodology needed to be developed that adequately addressed the questions of how or if steady state, representative soil gas samples could be obtained. The temperature response of the analytical equipment also needed to be accounted for. Once all of this was accomplished, it was possible to begin assaying the short term temporal and spatial variability associated with the sampling method itself.

It was initially expected that sampling induced variability would be almost statistically insignificant. Based on previous work on temporal and spatial variability of soil gas it was thought that sampling variability would be secondary to spatial variability induced by macro zonation throughout the soil column and short term temporal variability produced by changes in factors such as soil temperature, barometric pressure and soil moisture.

2.1.3 Pumping Equilibrium Time Investigation – Motivation

A major concern with the sampling method described below was that the pumping setup effectively and reproducibly sample soil gas at the desired depth. In order to do this it was necessary to insure that the soil gas that was being collected was representative of the actual composition. Efforts were made to determine the ideal number of tubing volumes to pump in order not to dilute air from the sampling point with either dead air in the sampling tube or air from surrounding zones in the soil, i.e. that pumping was not occurring for either too long or too short a time at a particular point.

Genereux (1988), in his studies of ^{222}Rn in soil gas, found significant variations in soil gas concentration versus pumping time profiles for three different sampling tubes. All three tubes showed a different time course. One suggestion for the differences was that soil layering could create preferential diffusion pathways near some sampling tubes. ^{222}Rn content in soil gas was found to be quite sensitive to the volume of gas withdrawn. Even in the cases where a steady state was, apparently, reached it did not occur at a consistent volume.

2.1.4 GC Temperature Response Investigation - Motivation

In addition to accounting for temperature in the determination of Henry's constants it was also necessary to account for the effect of temperature variability on the GC itself. It had been noted in early investigations that the sensitivity of the GC appeared to vary with temperature. It was necessary to understand this variation in order to accurately account for it when running standards and analyzing samples on the GC.

2.2 Materials and Methods

2.2.1 Sampling

The sampling and analytical techniques that were employed to delineate groundwater contamination, using soil gas monitoring, are based on the work of Spittler (1986, 1992b) and are representative of the techniques that are commonly used in soil vapor surveys (Kerfoot 1987, Marrin and Thompson 1987, Kerfoot and Soderberg 1988, Moseley and Meyer 1992). The method first involves making a hole in the ground down to the desired depth. Holes were made either with a 3.8 cm soil auger or a 1.1 cm diameter slide hammer tip. For

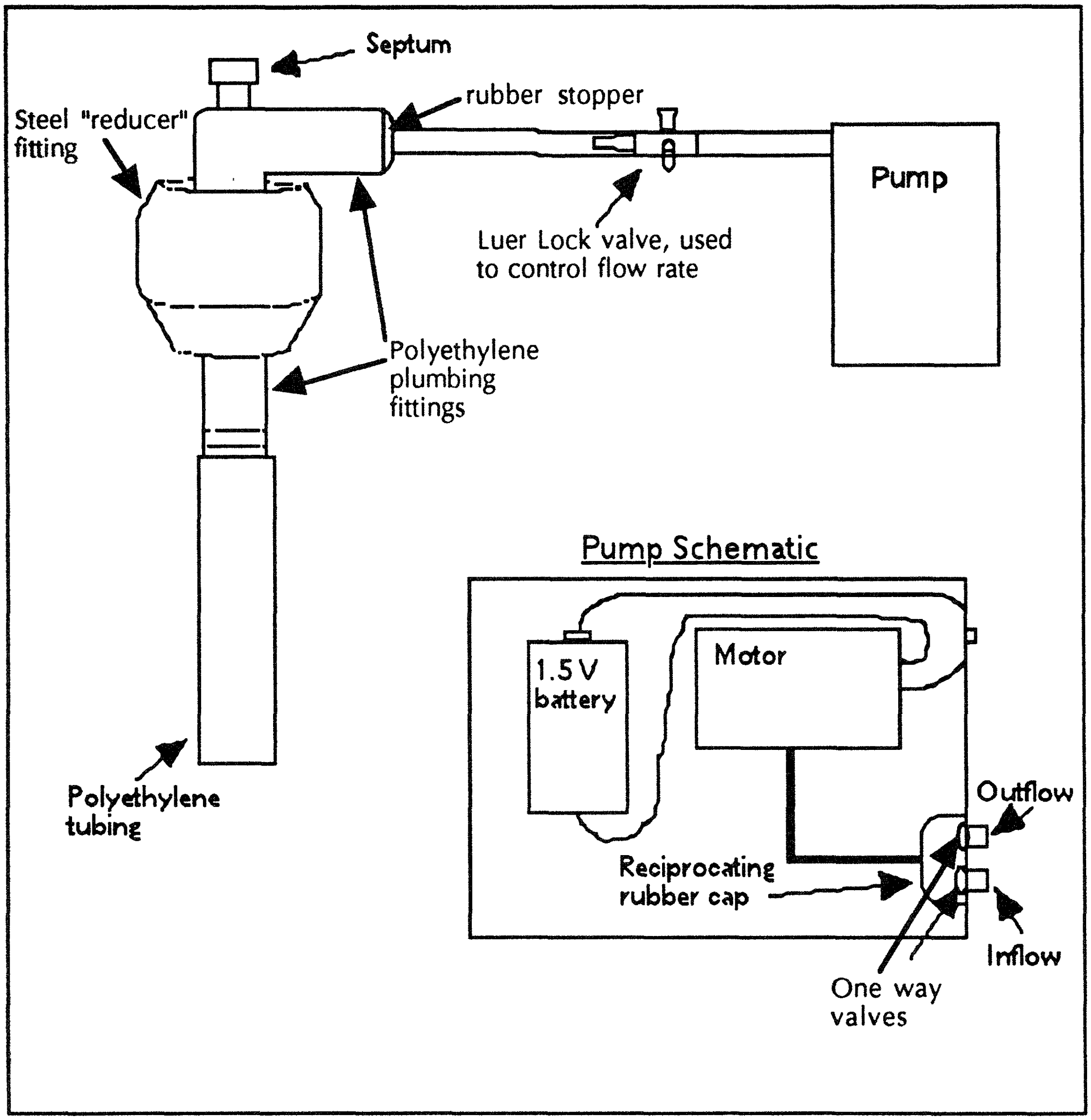

Figure 2.1: Gas sampling setup and pump schematic.

later studies the slide hammer was used exclusively because of the greater ease with which it went through rocky soils.

A length of polyethylene tubing (3.8 cm OD / 3.4 cm ID, or 1.1cm OD / 0.9 cm ID, depending on what size hole was made) which fit snugly in the hole was pushed down and capped with a sampling port which sealed the top of the hole (figure 2.1). The hole was then pumped out using a small battery powered pump attached to the sampling port (see section 2.3.1.1 for details on pumping). A Luer Lock® valve was installed in the pump line to control the pumping rate.

Gas samples were taken with one milliliter ground glass syringes sealed with house distilled water. The syringe needles were inserted through the sampling port septum and flushed five times with air from the pump stream just prior to sampling in order to allow sorptive equilibrium to be reached between the gas and the syringe walls (Spittler 1992b). Approximately 800 microliters of gas were pulled into the syringe and the needle of the syringe was sealed with a septum. The tubing was then removed from the ground, without turning off the pump. Several volumes of ambient air were pumped through the tubing in order to mitigate the problem of VOC sorption onto the tubing walls. Ambient air samples, taken between soil samples using this sampling setup and methodology, showed no contamination of the sampling port, tubing or syringes. After sampling was complete the holes were filled in with soil to avoid creating preferential diffusive pathways for the soil gas.

2.2.1.1 Testing for Variability Due to Sampling – Technique Descriptions

Three variations on the above technique were employed in order to determine where variabilities in sampling arose from. The first involved using the technique as presented above, filling and sampling the same point on the ground surface several times in a short period (1 to 2 hours); this is referred to as the ***same hole technique.*** During the same period, at the same intervals samples were taken at a fixed point. The ***fixed point technique*** employed the same sampling set up which was installed and then left in place. Sampling points were capped in order to assure that gases were not diffusing out through them between sampling. Using the results of these tests it was possible to determine the short term temporal variability of each technique, and a comparison could be made between the two.

The third method involved simultaneous sampling depth profiles of two points within 25 cm of each other. The two samplers were installed, within 30 seconds of each other, and the "simultaneous sampling" actually occurred 5 - 10 seconds apart. Only one depth profile was taken at each point in order to isolate the effects due purely to the initial punching of the hole in the ground. This is referred to as the ***simultaneous sampling technique.***

Soil gas sampling was performed on two separate sites on the Aberjona watershed. The first is on the old Woburn municipal landfill between a closed landfill cell and Landfill Creek. The soil at this location was a sandy loam with pebbles and cobbles which extended to a depth of approximately 1.5 meters, the maximum depth to the water table. The second site is located along a narrow section of land that runs between the East Drainage Ditch and Olin Inc. in Wilmington, MA. In this area the soil appeared to be a fairly homogeneous loam throughout the unsaturated zone. For more detailed site descriptions and maps see sections 3.1.1.1.1 and 3.1.1.2.

2.2.1.2 Monitoring Soil Temperature

Soil temperature was measured, at the landfill, using a six foot Omega 865™ temperature probe. The probe was placed in a hole, after soil vapor been sampled, and left for 5 minutes to allow thermal equilibrium to be reached. Temperature was recorded at 90 cm as very little spatial variation was observed at this depth.

2.2.2 Analysis

All analysis was performed on a Photovac 10A10™ photo-ionization gas chromatograph (GC) with a portable chart recorder. In the field both the GC and chart recorder were run off of a 125 watt ATR® 12 volt DC to 110 volt AC voltage inverter attached to a 12 volt marine battery. Nitrogen was used as the carrier gas for the GC. Over 90 percent of the time a 700 μL sample of soil vapor was injected, in all other cases the volume injected was less than this due to an error made in sampling or sample transport (correcting for different injection volumes is discussed in section 2.2.2.3). The maximum time between sampling and analysis was a half hour. The signal recorded was compared to the signal from a field standard which was run as conditions warranted (see section 2.3.1.2). The conversion between standard and gas sample signals and the correction for the various gas volumes injected is discussed in section 2.2.2.2. Because of ease of identification and its presence at several sites of interest 1,1,1-TCA was assayed as an indicator of overall variations in soil gas composition.

2.2.2.1 Standard Preparation and Use

All standards were prepared by diluting a known volume of the chemical or chemicals of interest in distilled deionized water. The initial dilutions for all standards were made at concentrations at least one order of magnitude below the solubility level of the solute in water. The solutions were then shaken lightly by hand and allowed to stand for 15 minutes to help insure complete dissolution. 10 mL of these dilute solutions were placed in 15 mL septa capped vials. The vials were inverted, so that the standard solution was in contact with the septa, in order to eliminate the flux from the gas phase through the septa. Any reduction in gas or water phase concentration in the standards was not detectable within the levels of analytical uncertainty.

By the knowing the water concentration of the VOC and the temperature, it was possible to obtain its Henry's constant and thus its gas phase concentration. Temperature dependent Henry's constants, for each compound of interest, were determined using a regression equation developed by Gossett (1987). The equation is as follows:

$$H = \exp[(A - B)/T] \ (\mathrm{m^3\ atm\ mol^{-1}}) \qquad \text{Equation 2.1}$$

A and B are empirical constants determined for each compound of interest and T is the temperature in Kelvin.

Volumes of headspace from the vials were injected into the GC as standards. Volumes injected ranged from 10 μL to 100 μL depending on the sensitivity of the GC to the compound. The GC was generally over an order of magnitude more sensitive to alkenes than alkanes.

2.2.2.3 Determination of Unknown VOC Concentrations

In order to determine the concentration of VOCs in a soil gas sample it was necessary to relate sample peak height to standard peak height. Measuring peak height was found to provide the same amount of precision as measuring peak area (for a discussion of method precision and accuracy see section 2.2.2.4). In many cases, it was in fact necessary to measure peak height because a crowding of neighboring peaks prevented accurate area measurement.

A relationship was developed which corrected for differences in the sample volume injected into the GC as it was not always possible to inject the same sample volume every time, and it was noted that the GC response to increase in injection volume was not linear. The equation which follows was developed based an equation suggested by Spittler (1992b):

$$C_{sample} = \left(\frac{H_{sample} * C_{std} * V_{std}}{H_{std} * V_{sample}} \right) * F_{vol} \qquad \text{Equation 2.2}$$

C_{sample} = Gas phase concentration a specific compound in the sample
H_{sample} = Peak height of sample
V_{sample} = Volume of sample injected
C_{std} = Gas phase concentration of compound in standard vial
H_{std} = Peak height of standard
V_{std} = Volume of standard injected
F_{vol} = Volume factor

The most important part of the equation was the development of F_{vol}. It was necessary to determine a different volume factor for each compound that expected to be encountered. A standard injection volume, for each compound, was determined based on the GC response to the compound. The volumes selected were 10 µL for Trichloroethylene (TCE), *cis* and *trans* 1,2-Dichloroethylene(DCE) and 100 µL for 1,1,1-Trichloroethane(TCA) and 1,1-Dichloroethane(DCA). Triplicate volumes of gas from standard solutions ranging from the standard volume up to 800 µL were injected and the peak heights were recorded. Thus equation 2.2 could be rearranged and F_{vol} could be determined for each volume. For *cis* 1,2-DCE and TCE the volume factor attained a constant value for volumes above 100 µL. Plots of F_{vol} versus volume

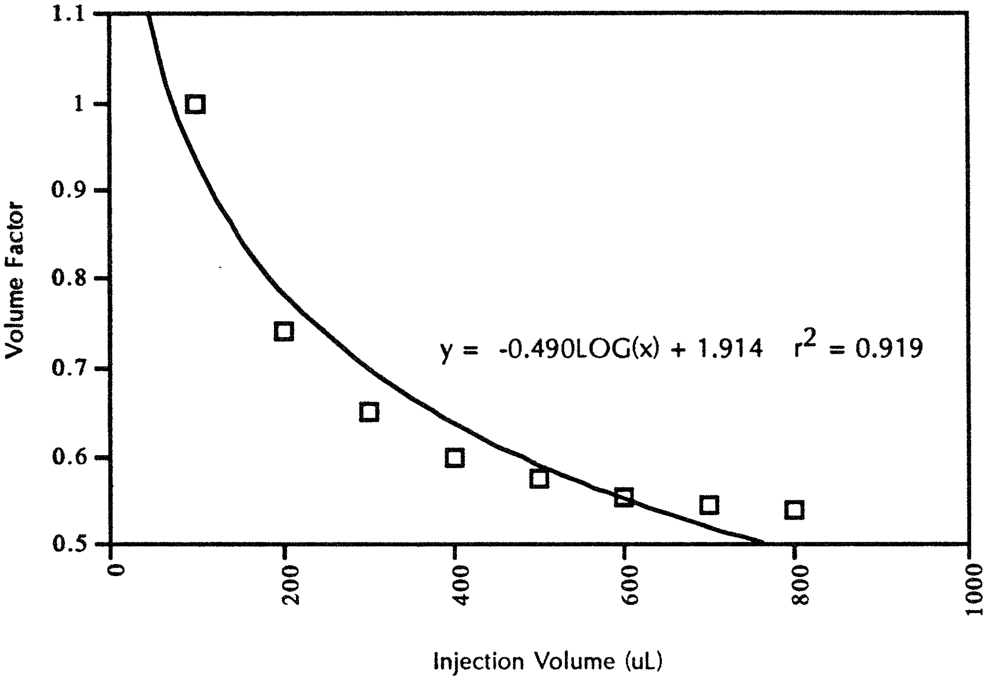

Figure 2.2: Volume factor determination for 1,1-DCA.

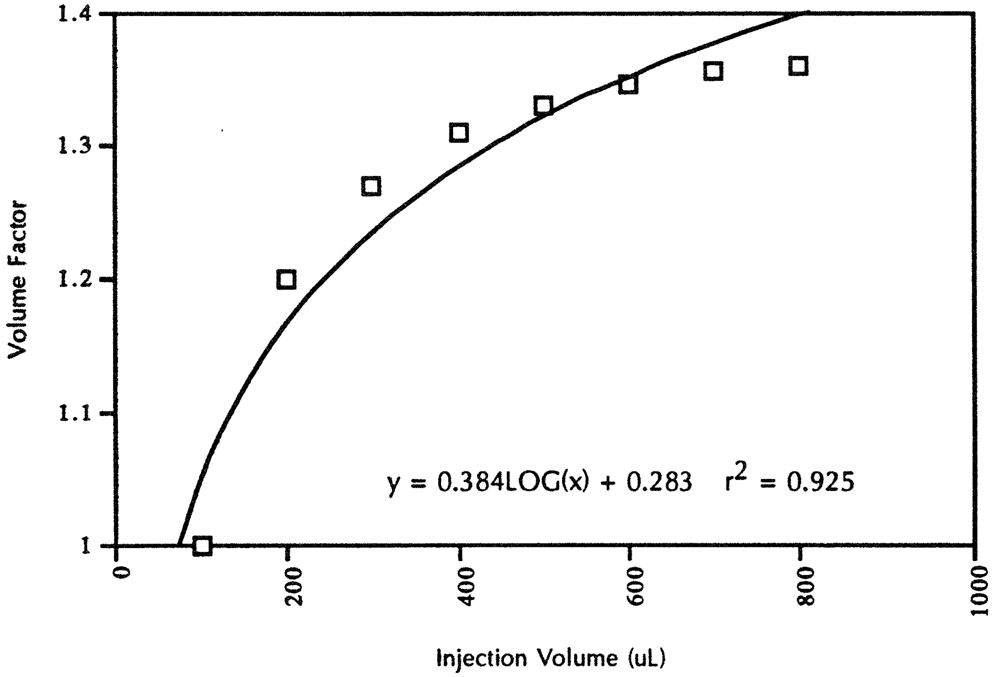

Figure 2.3: Volume Factor determination for 1,1,1-TCA.

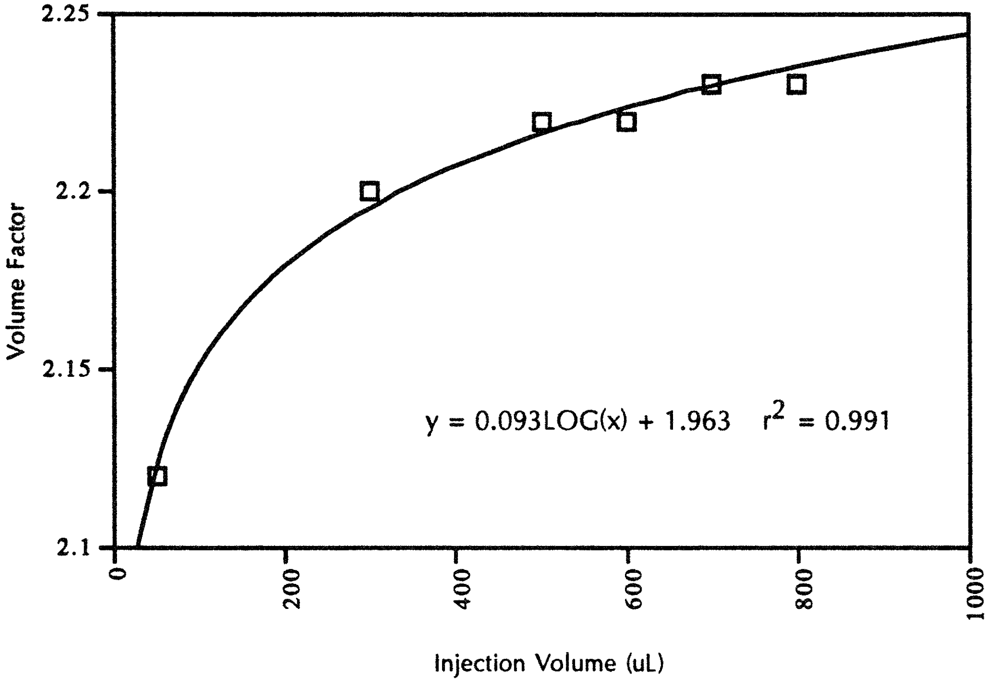

Figure 2.4: Volume factor determination for ***trans*** 1,2-DCE.

Compound	**Volume Factor**
trans 1,2-Dichloroethylene	1.963 + 0.093[Log(Volume)]
cis 1,2-Dichloroethylene	1.07
Trichloroethylene	1.11
1,1-Dichloroethane	1.914 - 0.49[Log(Volume)]
1,1,1-Trichloroethane	0.283 + 0.348[Log(Volume)]

Table 2.1: Volume Factor Summary.

for the other three compounds are presented in figures 2.2 through 2.4. The regression equations for F_{vol} obtained from these plots were used in determining the concentration of VOCs in soil gas samples. Table 2.1 presents a summary of the five volume factors that were obtained.

2.2.2.3 Analytical Precision

Any sample analyzed with the above methodology has a 95 percent confidence level of ±0.34 times the concentration value which was obtained. The 0.34 factor was calculated by running a 15 replicates of headspace above a standard solution on the GC and determining the standard deviation of the values obtained, the maximum deviation found was 16 percent. The 95 percent confidence level was then determined by multiplying the standard deviation by an empirical constant based on the number of standards run. For 15 runs this constant equals 2.12 (*Intro. Chem. Exper.* 1992) Because each data point from the field is the result of only one sample run the 95 percent confidence level is simply 2.12 times 16 percent, or 34 percent.

Statistical distinctions between data points were determined by evaluating the 95 percent confidence level of the difference of the two points. If y represents the absolute value of the difference between two data points, then in order for the points to be statistically different the value of y minus 2.13 times the standard deviation of y must be greater than zero. The statistical difference between two points is thus defined as this greater than zero value. The standard deviation of y is defined as follows:

$$\sigma_y = \sqrt{\sigma_{x_1}^2 + \sigma_{x_2}^2} \qquad \text{Equation 2.3}$$

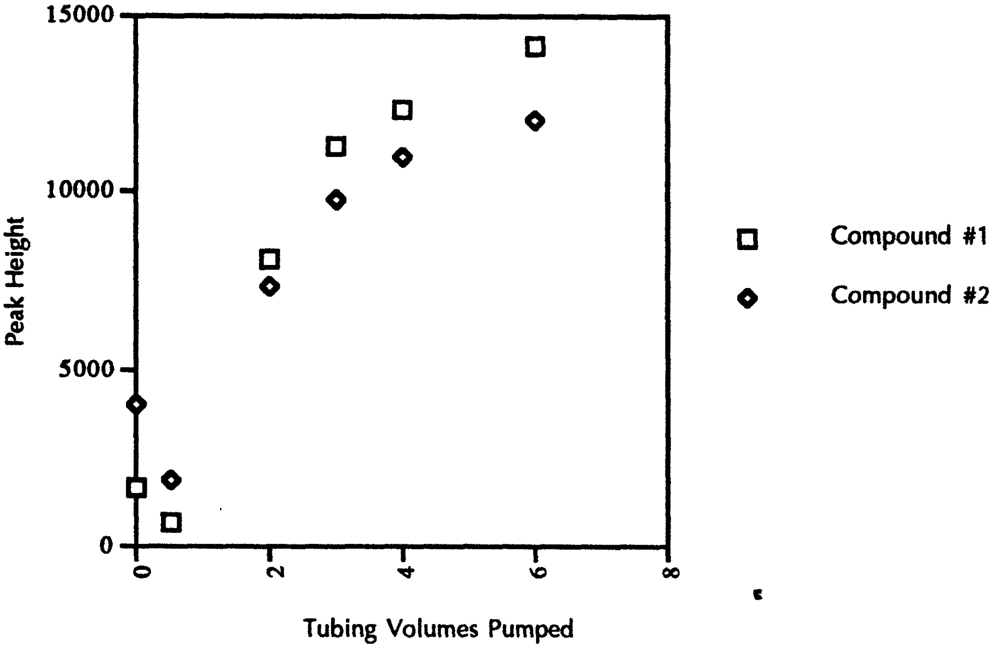

Figure 2.5: Peak height versus number tubing volumes pumped, point #1 (3.4 cm ID tubing).

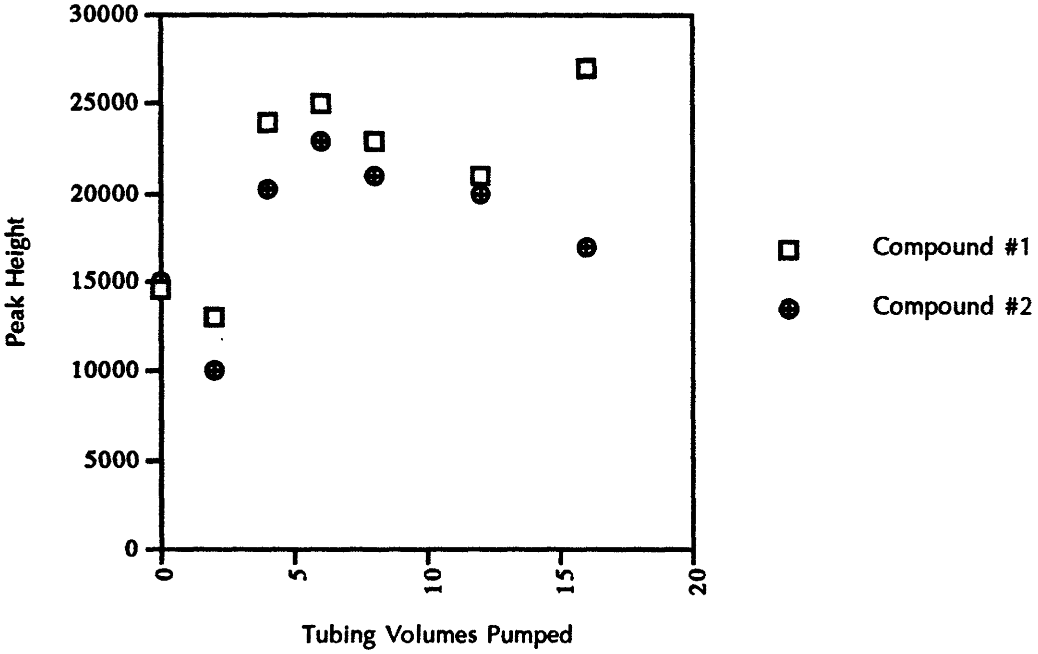

Figure 2.6: Peak height versus number of tubing volumes pumped, point #2 (0.9 cm ID tubing).

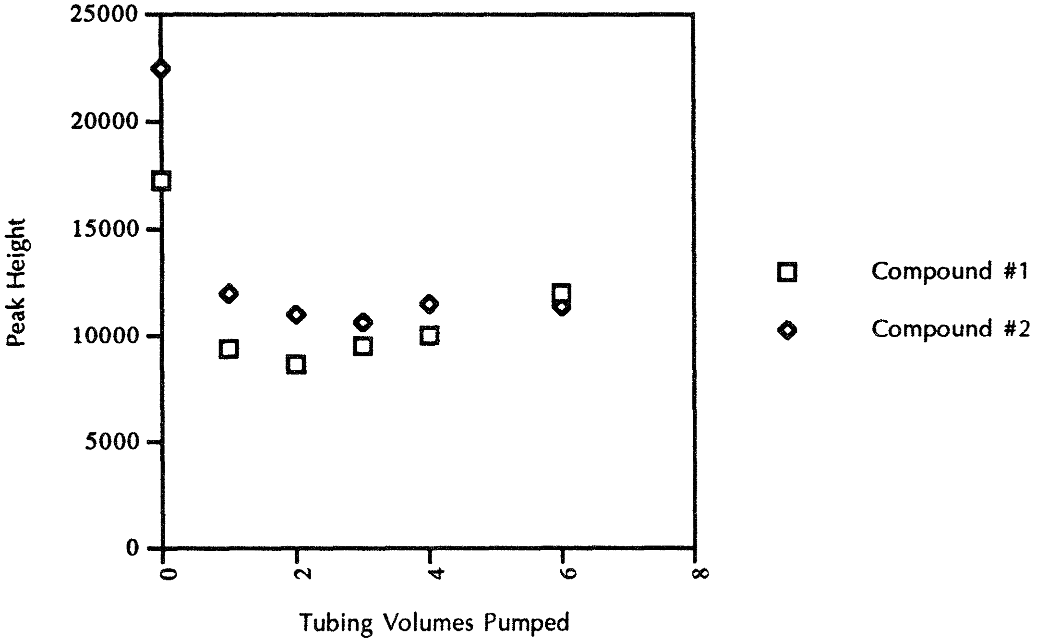

Figure 2.7: Peak height versus number of tubing volumes pumped, point #3 (3.4 cm ID tubing).

Where σ_{x_1} and σ_{x_2} are the standard deviations of the two data points. It was noted that precision appeared to increase as the operating temperature of the GC decreased during the fall and winter.

2.3 Results

2.3.1 Soil Gas Monitoring Methodology

2.3.1.1. Pumping Equilibrium Time

Profiles of gas concentration with time were determined at three sampling points adjacent to Landfill Creek. The three sites were chosen in different areas of the landfill in order to pump through zones which may have different characteristics. Two unknown compounds that provided extremely good sensitivity in gas chromatographic analysis, and were noted to occur at all sites that were investigated, were chosen for analysis. This was done in order to assure that low VOC concentrations, which were expected at early pumping times, could be accurately assayed.

Results of these tests are shown graphically in figures 2.5 through 2.7. (For discussion of expected error of the analytical technique see Section 2.2.2.3.) A 0.5 meter length of 3.4 cm ID tubing was used at points #1 and #3. a 1 meter length of 0.9 cm ID tubing was used at point #2. Graphs of the peak height profiles from points #1 and #2 (figures 2.5 and 2.6) show similar trends. Both start at low values and then after approximately three volumes have been pumped they both reach "steady state," i.e. statistically indistinguishable values. It should be noted that the second set of data values in both figures 2.5 and 2.6 are not statistically distinguishable from the initial ($t = 0$) points. Point #3 (figure 2.7) reaches "steady state" at approximately the same number of pump volumes as points #1 and #2, it however starts off with a high value at $t=0$ and

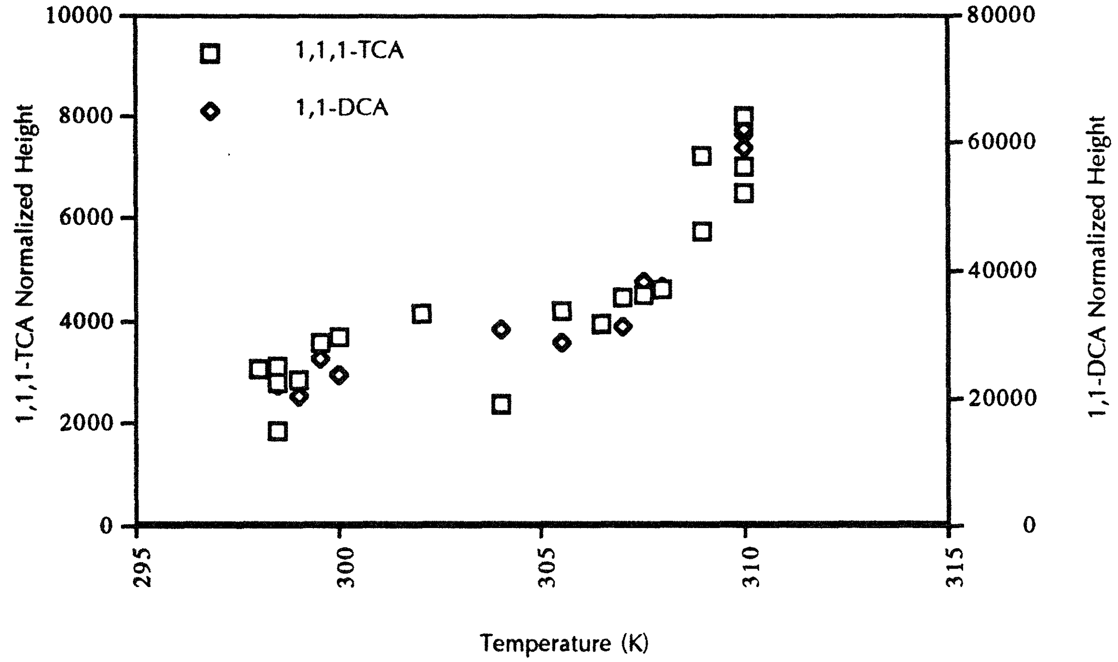

Figure 2.8: GC response as a function of temperature.

then decreases to this constant value. It is interesting to note that at all three points the concentration trends of the two compounds closely mirror each other, except at the final sampling of point #2.

Genereux (1988) in his study of radon, noted much greater variation in pumping / time profiles. Because in all three of the above test cases a steady state value appeared to be reached after approximately three pump volumes it was decided, following Genereux's advice, to only pump for a time sufficient to flush three volumes of air through the tubing, (a volume large enough to flush the tube but small enough to avoid flushing out much of the surrounding soil (Genereux, 1988)). It was necessary to avoid over flushing of the soil in order to assure that adequate resolution between the points in a vertical profile (usually 20 to 30 cm apart) was obtained. For a one meter length of 1.1 cm OD tubing 90 mL of air was pumped before sampling.

2.3.1.2 GC Temperature Response

The relationship of temperature to GC response is presented in figure 2.8. The same volumes of a standard solution of 1,1,1-Trichloroethane (1,1,1-TCA) and 1,1-Dichloroethane (1,1-DCA) were run during a two hour period on a summer day. Temperature increased as the van in which the GC was located sat in the sun with the doors and windows closed. The van was then allowed to cool back to its original temperature. 1,1,1-TCA and 1,1-DCA heights in the figure 2.8 were normalized to account for the effect of temperature on the Henry's constant; thus only behavior of the GC, and not of the standard solutions, is represented. The trend for both compounds shows a slight increase in peak height with increasing temperature up until approximately 309 K. At 309 K the GC appears to become extremely sensitive to temperature. This finding led to two actions. First the GC temperature was never allowed to exceed 309 K.

Secondly it was decided to run standards every time the temperature changed by two degrees in order to quantify the expected changes in GC response. When temperature remained constant standards were run every 1.5 to 2 hours. It was noted that cooler temperatures during the fall and winter appeared to reduce the absolute variability in the GC response.

2.3.2 Variability in Soil Gas Composition Due to Sampling Method

It should be noted that the error bars in figures 2.9 through 2.23 represent only the 95 percent confidence level associated with each sampling point. The actual statistical difference between points (or lack there of) is determined by the 95 percent confidence level of the difference of two points, and is not actually represented on the graphs. Values of the statistical differences between all sets of two points which were compared are presented in appendix 1.

2.3.2.1 Sampling Using Same Hole Technique

The results for sampling of a point then filling the hole immediately after initial sampling and sampling again at a later time (same hole technique) are presented in figures 2.9 through 2.14. Figures 2.9 and 2.10 show the changes in 1,1,1-TCA concentration, at the landfill, throughout the day on 12/8/93. The two points sampled that these figures were located 25 cm apart and were sampled simultaneously. Different trends with time are noted both between the two sampling points as well as between different depths in the same profile.

Figures 2.11 and 2.12 (landfill 12/10/93) and 2.13 and 2.14 (East Drainage Ditch 12/12/93) present the differences in profiles obtained at single points using the same hole technique. Each of the figures shows a different pattern through the depth profile. In no place was there agreement between all points within a profile.

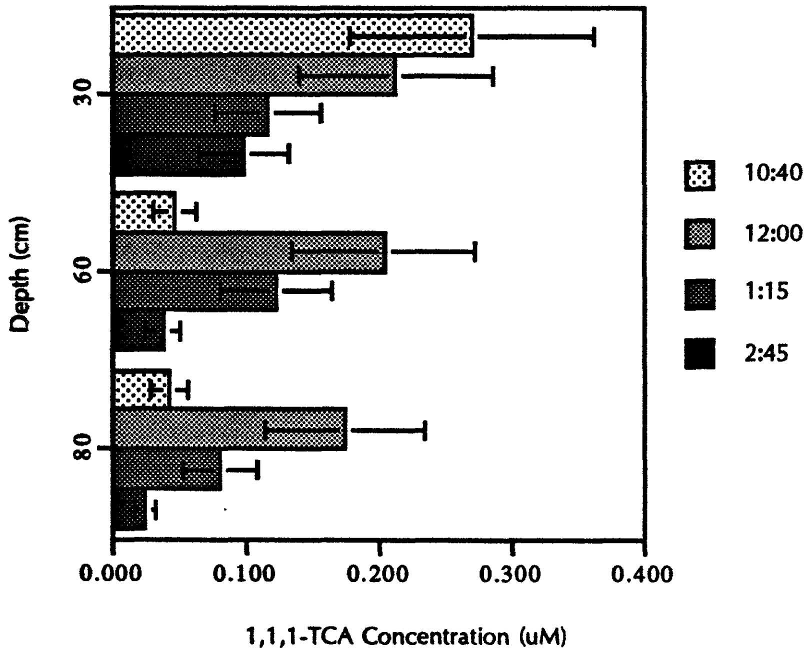

Figure 2.9: Point I-west (located 25 cm from I-east {figure 2.10}, sampled simultaneously) gas concentrations at three depths at 10:40. 12:00, 1:15 and 2:45 (landfill 12/08/93). Error bars indicate the 95 percent confidence level associated with each point.

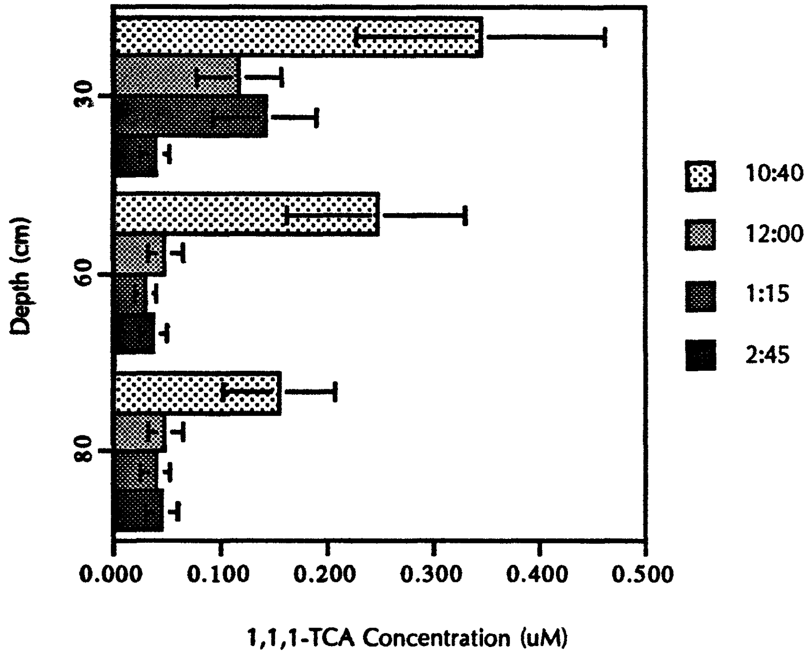

Figure 2.10: Point I-east (located 25 cm from I-west {figure 2.9}, sampled simultaneously) gas concentrations at three depths at 10:40. 12:00, 1:15 and 2:45 (landfill 12/08/93). Error bars indicate the 95 percent confidence level associated with each point.

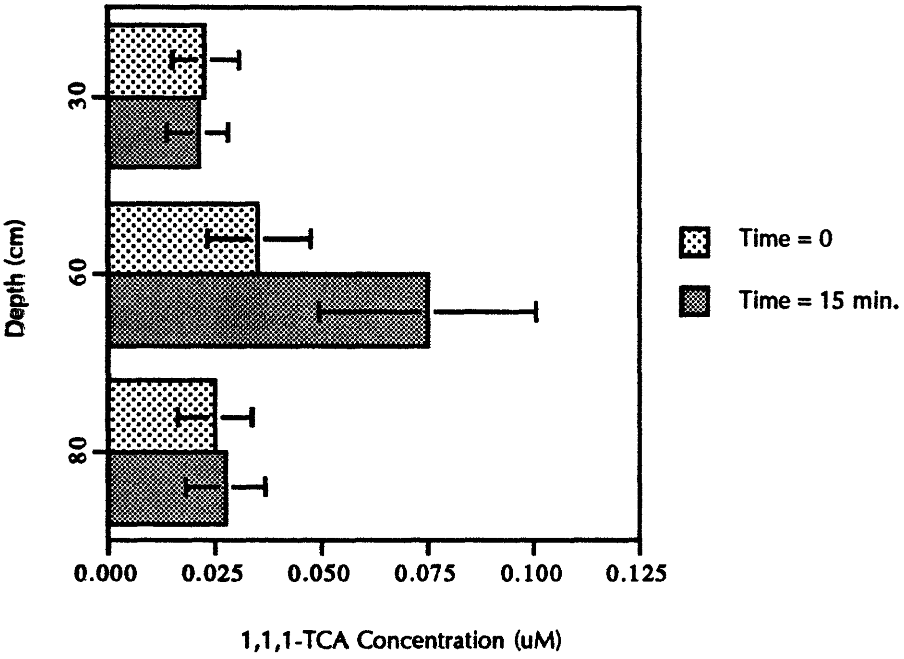

Figure 2.11: Variation in vertical soil gas profile obtained by sampling a point, filling it in and sampling again in 15 minutes, (landfill 12/10/93). Error bars indicate the 95 percent confidence level associated with each point.

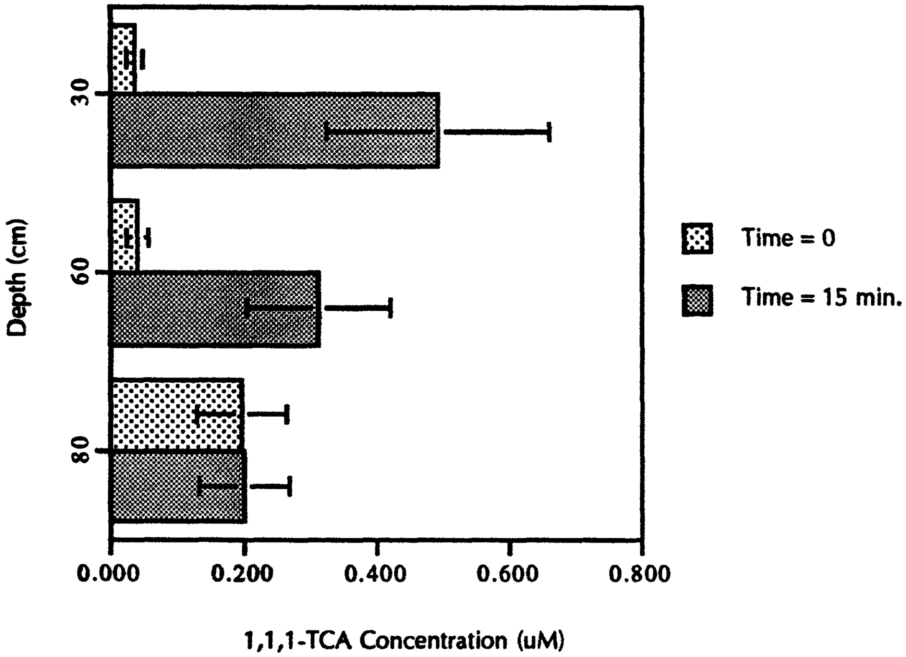

Figure 2.12: Variation in vertical soil gas profile obtained by sampling a point, filling it in and sampling again in 15 minutes, (landfill 12/10/93). Error bars indicate the 95 percent confidence level associated with each point.

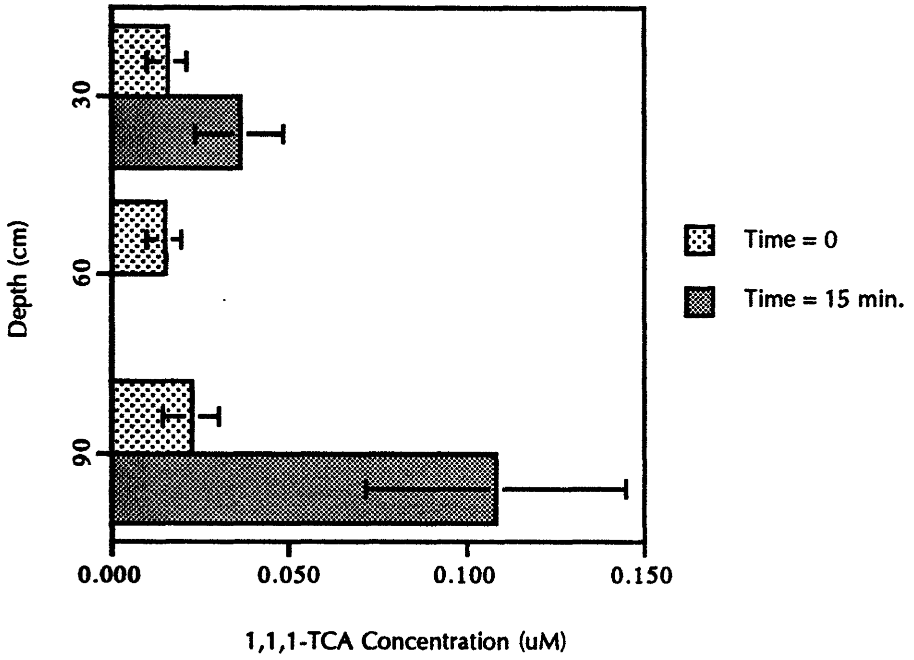

Figure 2.13: Variation in vertical soil gas profile obtained by sampling a point, filling it in and sampling again in 15 minutes, (East Drainage Ditch 12/12/93). No data for 60 cm at t = 15 min. Error bars indicate the 95 percent confidence level associated with each point.

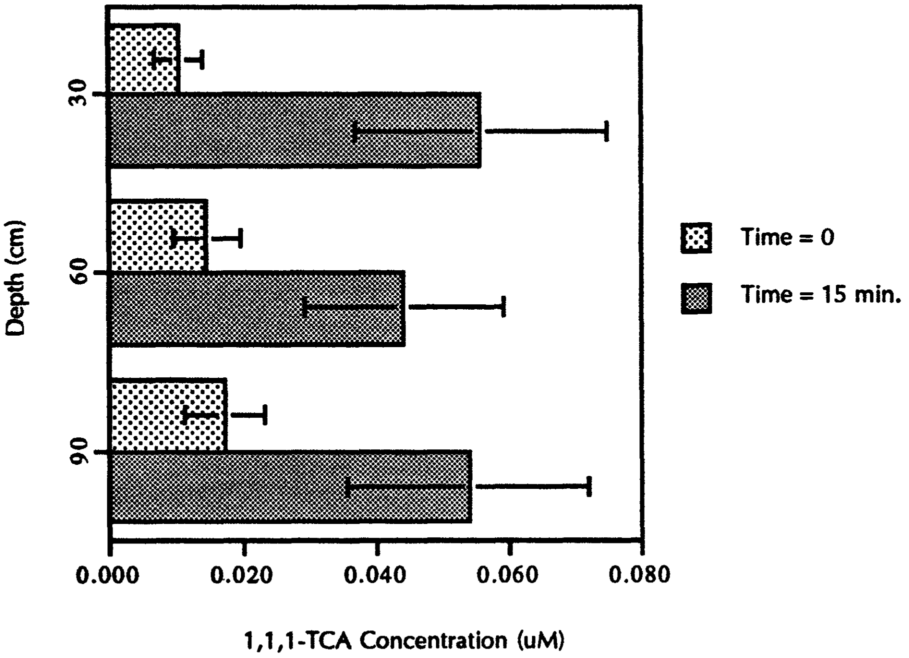

Figure 2.14: Variation in vertical soil gas profile obtained by sampling a point, filling it in and sampling again in 15 minutes, (East Drainage Ditch 12/12/93). Error bars represent the 95 percent confidence level associated with each point.

2.3.2.2 Sampling Variability of the Fixed Point Technique

2.3.2.2.1 Short Scale

The initial data that were taken on the variation at a fixed point were presented in section 2.3.1.1 in looking at pumping times. Samples were taken from a fixed point at zero to eighteen volumes pumped (0 - 240 seconds). In all cases after 3 volumes were pumped the gas concentrations did not experience any statistically distinguishable fluctuation.

2.3.2.2.2 Longer Scale

The data obtained at the landfill and East Drainage Ditch, with fifteen minute intervals between sampling are presented in figures 2.15 through 2.17. Again, as with the shorter term case, no statistical variability was noted between the data points.

2.3.2.3 Variability of the Simultaneous Sampling Technique

The variation in 1,1,1-TCA concentration in soil gas at two points located 15 to 25 cm from each other and sampled at the same time (simultaneous sampling technique) is presented in figures 2.9, 2.10 and 2.18 through 2.23. Figures 2.9, 2.10 and 2.18 through 2.20 present data from the landfill, the data in figures 2.21 through 2.23 were obtained at the East Drainage Ditch.

Each of the profiles obtained at the landfill show apparently random variability between points at the same depth. Profiles from the East Drainage Ditch show almost complete agreement, within the 95 percent confidence level, between points at the same depth.

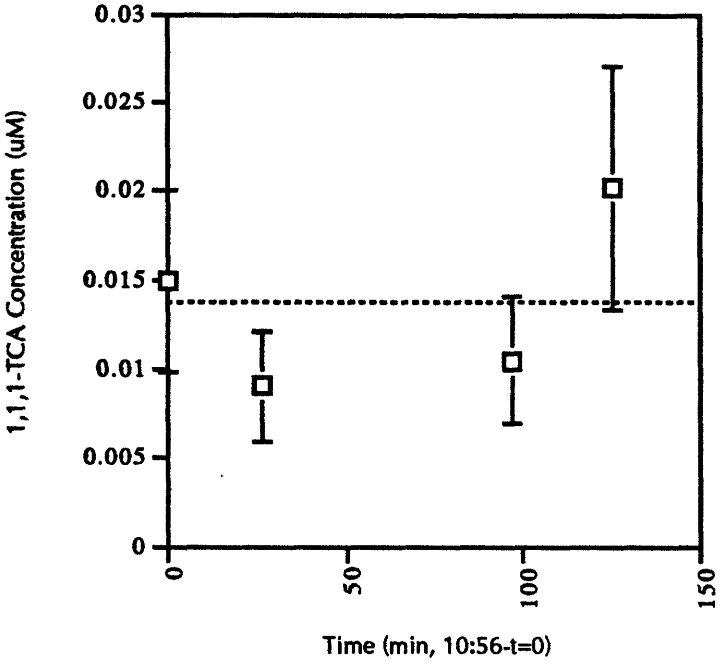

Figure 2.15: Change in 1,1,1-TCA concentration with time at a fixed sampling point (East Drainage Ditch 12/12/93). Dashed line indicates the average gas concentration. Error bars represent the 95 percent confidence level associated with each point.

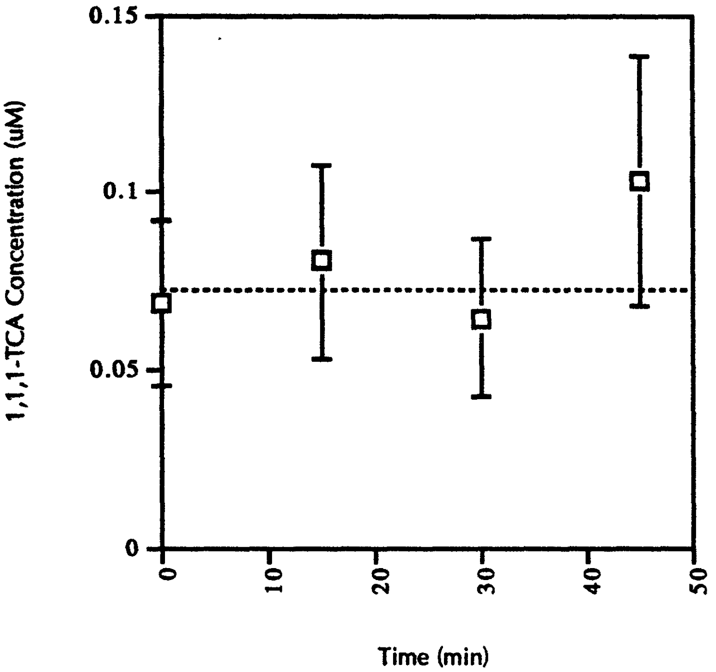

Figure 2.16: Change in 1,1,1-TCA concentration with time at a fixed sampling point (landfill 12/16/93). Dashed line indicates the average gas concentration. Error bars represent the 95 percent confidence level associated with each point.

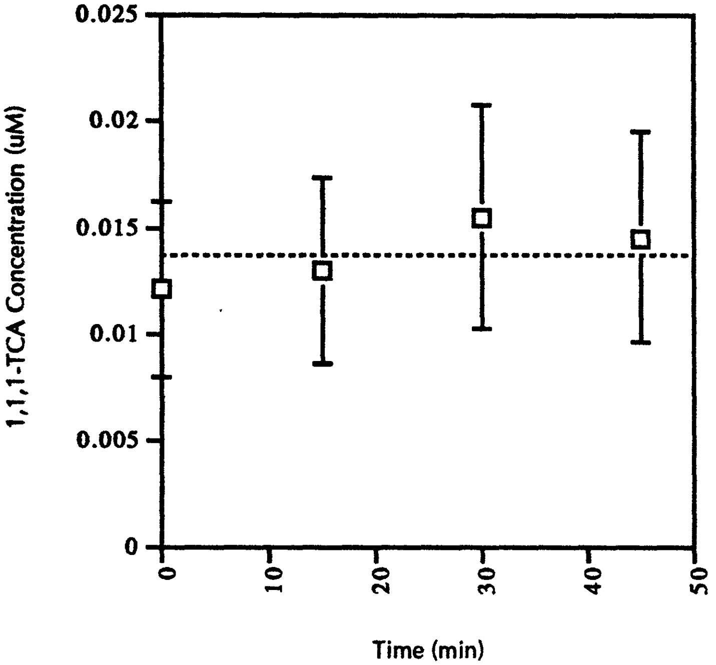

Figure 2.17: Change in 1,1,1-TCA concentration with time at a fixed sampling point (landfill 12/16/93). Dashed line indicates the average gas concentration. Error bars represent the 95 percent confidence level associated with each point.

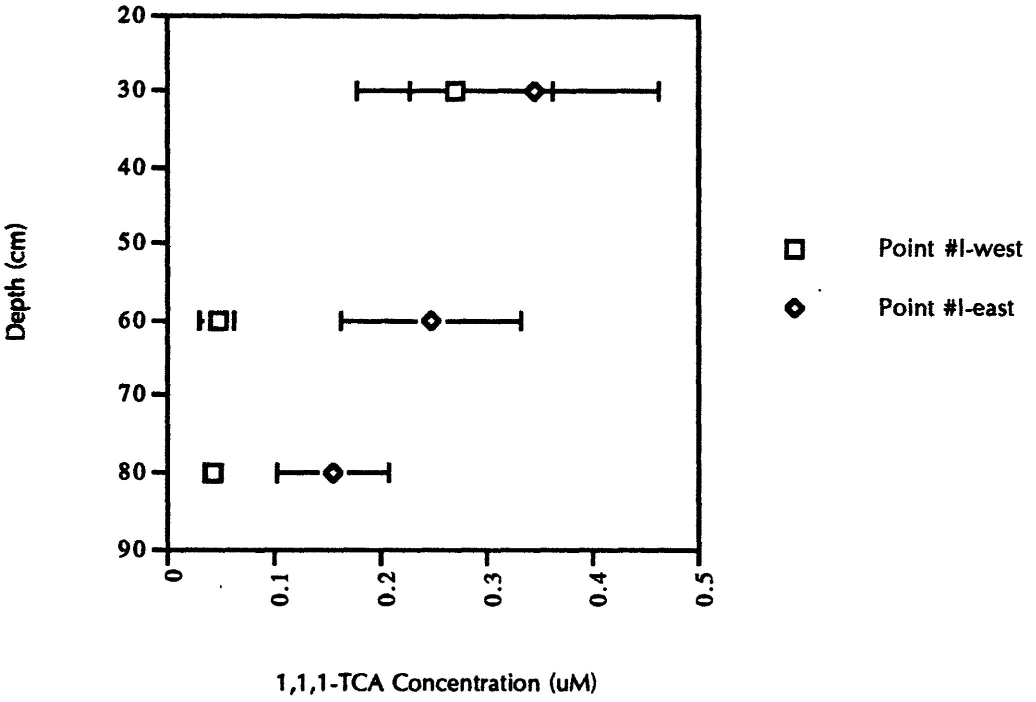

Figure 2.18: Variation in 1,1,1-TCA concentration profile at two points 25 cm apart, sampled simultaneously (landfill 12/08/93). Error bars represent the 95 percent confidence level associated with each point.

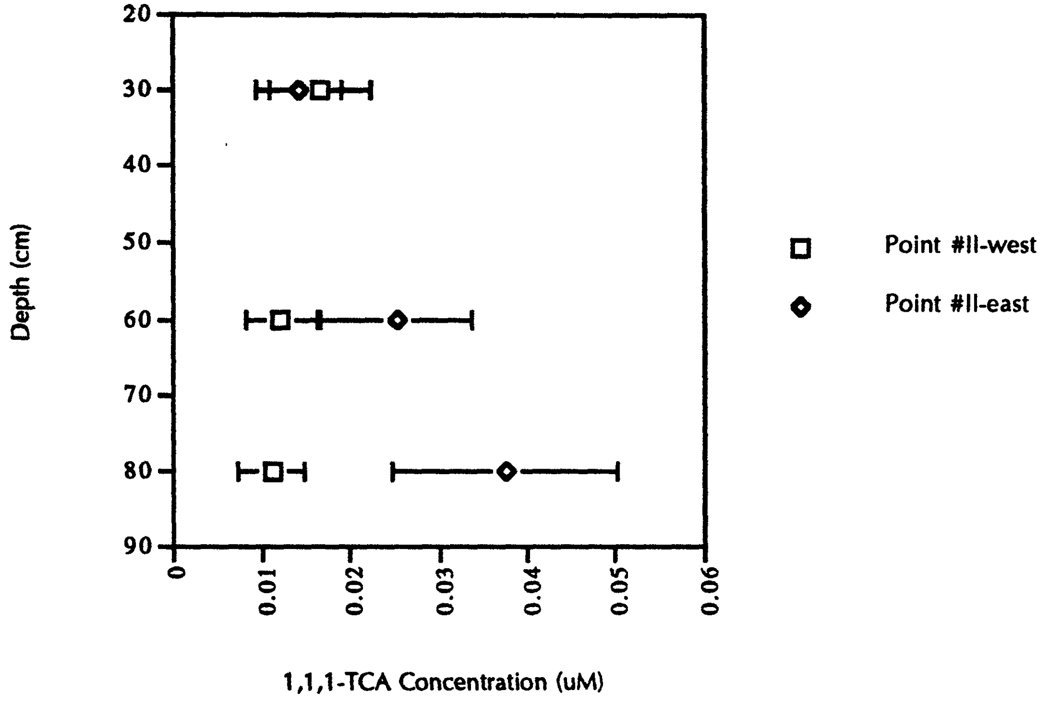

Figure 2.19: Variation in 1,1,1-TCA concentration profile at two points 15 cm apart, sampled simultaneously (landfill 12/10/93). Error bars represent the 95 percent confidence level associated with each point.

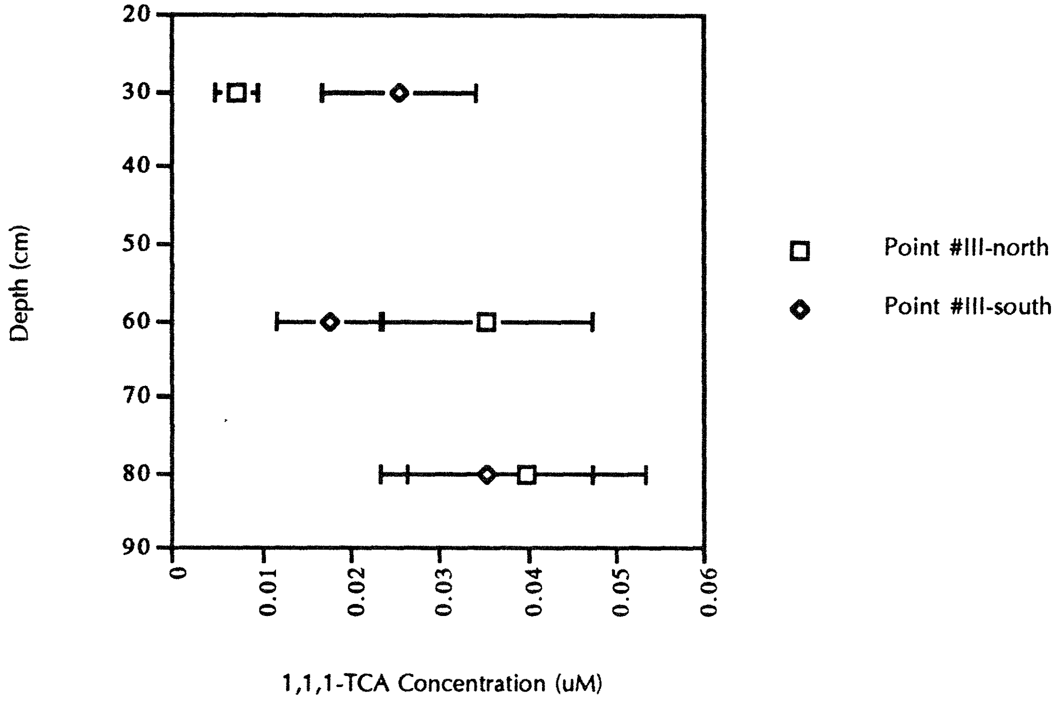

Figure 2.20: Variation in 1,1,1-TCA concentration profile at two points 15 cm apart, sampled simultaneously (landfill 12/10/93). Error bars represent the 95 percent confidence level associated with each point.

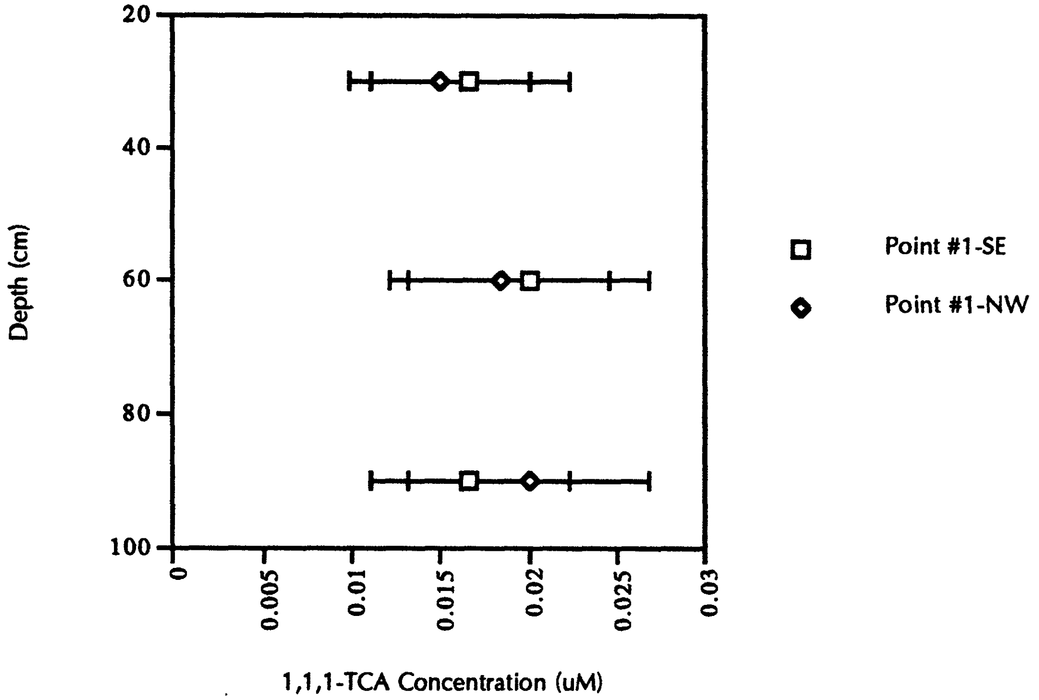

Figure 2.21: Variation in 1,1,1-TCA concentration profile at two points 15 cm apart, sampled simultaneously (East Drainage Ditch 12/12/93). Error bars indicate the 95 percent confidence level associated with each point.

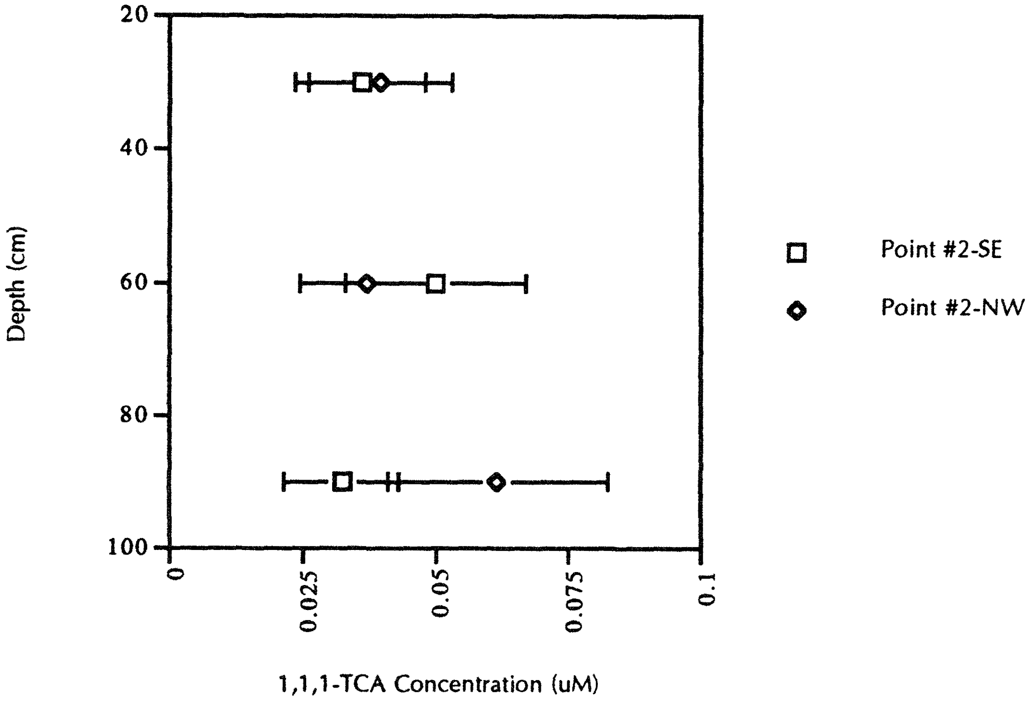

Figure 2.22: Variation in 1,1,1-TCA concentration profile at two points 15 cm apart, sampled simultaneously (East Drainage Ditch 12/17/93). Error bars indicate the 95 percent confidence level associated with each point.

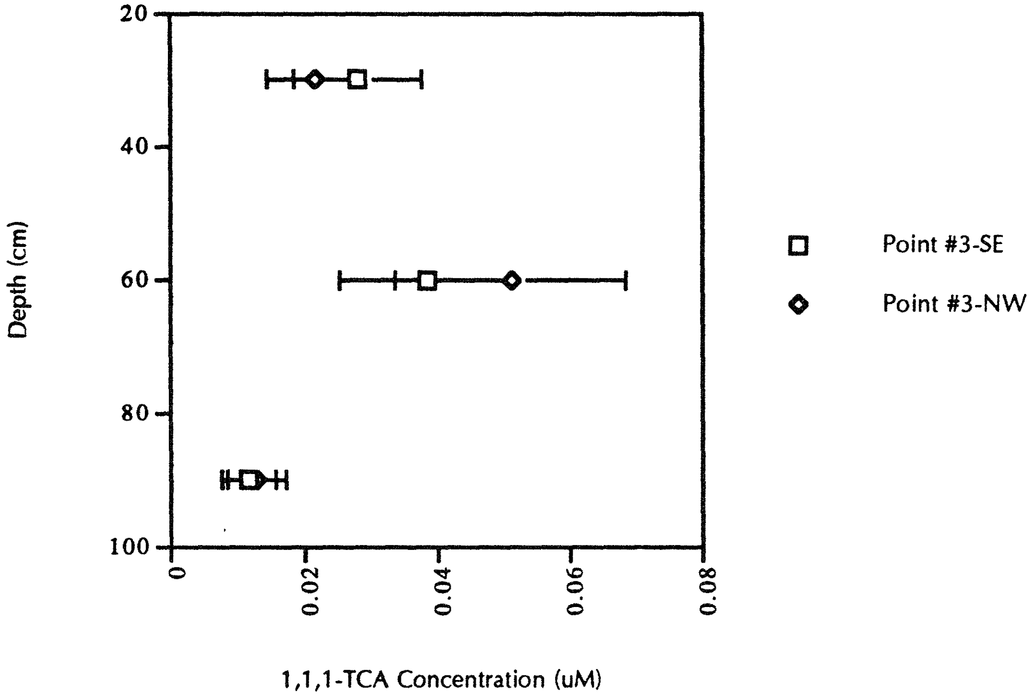

Figure 2.23: Variation in 1,1,1-TCA concentration profile at two points 15 cm apart, sampled simultaneously (East Drainage Ditch 12/17/93). Error bars indicate the 95 percent confidence level associated with each point.

2.3.3 Variability in Temperature and Soil Gas Signal

The trend in soil temperature at 90 cm and average daily concentration of 1,1,1-TCA in soil gas from September through December 1993, at the landfill, is presented in figure 2.23. Although the fluctuation of temperature and concentration may vary between points, there is no doubt that the general trend in the two is the same. An approximate 15 °F drop in temperature is accompanied by a 0.76 μM drop in 1,1,1-TCA concentration.

A more interesting and perhaps more informative comparison, between 1,1,1-TCA concentration and the temperature dependent Henry's constant, is shown in figure 2.24. The Henry's constant decreases by 40 percent while 1,1,1-TCA concentration falls by almost two orders of magnitude. Even if the first point in TCA concentration, which appears to be anomalously high, is ignored the concentration decrease is still over an order of magnitude.

2.4 Discussion

2.4.1 Methodological Precision in Assaying Temporal Variability in Soil Gas

From section 2.3.2.1 it can reasonably be concluded that variations of up to 800 percent may be encountered due to the same hole technique. Typical values of the variability between points are from 100 to just over 200 percent. The variability does not appear to be site specific, as similar percentage differences are seen at each of the two sites. Any data obtained using such a method must be interpreted in light of this sampling error. For the evaluation of some longer term temporal variability in soil gas composition, where changes of over an order of magnitude are observed, such as is presented in section 2.3.3, this technique may prove entirely adequate. In the interpretation of most shorter term temporal variability this technique may not provide the precision necessary for a meaningful interpretation of the data.

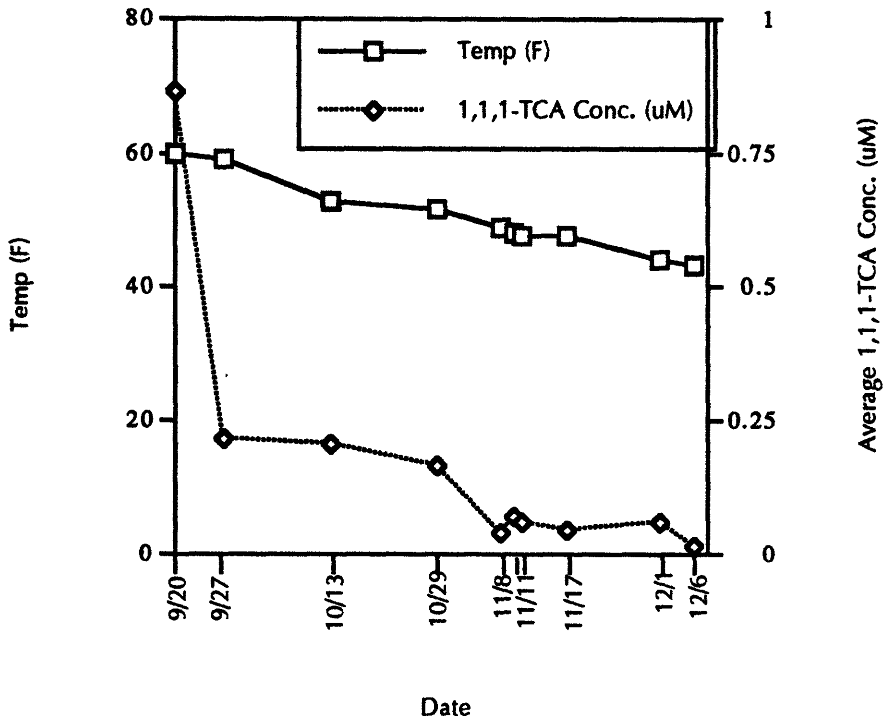

Figure 2.24: Variation in soil temperature and average 1,1,1-TCA concentration with time (landfill). Lines are merely meant to accentuate the general trend and do not indicate the actual changes between points.

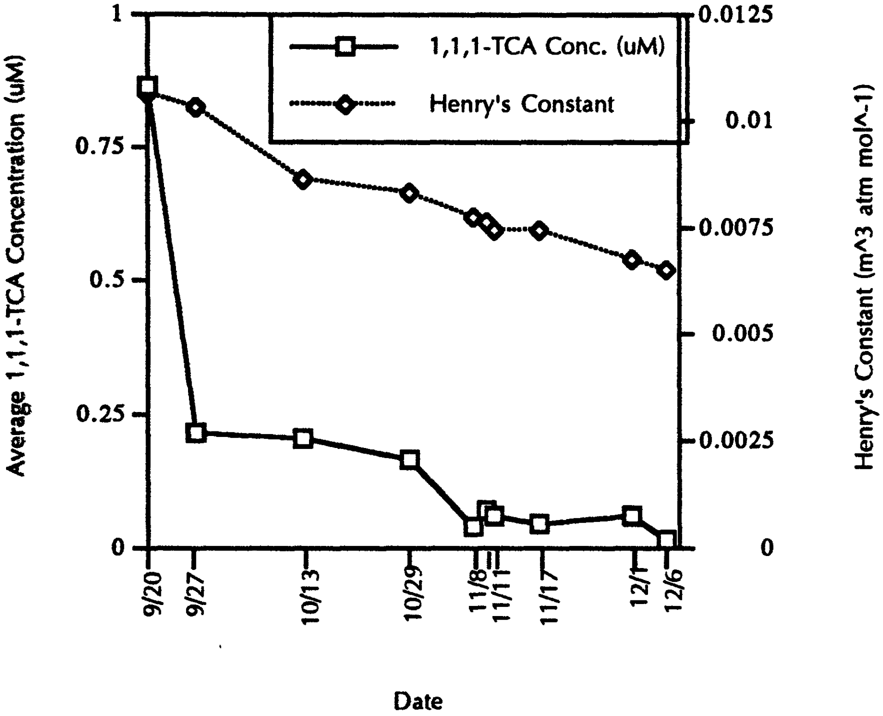

Figure 2.25: Variation in Henry's Constant and average 1,1,1-TCA concentration with time (landfill). Lines are merely meant to accentuate the general trend and do not indicate the actual changes between points.

The fixed point sampling technique in which capped probes are placed in the ground and sampled periodically provides adequate precision to determine any temporal variability above the level of analytical uncertainty. As with the same hole technique the results are consistent between the two sites. Fixed point sampling provides significantly more precision than continual sampling and filling at a point. For monitoring temporal changes, fixed point sampling is vastly superior to filling in and sampling repeatedly at the same point. In order to monitor temporal changes it is suggested that an array of fixed sampling points at various depths be used, in order to get the best possible resolution of changes throughout the soil profile.

2.4.2 Soil Structure Relationship to Spatial Sampling Variability

Simultaneous sampling of closely spaced points at the landfill yielded quite different concentration versus depth profiles between the points. Variations of up to 260 percent were noted at the same depth sampled at the same time. Data from the East Drainage Ditch showed excellent correlation between points with a variation of 22 percent occurring only once. The difference in the data obtained from the two sites, indicates that a site specific phenomenon may be responsible.

The difference between the two sites is hypothesized to be due to the degree of disruption of the soil that occurred during sampling and appears to be related to soil structure. The coarse, rocky soil of the landfill could be expected to be significantly disturbed from its natural state when holes were punched in it. The degree of disruption would vary greatly, as the exact composition of the soil varied spatially and with depth. The fine grained, fairly homogenous soil at the East Drainage Ditch would be expected to be perturbed to a much smaller extent mainly due to its spatial uniformity. If this correlation does indeed exist between sampling disturbances and soil type it indicates that the precision and spatial resolution of a sampling method will not only be site dependent but that they may actually be predictable on a site to site basis, if information on soil type and structure is available.

Table 2.2 presents an error budget associated with field analysis of VOCs in soil gas.

2.4.3 Correlation Between Temperature and Daily Averaged 1,1,1-TCA Soil Gas Concentration

Soil gas concentration of 1,1,1-TCA follows a seasonal decreasing trend from September through December. The trend appears to be correlated with a similar trend in temperature and thus the temperature dependent Henry's constant. The fact that the Henry's constant changes by 40 percent as compared to close to a 100 fold decrease in 1,1,1-TCA concentration indicates that temperature may not be the only seasonally changing variable that effects soil gas composition. It is possible that part of the effect is due to temperature dependent changes in K_{oc} of the soil. Sufficient data on the temperature dependence of K_{oc} or K_{ow} for 1,1,1-TCA or similar compounds, however, are not available to support or refute this theory. Changes due dilution of 1,1,1-TCA concentration in the underlying groundwater because of rains in the fall and early winter may also provide part of the answer. The decreasing trend in TCA concentration does not appear to be due seasonal variations in either soil moisture content or atmospheric pressure.

2.5 Conclusions

When sampling soil gas it is necessary to account for all sources of error due to probe installation and sampling. Coarser, rockier soils appear to have

Source	**Variability (percent)**
Analytical (95 Percent Confidence Level)	34
Same Hole - Temporal Variability (maximum sampling induced variability above analytical error)	800
Fixed Point - Temporal Variability (maximum sampling induced variability above analytical error)	*
Fixed Point - Variability After Purging of Three Tubing Volumes (maximum sampling induced variability above analytical error)	*
Simultaneous Sampling Technique - Site Dependent Spatial Variability (maximum sampling induced variability above analytical error)	22-260

* Within the range of analytical error.

Table 2.2: Soil gas sampling error budget.

more error associated with probe installation than homogeneous finer grained soils. It is necessary to assay both temporal and spatial variability in order to properly understand the resolution of the sampling technique that is being employed. When sampling for temporal variation in soil gas composition, especially on the short term, it is suggested that capped fixed samplers be used in order to increase precision. It may be useful to do further research on the effect of soil properties on sampling precision in order to develop a more systematic predictive capability.

Variations in mean average soil gas concentration of 1,1,1-TCA show that temperature may not be the only variable which controls seasonal variations in VOC concentrations in soil vapor. Its is suggested that further study be done in order to gain a better understanding of the temporally fluctuating variables that control VOC distribution in soil.

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Chapter 3. Relationship Between VOCs in Soil Gas and Stream Inflow

3.1 Introduction

Several authors have proposed using stream reconnaissance as a tool for detecting contaminants flowing with the groundwater into surface streams (Lee and Cherry 1978, Muraoka and Hirata 1989, Vroblesky et al. 1991, Kim 1992). Vroblesky et al. (1991) used passive vapor sampling in creek bottom sediment to map out an area of VOC inflow into a creek in Aberdeen, Maryland; inflow area and inflow contaminants were found to closely correspond to groundwater contaminant distribution on the site. A similar method was employed by Muraoka and Hirata in a study in Japan (1989). Lee and Cherry (1978) have discussed the possibility of using stream bottom seepage meters to sample chemicals in the stream inflow. Genereux (1991) and Kim(1992) used conservative (NaCl) and nonconservative (propane gas) tracers to assay the rates of radon and VOC inflow, respectively, from the subsurface into surface waters.

Soil gas monitoring has proven to be an extremely effective method for determining the presence of VOCs in underlying groundwater (Swallow 1983, Marrin 1987, Crockett and Taddeo 1988, Tillman et al. 1989). The goal of the present study was to determine how well VOC inflows would correlate with the distribution of soil gas contamination adjoining the stream reaches. It was initially expected that VOCs encountered by soil gas surveys, in these areas, would mirror those found in the inflow. A methodology for soil gas collection and analysis was developed based on the work of Spittler (1986, 1992).

3.1.1 Site Selection

Four study sites were chosen. At each of these sites Kim (1992) had found an inflow of one or more VOCs from the groundwater into the surface water. All four sites are located on the Aberjona watershed (figure 1.1), two in the town of Woburn, one in Wilmington and one in Stoneham. Two of the areas of interest are located along the at the upper and lower ends of the East Drainage Ditch (figure 3.1). One runs between Landfill Creek and a closed cell on the old Woburn Municipal Landfill(figure 3.1) and the last is situated approximately 0.3 km east of the Woburn - Stoneham line, along Sweetwater Brook (figure 3.2). More detailed site maps are presented in figures 3.3 through 3.6

3.1.1.1 East Drainage Ditch (EDD)

The East Drainage Ditch is a small stream which runs for approximately 2. 7 kilometers in a southeasterly direction. For much of its length the stream flows alongside the Boston and Maine Railroad tracks. The East Drainage Ditch is approximately 1.5 meters across and 0.5 meters deep, with a soft, silty bed for much of its length, but in several places it flows through buried culverts.

3.1.1.1.1 EDD Upstream

The upstream site on the East Drainage Ditch is located just to the southeast of the Eames Street Bridge in Wilmington, MA. The study location occupies an area 120 meters by 7 meters, between the steep bank of the stream and a fence demarcating the Olin Corporation property line. The Olin property is currently abandoned except for a small crew operating a pump and treat cleanup of the underlying groundwater. Soil cores form this location indicated that the soil a fairly homogeneous loam which extends approximately 2.5 meters down to the water table.

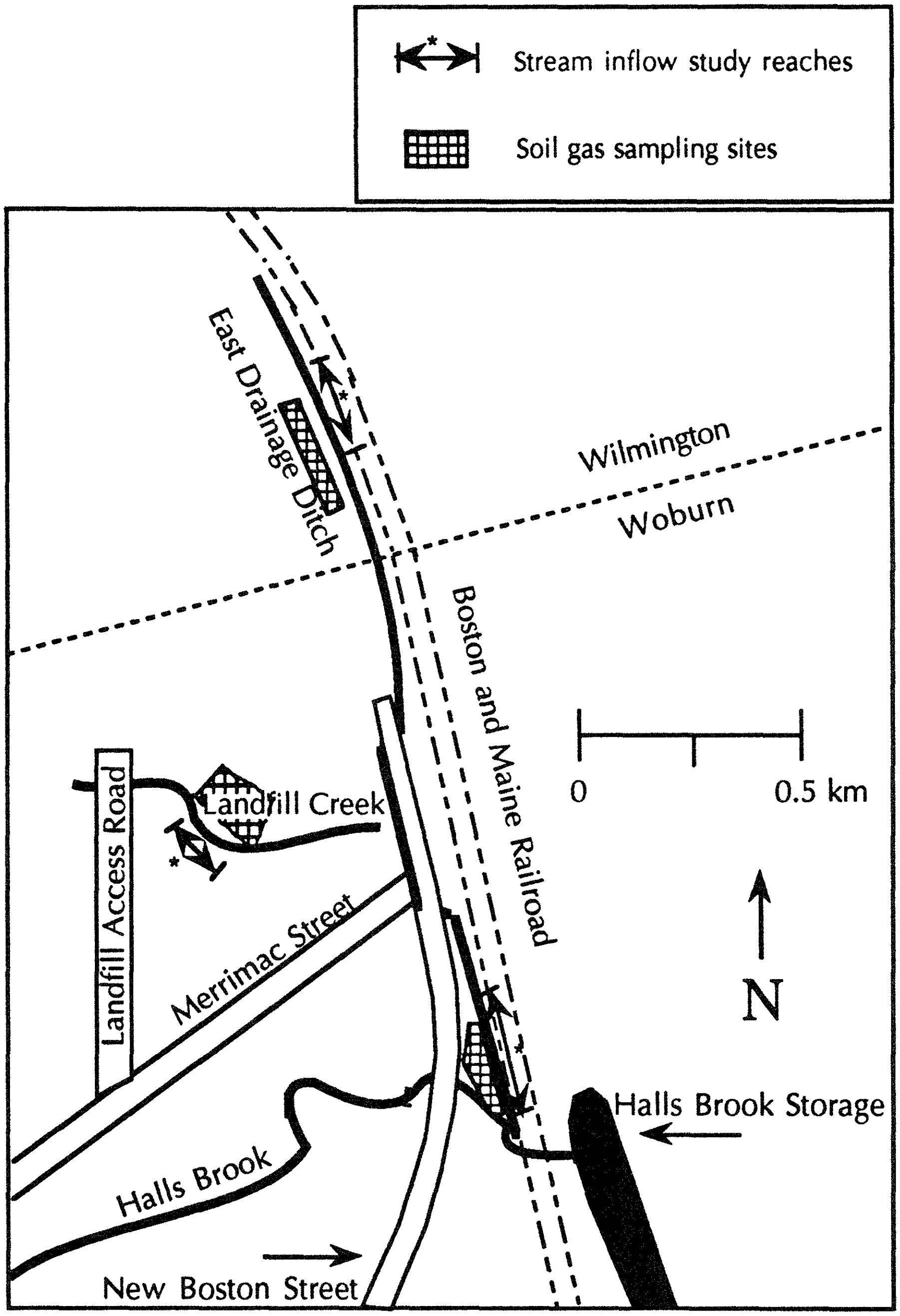

Figure 3.1: East Drainage Ditch and Landfill Creek

3.1.1.1.2 EDD Downstream

The downstream sampling area on the East Drainage Ditch is situated between the Boston and Maine Railroad tracks and the ditch in Woburn, 30 meters upstream from the Halls Brook Storage Area. Between the East Drainage Ditch and Halls Brook is a small wooded area. Halls Brook is bounded on the southwest side by a parking lot. A substantial quantity of railroad debris (railroad ties and sections of track) has been dumped along the bank of the East Drainage Ditch at this location. The soil in this area is a fairly homogenous sandy loam with the water table at a 1 meter depth.

3.1.1.2 Landfill Creek

Landfill Creek, as its name implies, runs through the old Woburn Municipal Landfill, which has been closed since the early 1980's. The creek is 1.5 to 2 meters wide and 0.5 meters deep with a very soft, silty bed. From late spring through early fall the area is covered by herbaceous vegetation. The marshy areas indicated in figure 2.5 are at a slightly lower elevation than the rest of the site and are actually "marshy" for approximately six months, from late fall to late spring. The elevation of the land surface rises to the north from well before the base of the closed cell up to the top of the cell. The south side of the creek is bordered by a small wooded area. The soil in the sampling area is a sandy loam strewn with pebbles and cobbles. The water table was from 1.5 to 2.5 meters below the ground, due to the topography of the site.

3.1.1.3 Sweetwater Brook

Sweetwater Brook is a small stream which runs southwest through Stoneham and crosses into Woburn just to the south of Montvale Avenue. The width of the brook ranges from 1.5 to 3 meters with a depth of 0.5 meters and

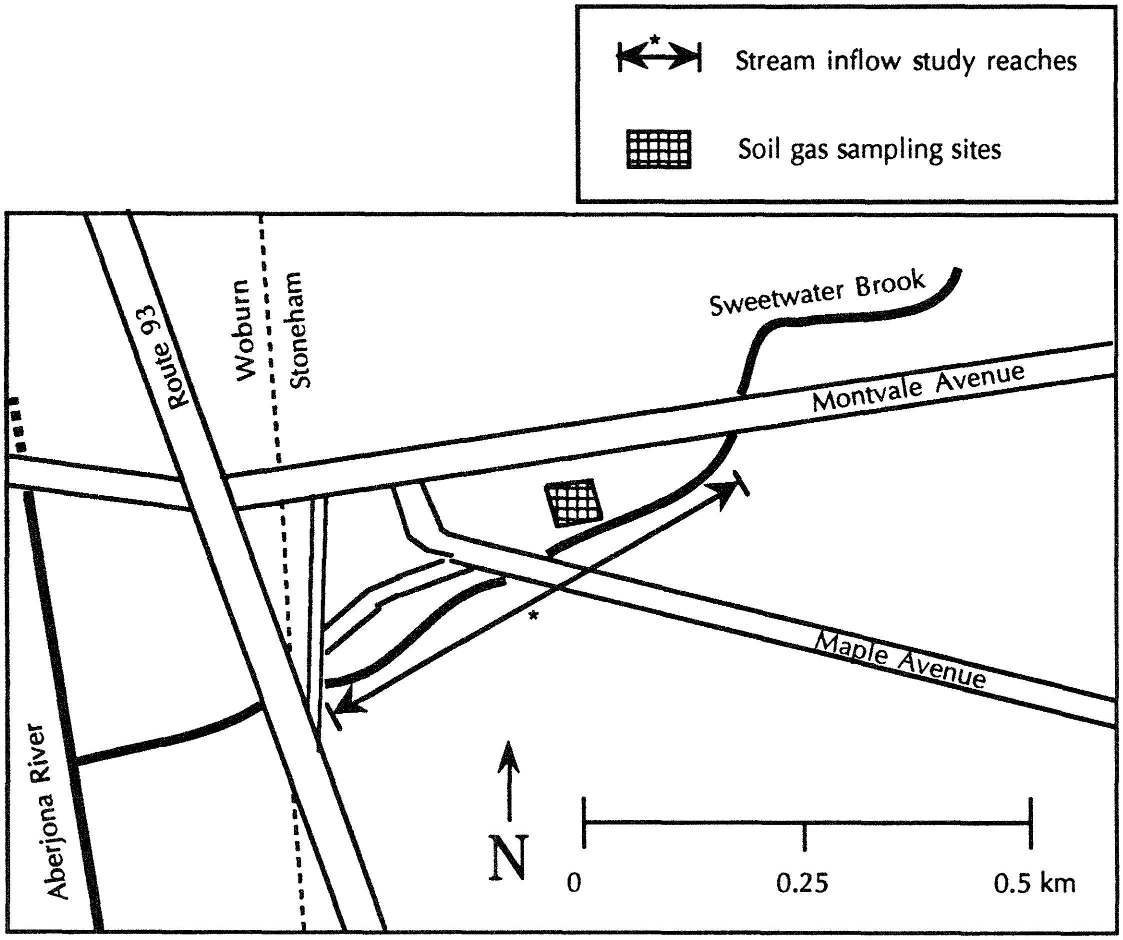

Figure 3.2: Sweetwater Brook.

rocky bed. The area of interest is located on a vacant lot behind Montvale Avenue between an office building and a strip of pavement on the northwest side of the stream. The southeast bank of Sweetwater Brook is bordered by a truck depot. The soil at this location is a sandy loam with pebbles and cobbles near to the stream bank; farther away it becomes a loamy clay with a considerable amount of pebbles and cobbles. During the sampling period punching a slide hammer through the ground at a distance from the stream bank was extremely difficult.

3.2 Materials and Methods

3.2.1 Sampling

Soil gas sampling was performed by creating a small hole in ground with either 3.8 cm auger or a 1.1 cm slide hammer. A length of appropriate diameter tubing (large enough to fit snugly in the hole and prevent gaseous diffusion up the sides of the hole) was inserted into the hole. A pumping / sampling port was attached to the tubing and three volumes of air were pumped. Approximately 800 µL of air was sampled from the pump stream into a 1 mL glass syringe which was capped with a septum and taken for GC analysis. In all cases where samples were taken from one site, on different days, points indicated as the same were actually different points within a 0.5 meter radius of each other. All holes were filled in after sampling. Samples were taken at the following depths above the water table EDD upstream: 1.5 meters, EDD downstream: 20 cm, Landfill Creek: 20 cm, Sweetwater Brook: 20 cm (along streambank), 90 cm (away from streambank). For a more complete description of the sampling technique see chapter 2, sections 2.2.1 and 2.3.1.1.

3.2.2 Analysis

All analysis was performed on a Photovac 10A10® portable gas chromatograph (GC) equipped with a photoionization detector, attached to a portable chart recorder. Approximately 700 µL of the sampled soil gas was injected into the GC, with the exact volume recorded each time. The maximum time between sampling and GC analysis was half an hour. Standards, of all appropriate compounds at a particular site, were run throughout the day whenever the ambient temperature changed by 2 °C or more, or every 1.5 to 2 hours if temperature remained constant. Sample concentrations were obtained by counting peak heights obtained from the chart recorder and comparing them to the heights of the standards. The 95 percent confidence level for data obtained with this technique was 34 percent. For a more complete discussion of the analytical technique see chapter 2, sections 2.2.2 and 2.3.1.2.

3.3. Results

Results of soil gas surveys at each of the four study sites are presented below and in figures 3.3 through 3.6. Tables 3.1 and 3.2 summarizes the VOCs which were encountered using soil gas monitoring and stream inflow monitoring.

3.3.1 East Drainage Ditch Upstream

Soil gas monitoring at the East Drainage Ditch upstream site on 6/2, 6/7, and 6/16/93 indicated the presence of 1,1,1-TCA. The highest concentrations were found on 6/16/93. The 1,1,1-TCA distribution found on 6/7/93 indicated a concentration drop of approximately an order of magnitude had occurred since

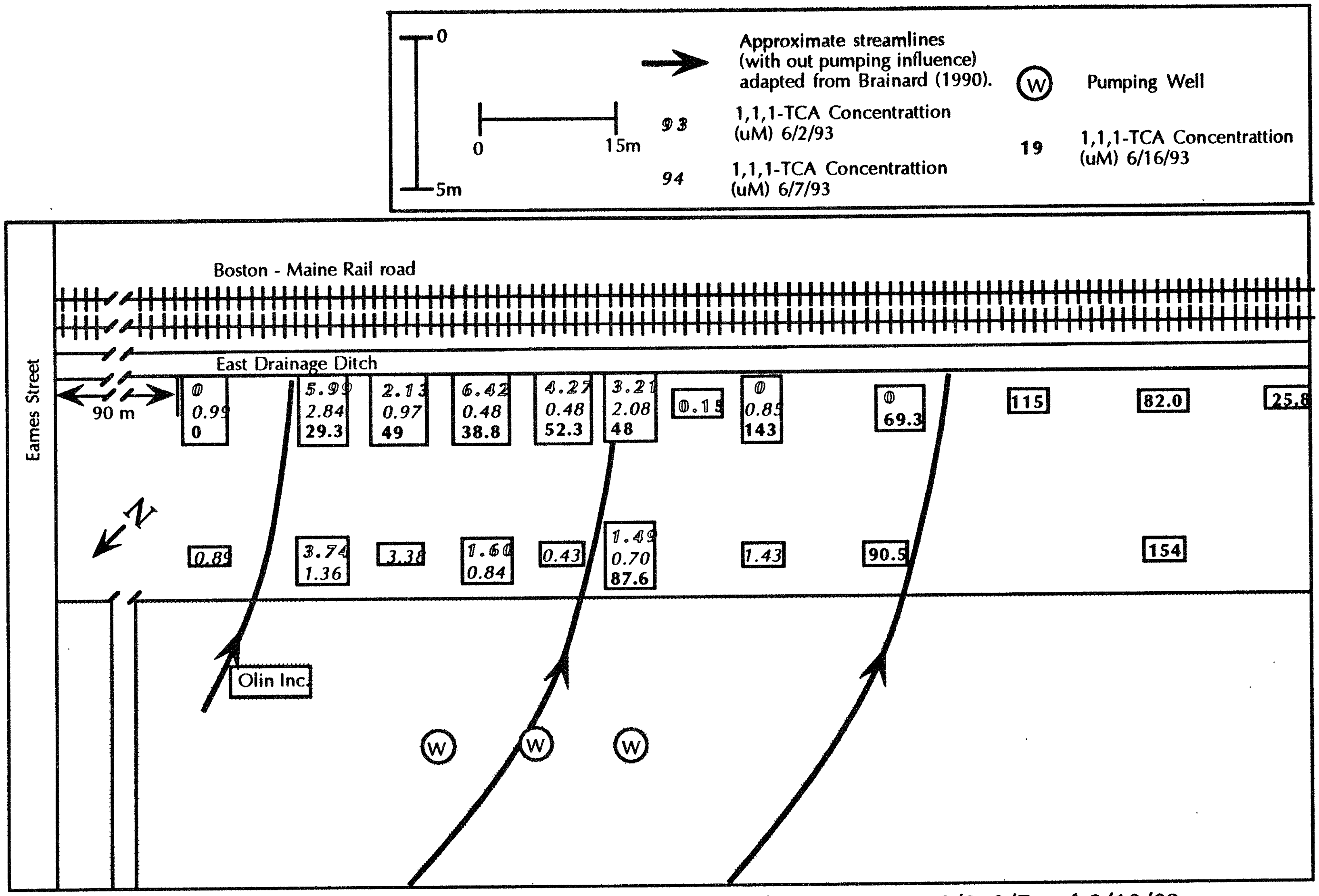

Figure 3.3: Soil gas distribution of 1,1,1-TCA at East Drainage Ditch upstream on 6/2, 6/7 and 6/16/93.

6/2. A rise in concentration of over an order of magnitude was noted between the mean gas concentrations obtained on 6/7 and 6/16. A site map containing the results of the surveys as well as the estimated natural groundwater flow regime (adapted from Brainard, 1990) is shown in figure 3.3.

A stream inflow study performed on 10/27/90 indicated that 1,1,1-TCA and TCE were present in the inflow in concentrations of approximately 22.2 ±11.7 and 12.3 ±9.6 μg/L respectively Kim (1992). As indicated in figure 3.3 there are three groundwater extraction wells located approximately 5 meters across the fence line, on Olin's property.

3.3.2 East Drainage Ditch Downstream

Both TCE and benzene were found in the soil gas downstream at the East Drainage Ditch. TCE was detected during investigations on 6/12 and 6/29/93. The measured concentration values were over an order of magnitude higher on the second date then on the first. Benzene was detected on 6/29/93, but none was found on 6/12/93. In addition, no benzene was detected close to the stream. Soil vapor results and approximate groundwater flow streamlines (adapted from Brainard, 1990) are presented on a site map in figure 3.4. Benzene concentrations are expressed in relative units because benzene standards were not run on 6/29, and thus only represent relative concentrations of benzene.

Kim (1992), in a study performed on 10/1/90, found TCE and benzene in the stream inflow at concentrations of 2.2 ±0.3 and 0.05 ±0.02 μg/L respectively.

3.3.3 Landfill Creek

Figure 3.5 summarizes the soil gas data obtained from Landfill Creek on 5/17 and 7/19/93. 1,1,1-TCA was detected on both days, although a mean

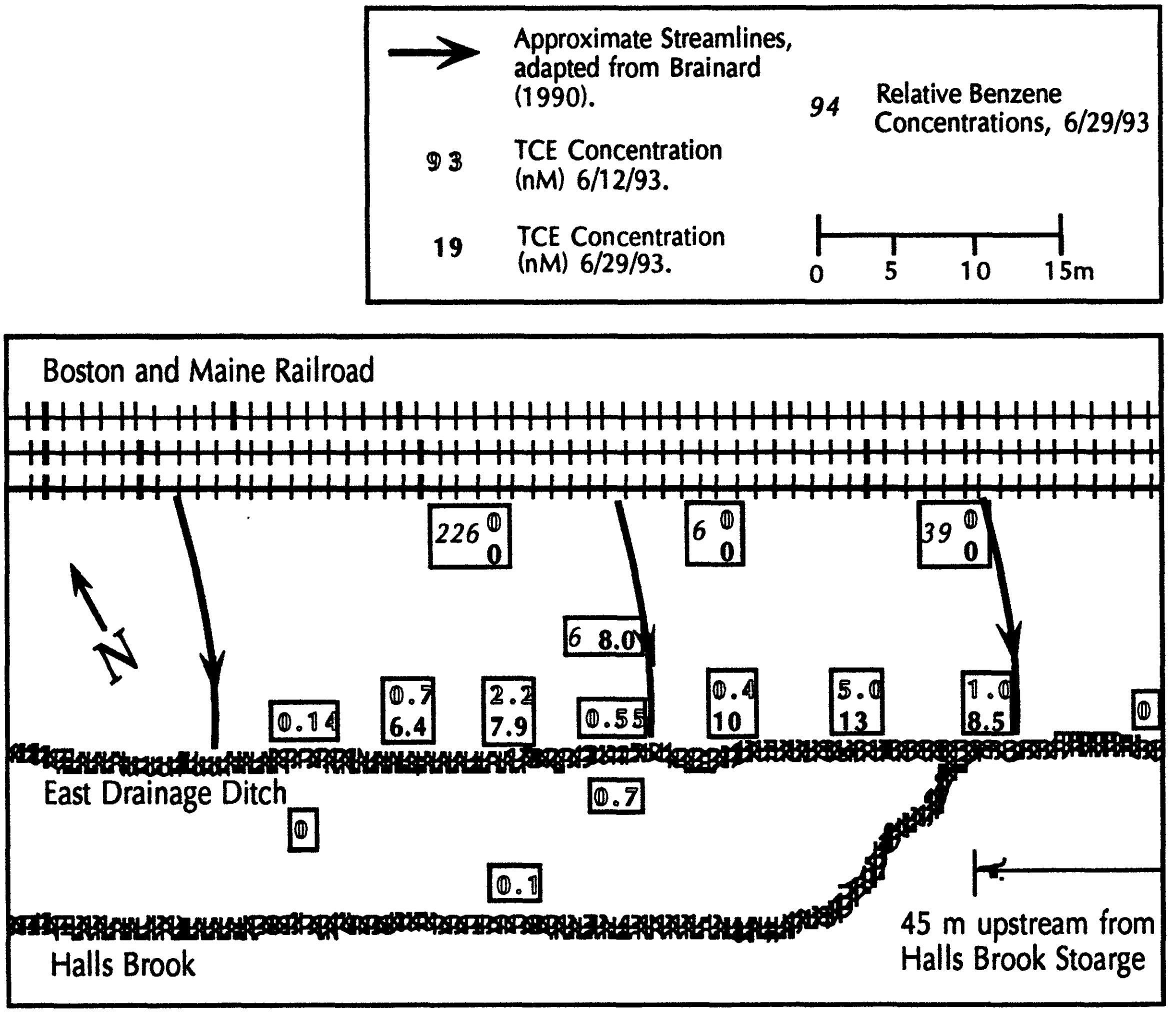

Figure 3.4: Soil gas distribution of 1,1,1-TCA and benzene at East Drainage Ditch downstream on 6/12 and 6/29/93.

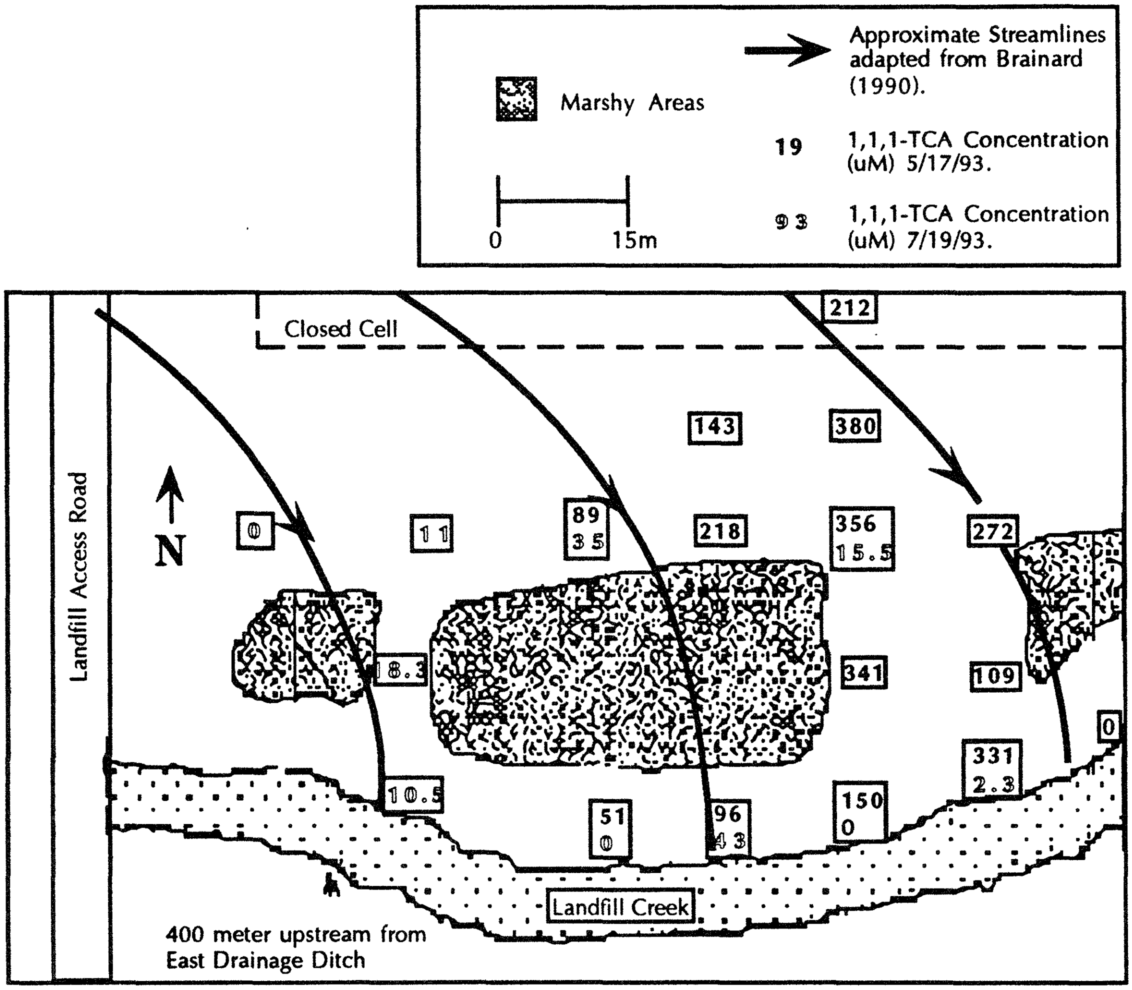

Figure 3.5: Soil gas distribution of 1,1,1-TCA at Landfill Creek on 5/17 and 7/19/93.

concentration decrease of over an order of magnitude noted between the two days. Approximate streamlines (adapted from Brainard, 1990) and soil gas profiles are presented on the site map in figure 3.5.

Both 1,1,1-TCA and 1,1-DCA appeared in a stream inflow study conducted by Kim (1992) on 9/23/90. Concentrations of 0.7 ±0.5 and 0.5 ±0.4 µg/L for 1,1,1-TCA and 1,1-DCA respectively were found in the inflow.

3.3.4 Sweetwater Brook

Toluene and 1,1,1-TCA were both observed in the soil gas at Sweetwater Brook. Because of the hard rocky soil, which was encountered 10 meters from the stream bank, all samples at distances greater than 10 meters from the stream were only taken at a depth of 30 cm. Gas along the stream bank was sampled at a depth of 1 meter. Because of the sampling difficulty samples were only taken on 6/19/93. The results of this soil vapor survey as well as the approximate groundwater flow path (adapted from Brainard, 1990) are presented on the site map in figure 3.6.

Kim (1992) has observed, in several studies from 6/90 through 3/92, that 1,2-DCE and TCE appear to be present in the stream inflow. The in-stream concentrations of these two compounds did not appear to change statistically over this period. The mean values observed were 32.6 ± 4.21 and 248 ± 32.2 for 1,2-DCE and TCE respectively. 1,1,1-TCA was observed in the stream in concentrations from 1.0 to 2.3 µg/L but did not appear to be inflowing in the study reach. Toluene was observed in the stream but no concentration values were reported (Kim, 1993).

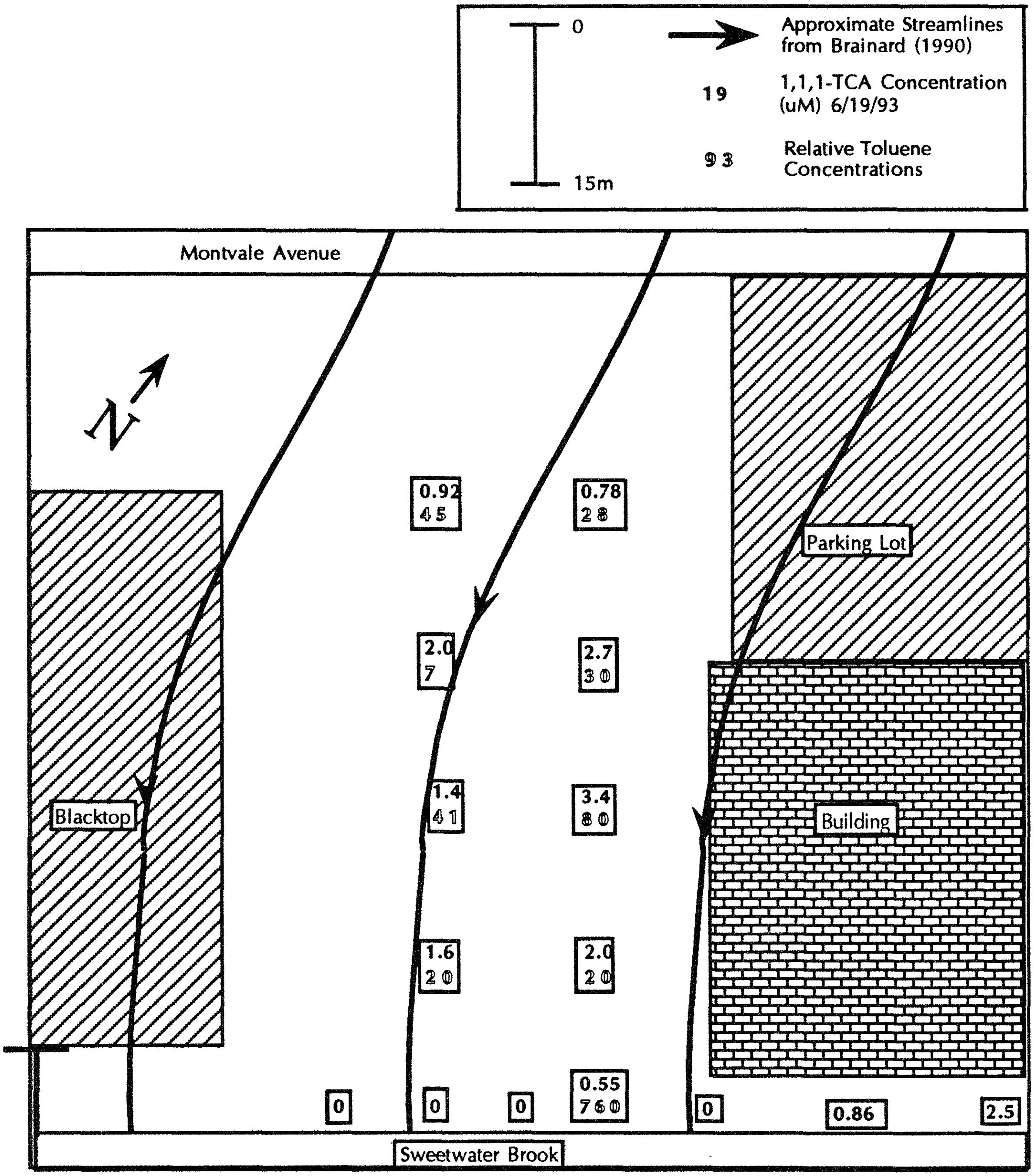

Figure 3.6: Soil gas distribution of 1,1,1-TCA and toluene at Sweetwater Brook on 6/19/93.

Location	Soil Gas Contaminants	Stream Inflow Contaminants
Sweetwater Brook	1,1,1-TCA, Toluene	1,1,1-TCA, 1,2-DCE, TCE
Landfill Creek	1,1,1-TCA	1,1,1-TCA, 1,1-DCA
East Drainage Ditch (upstream)	1,1,1-TCA	1,1,1-TCA, TCE
East Drainage Ditch (downstream)	TCE, (Benzene)	TCE, Benzene

Table 3.1: Presence of VOCs in soil gas versus stream inflow at four sites on the Aberjona watershed.

Location - Contaminent	Mean Soil Gas Concentration (uM)	Stream Inflow Concentration (uM)
East Drainage Ditch upstream - TCA	23.26	22.9±11.7
- TCE		12.3±9.6
East Drainage Ditch downstream -TCE	0.00287	2.2±0.3
- Benzene		0.5±0.02
Landfill Creek - TCA	100.4	0.7±0.5
- DCA		0.5±0.4
Sweetwater Brook - TCA	1.47	
- TCE		248±32.2
- DCE		32.6±4.2

Table 3.2: Concentrations of VOCs in soil gas and stream inflow at four sites on the Aberjona watershed

3.4 Discussion

A quantitative comparison of stream inflow and mean soil gas VOC concentrations is presented in table 3.2. As can be seen from the data there is no apparent correlation between the two. Inflow concentrations are their lowest at the East Drainage Ditch downstream and Landfill Creek. Soil gas concentrations reach relative minimum and maximum values at these two sites respectively. The daily variability in soil gas makes any correlation with the relatively invariant stream inflow data more difficult. Lack of quantitative correlation leaves the door open, however, for a qualitative assessment of the differences in soil gas and stream inflow composition at each of the sites.

The results which are described above show that there may not be a correlation between VOC composition of stream inflow and soil gas. Agreement between stream inflow and soil gas surveys was only found 50 percent of the time (see table 3.1). There may be several explanations for these differences ranging from changes in groundwater composition in the time between soil and groundwater monitoring was performed to bio-mediated reductive transformations.

In order to accurately comment on the connection between soil gas and stream inflow studies it is necessary to understand the precision of the soil gas method at each of the sites. Determinations of the error inherent in the soil vapor surveys performed at each site can be made based on the results of chapter 2. Any mean temporal variability above analytical uncertainty is considered to be statistically significant. The spatial resolution attained at each site will vary depending on soil type and homogeneity. Both of the East Drainage Ditch sites have fairly homogenous soil, thus it may be possible to spatially distinguish points whose concentrations differ by over 25 percent. At Landfill Creek the studies done in chapter 2 indicate that concentrations must differ by 260 percent in order to be spatially distinguishable. Because of the extremely hard and rocky soils present at Sweetwater Brook it is estimated that concentrations must differ spatially by over 300 percent in order indicate any real difference in soil vapor compositions. It is in light these criteria that the soil gas data were interpreted.

3.4.1 Landfill Creek

It is possible that anaerobic biotransformations are responsible for some of the differences which have been noted between soil gas and stream inflow VOC data. Several laboratory and field studies have shown that halogenated alkanes and alkenes may be reductively bio-transformed by bacteria such as *Clostridium* sp. (Galli and McCarty 1989 a & b). TCE has been found to degrade to form *cis* and *trans* 1,2-DCE (Vogel and McCarty 1985, Parsons et al. 1982 & 1984). 1,1,1-TCA may transform to 1,2-DCE or 1,1-DCA (Galli and McCarty, 1989 a & b, Bower 1983, Parsons et al. 1982 & 1983). Toluene catabolism by a TCE degrading bacterium has been noted by Shields et al. (1989).

The variation in VOC composition in soil vapor and stream inflow at Landfill Creek is consistent with such transformations. 1,1,1-TCA and 1,1-DCA appear in the stream inflow, but only 1,1,1-TCA was detected in the soil gas. It appears that 1,1,1-TCA is transformed as the groundwater moves through the creek bed into the creek (if such a transformation was occurring in the ground 1,1-DCA would have been detected in soil gas). If this is the case it indicates the need to assay conditions in both the streambed and the soil, when performing stream inflow surveys, in order to account for possible transformations that may produce erroneous predictions of groundwater contaminants.

Because of the nature of the soil at the Landfill it is not possible to say anything about the spatial distribution of 1,1,1-TCA in the soil gas other than that it is present in the area where stream inflow studies were conducted and that its presence further indicates that 1,1,1-TCA may be present in the groundwater in this area. The data does show a significant drop in gas concentration between 5/17 and 7/19 (see figure 3.7).

3.4.2 Sweetwater Brook

In the case of Sweetwater Brook soil gas monitoring and stream monitoring were in complete disagreement about the composition of groundwater contaminants. 1,2-DCE and TCE appeared to be flowing into the brook, while TCA and toluene were found in the soil gas. It is important to note that TCA and toluene were present in the stream although they didn't appear to be flowing along the study reach (Kim, 1993). This may indicate one of two things. Either the contaminants which appear in the soil gas aren't flowing into the stream along the reach which was studied, or the inflow monitoring method may not provide adequate sensitivity to detect these compounds. In the first case, the fact that 1,2-DCE and TCE weren't detected in the gas survey area may not reflect on the accuracy of the inflow method. Because of the large number of buildings and paved areas which border Sweetwater Brook it was only possible to perform soil gas monitoring on a small section of the reach which surveyed with the stream inflow technique. Without a better notion of the soil gas composition along the rest of this stretch of the brook it is not possible to make any strong statements about the correlation between soil gas and stream inflow data in this area. The nature of the soil in this area made it impossible to say anything about the distribution of contaminants in ground other than that 1,1,1-TCA and toluene were present in the soil gas and thus possibly in the groundwater.

3.4.3 East Drainage Ditch Upstream

The upstream East Drainage Ditch site showed the presence of 1,1,1-TCA in the soil gas, but both 1,1,1-TCA and TCE appeared in the stream inflow. One reason for the observed difference may be the passage of time between stream inflow and soil gas sampling (over 2.5 years) coupled with the pump and treat cleanup which was going on at Olin Inc. Olin's groundwater treatment may have removed most or all of any TCE which was present in the groundwater. From the stream inflow data, TCE concentration in the inflow appeared to be only half that of 1,1,1-TCA, indicating TCE concentrations in the groundwater may have been lower than 1,1,1-TCA concentrations. If this were the case it may be assumed that TCE would be cleaned up from the groundwater more quickly than 1,1,1-TCA, leaving TCA in the groundwater when TCE had been "cleaned up." The soil at this site is fairly homogeneous, this may indicate that points which differ by over 25 percent, above the 95 percent confidence level associated with the analytical technique, are statistically distinguishable. Concentration of 1,1,1-TCA appears to behave somewhat erratically throughout the sampling area. It should also be noted that mean 1,1,1-TCA concentrations on 6/2 and 6/7 differ by 60 percent. Between 6/7 and 6/16 a mean concentration increase of over an order of magnitude appears to occur. These differences in soil vapor composition may be due to the influence of temporal variables on the gas. It is also possible that they reflect changes in groundwater composition due to the treatment occurring at Olin Inc.

3.4.4 East Drainage Ditch Downstream

The East Drainage Ditch was the only one of the four study sites which showed agreement between soil gas and stream surveys. TCE and benzene were found in both the stream inflow and in the soil gas. It is unknown, however, why benzene appeared on only one of the two days when soil gas was sampled. Gas sampling was done within 20 cm of the water table in an effort to mitigate any problems due to possible oxidative transformation of benzene above the water table. It is also interesting that when benzene was found it only occurred at a distance from the stream bank which would indicate that it wasn't flowing into the stream. The most statistically significant spatial differences (a greater than 25 percent difference above the 95 percent level of analytical uncertainty) in soil gas TCE concentration occurred on 6/12. These points indicate the possible presence of a wide, squat groundwater plume centered near the confluence of the East Drainage Ditch and Halls Brook. A statistically significant mean increase in 1,1,1-TCA concentration of approximately an 300 percent was noted between 6/12 and 6/29. The fact that benzene was only observed on the day with higher TCA concentrations may mean that whatever mechanism caused the increase in TCA may also have increased benzene concentrations from their undetectable levels on 6/12.

3.4.5 Changes in Mean VOC Concentration in Soil Gas

As was noted in sections 3.3.1 through 3.3.4, large changes in mean soil gas concentration occurred between sampling dates, figure 3.7 shows the relative changes at points that were sampled on all sampling dates, at each site. Similar magnitude changes have been observed for both VOCs (Davis et al. 1991) and radon (Schery et al. 1984). The magnitude of the observed changes appears to preclude any physical / chemical explanation. For example the small changes that may have occurred in the temperature dependent Henry's can not explain order of magnitude changes in soil gas concentrations. Soil at the three sites never appeared to become dry enough for drastic changes in the sorptive properties of the soil to occur. GC response between any of the sampling days had a maximum variation of 20 percent.

There does appear to be an inverse correlation between changes in barometric pressure (figures 3.8 through 3.11) on the day prior to sampling and the changes noted in gas concentrations. For example a upward pressure trend is noted on 6/6 and the mean 1,1,1-TCA concentration on 6/7 is observed to be at a lower value than on 6/2. Conversely a downward pressure trend is noted on 6/15 and the mean 1,1,1-TCA concentration on 6/16 is over an order of magnitude higher than on 6/7. This would indicate that changes in atmospheric pressure may be responsible for the advection of gas into and out of the soil. One model for this behavior is that the sampling holes made on the previous day or days would provide conduits for transport of soil gas. Changes in barometric pressure would thus flush air into or out of these holes, slowly perturbing the gas concentration in the sampling area. Over a period of a day this change in concentration could become substantial. Although holes were filled in after sampling, the mere disturbance of the soil could create pathways for this advective transport. It is also possible that these fluctuations are present throughout the soil profile and are not sampling artifacts. It is much more difficult to predict a physical model of this kind of wide spread change. Without preferential pathways for gas transport in the soil changes in barometric pressure would only produce small (less than 1 percent) variations in the mass of air in soil pore space and thus changes gas concentration would be correspondingly small. The studies which have previously looked at the correlation between atmospheric pressure and soil gas composition for pesticides (Spencer 1970) radon (Kraner et al. 1964) and CO_2 (Reardon et al. 1979, Schery et al. 1984) do not provide convincing data on the matter.

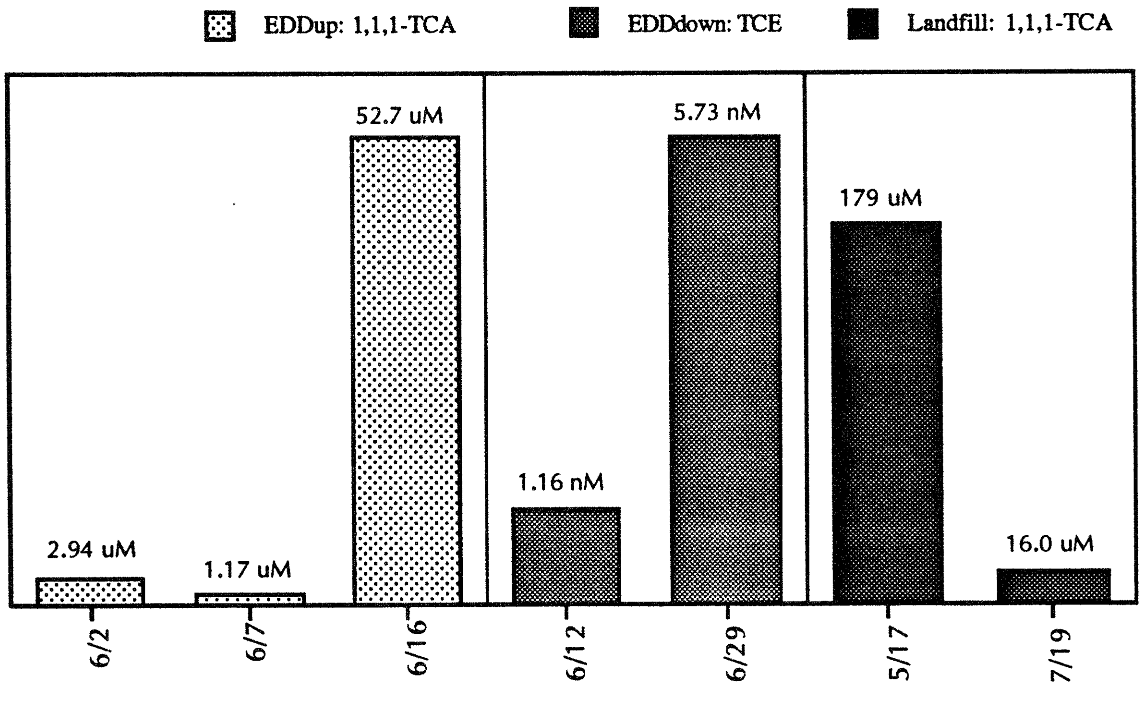

Figure 3.7: Variation in mean soil gas concentration of points sampled on all two or three sampling days, at three sites on the Aberjona watershed. EDD down concentrations are in nM.

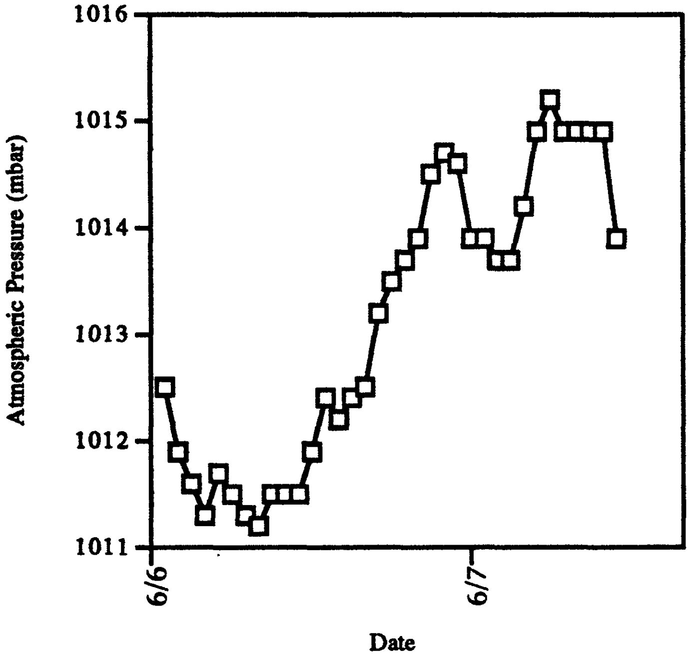

Figure 3.8: Variation in atmospheric pressure from 6/6 to 6/7/93.

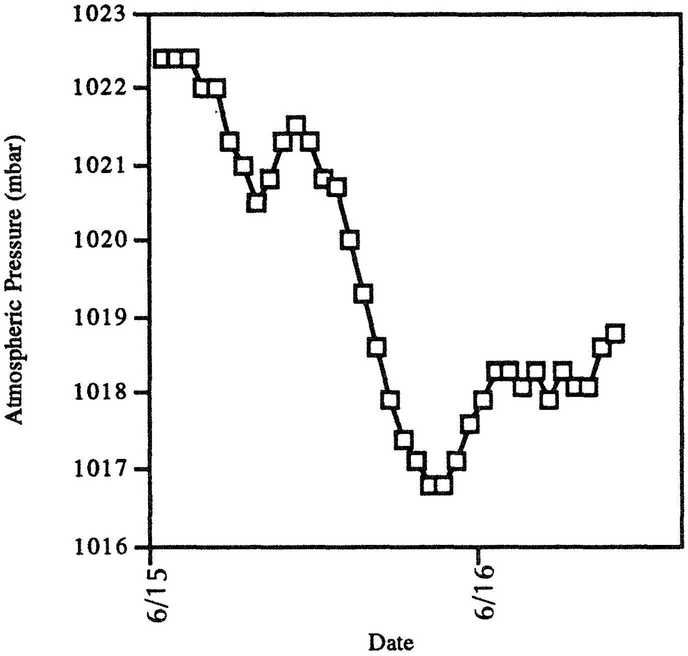

Figure 3.9: Variation in atmospheric pressure from 6/15 to 6/16/93.

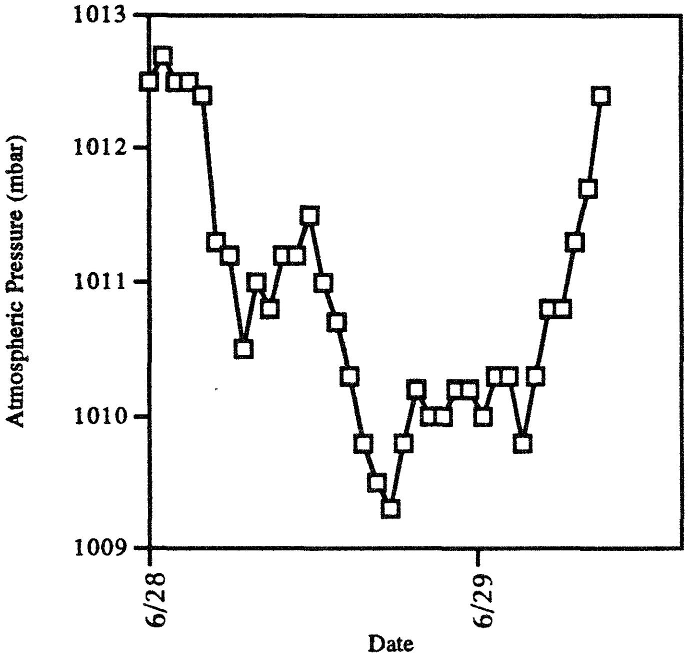

Figure 3.10: Variation in atmospheric pressure from 6/28 to 6/29/93.

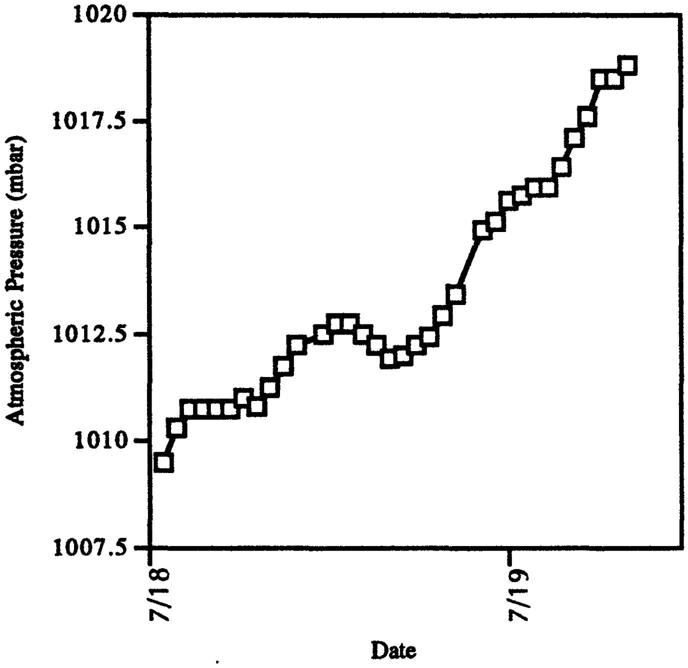

Figure 3.11: Variation in atmospheric pressure from 7/18 to 7/19/93.

3.5 Conclusions

Stream inflow and soil gas do not appear to be well correlated either quantitatively or qualitatively. Due to usually high correlation of VOC presence in soil gas and groundwater, this provides an indication that stream inflow monitoring may not be an effective method in predicting the composition of VOCs in groundwater. Stream inflow data does, however, seem to effectively predict the presence of areas of contaminated soil gas. Adjacent to all four stream reaches in which VOCs appeared in the stream inflow areas of VOC contaminated soil gas was found. This indicates that stream inflow monitoring may prove useful in detecting areas of non-specific anthropogenic VOC contamination. It is recommended that further studies be done to determine whether the lack of correlation between stream inflow and soil gas is indeed indicative of the relationship between stream inflow and groundwater.

It may be possible to increase the accuracy of stream inflow monitoring as a tool in the search for groundwater pollution by accounting for chemical transformations which may introduce chemicals to the stream which were not present in the groundwater. Smith and Dragun (1985) provide a review of anaerobic biotransformations of halogenated alkene and alkanes, while Nielson (1990) has a summary of a wide range of biotransformations which have been observed for halocarbons. In some cases stream inflow data may indicate the presence of areas of contaminated groundwater which have not been detected with smaller range soil gas / groundwater surveys. Further studies are recommended to order to better understand the factors which cause the apparent differences in VOC composition between soil gas and stream inflow.

Results obtained on the fluctuation of VOC concentrations in soil gas which has been sampled on multiple days at the same site appear to indicate a correlation with changes in atmospheric pressure. It is recommended that further studies be done to determine whether these variabilities are due to disturbance of the soil during sampling, and to better determine the overall effect of atmospheric pressure on soil gas composition.

If implemented in a careful and thoughtful manner stream inflow monitoring may yet prove to be useful tool for discovering areas of fouled groundwater. If the technique can be improved in order to account for possible chemical transformations it may become useful in detecting areas of groundwater contaminated with metals, and other pollutants, which do not lend themselves to other remote sensing techniques such as soil gas monitoring.

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Appedix 1: Statistical Summary of Sampling Points

Same Hole Technique

y-2.13*stdev(y)	12/8/93 (figs 2.10 & 2.11)	Statistical Difference (fraction of data value)
-0.053255231	west 10:40-12:00 (30cm)	*
0.018149364	west 12:00-1:15 (30cm)	0.16
-0.031193803	west 1:15-2:45 (30cm)	*
0.09069136	west 10:40-12:00 (60cm)	1.95
0.00569974	west 12:00-1:15 (60cm)	0.05
0.043415061	west 1:15-2:45 (60cm)	1.15
0.074769609	west 10:40-12:00 (80cm)	1.74
0.032802851	west 12:00-1:15 (80cm)	0.41
-0.021081225	west 1:15-2:45 (80cm)	*
0.109521178	east 10:40-12:00 (30cm)	0.92
-0.035438272	east 12:00-1:15 (30cm)	*
0.055568228	east 1:15-2:45 (30cm)	1.40
0.118255562	east 10:40-12:00 (60cm)	2.43
-0.000342101	east 12:00-1:15 (60cm)	*
-0.008255619	east 1:15-2:45 (60cm)	*
0.054247816	east 10:40-12:00 (80cm)	1.12
-0.011175703	east 12:00-1:15 (80cm)	*
-0.013539637	east 1:15-2:45 (80cm)	*

	12/10/93 (figs 2.12 & 2.13)	
-0.008235691	(30cm)	*
0.013196823	(60cm)	0.62
-0.009541478	(80cm)	*
0.2973503	(30cm)	8.04
0.170564654	(60cm)	4.08
-0.086668787	(80cm)	*

	12/12/93 (fig 2.14 & 2.15)	*
0.00775056	(30cm)	0.49
0.050350854	(90cm)	2.24
0.027230624	(30cm)	2.62
0.014711415	(60cm)	1.00
0.018392703	(90cm)	1.05

Statistical difference is expressed as a fraction of initial data point at a particular depth.

* No statistical difference (above analytical uncertainty) between points.

Fixed Point Technique

y-2.13*stdev(y)	12/12/93 (fig 2.16)	Statistical Difference (fraction of data value)
-0.005225378	t=0	*
-0.000620738	t=26	*
-0.002345345	t=97	*
-0.001263455	t=125	*
	12/16/93 (figs 2.17 & 2.18)	
-0.00267656	t=0	*
-0.034724165	t=15	*
-0.017957255	t=30	*
-0.017627815	t=45	*
-0.004200238	t=0	*
-0.005179048	t=15	*
-0.004882295	t=30	*
-0.005628141	t=45	*

Statistical difference is expressed as a fraction of initial data point at a particular time.

* No statistical difference (above analytical uncertainty) between points.

Simultaneous Sampling Technique

y-2.13*stdev(y)	12/8/93 (fig 2.19)	Statistical Difference (fraction of data value)
-0.065180843	I-30cm	*
0.120556836	I-60cm	2.60
0.060832651	I-80cm	1.43
	12/10/93 (figs 2.20 & 2.21)	
-0.004464158	II-30cm	*
0.004044783	II-60cm	0.33
0.013909732	II-80cm	1.25
0.009935835	III-30cm	1.40
0.005025789	III-60cm	0.28
-0.012603023	III-80cm	*
	12/12/93 (fig 2.23)	
-0.00551313	#1-30cm	*
-0.007021141	#1-60cm	*
-0.00500171	#1-90cm	*
	12/17/93 (fig 2.24)	
-0.004976073	#2-30cm	*
-0.007661546	#2-60cm	*
-0.004220439	#2-90cm	*
-0.013284797	#3-30cm	*
-0.007089652	#3-60cm	*
0.007227104	#3-90cm	*

Statistical difference is expressed as a fraction of initial data point at a particular time.

*** No statistical difference (above analytical uncertainty) between points.**