

**^{13}C AND ^{37}Cl CHARACTERIZATION OF PCE AND APPLICATION TO
CONTAMINATION OF THE HARRISON LANDFILL: TUCSON, ARIZONA**

by

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STATEMENT BY AUTHOR

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DEDICATION

This thesis is written in memory of my father, Arne Rosengreen, and is dedicated to my mother and brother, Annemarie Rosengreen and Lars Thomas Rosengreen.

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ABSTRACT

Tetrachloroethene (PCE) contamination of groundwater and soil air underneath Harrison Landfill in Tucson, Arizona, likely occurred by downward vapor phase transport of PCE dumped in the landfill. This study has explored the possibility of using isotopic techniques to better understand this process.

The author designed and used a technique for the extraction of PCE vapors from soil air, for $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ analysis. It involved collecting PCE vapors by passing soil air through PCE adsorbent traps, then processing and transferring the PCE to a combustion tube. The author also measured for $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ values from manufactured trichloroethene (TCE, same as measured by another lab) and PCE samples. An additional experiment measured the $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ values of the liquid PCE residual after evaporating various fractions of PCE.

$\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ values of the TCE samples previously described were similar to the earlier values, indicating that $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ measurements of solvents (including PCE) were reproducible. Successive evaporation of PCE followed a Rayleigh trend, indicating α values of 1.0006 for carbon and 0.9992 for chlorine. The author simulated the PCE soil vapor sampling in the laboratory, achieving high yields and good separation of PCE. $\delta^{13}\text{C}$ values from Harrison soil PCE vapors ranged from -27.3 to -25.1 ‰ and were within previous values for PCE. $\delta^{37}\text{Cl}$ values were at least 2.3 ‰ higher than any previously reported for PCE samples. $\delta^{37}\text{Cl}$ values for PCE, indicated that either the PCE in Harrison landfill became fractionated in situ, or was already ^{37}Cl rich when dumped at the site.

CHAPTER ONE

INTRODUCTION

Twenty-three municipal solid waste landfills (Tucson OEM, 2000) are in the southeastern Arizona city of Tucson. It is likely that solvents such as tetrachloroethylene (PCE) and trichloroethylene (TCE) have been illegally dumped in the landfills during their operation. Groundwater pumped from monitoring wells at four of these landfills exceeded the aquifer water quality standard (.005mg/L for PCE and TCE) for volatile organic carbon compounds (VOCs). At three landfills, PCE and TCE were specifically detected (Tucson OEM, 2000). None of the landfills in Tucson is lined with membranes or low-permeability barriers to prevent or inhibit the flow of fluids from the solid waste into the underlying ground and groundwater.

In September of 1995, a well supplying water to St. Joseph's hospital in Southeast Tucson was found to contain PCE concentrations approaching the drinking water standard (Tucson OEM, 2000). St. Joseph's is a private hospital located 1 mile west of Tucson's Broadway landfill. It has been suggested that PCE originating in the landfill migrated 99 m (325 ft.) down from the landfill to the aquifer by gas phase transport and then to the affected well (Camp Dresser & McKee, Inc. [CDM], 1998). Production from this well was stopped until installation of a carbon filtration system was set up to clean the water before delivery.

Until 1992, all of the water supplied to the public in Tucson came from groundwater. Since 1900, the city drilled 585 production wells to fulfill the municipal water needs. Numerous private wells are still active in Tucson and the use and

locations of many of these are not on record. It is feared that such wells might become/have already become contaminated by gas phase transport of PCE and TCE from nearby landfills, and many additional wells may require carbon filter treatment. Thus it is necessary to identify and understand the source of the contamination, whether it is the landfill or other sources in the immediate surroundings. Recognizing that PCE or TCE will be a persistent problem in ground water of the Tucson region, the hypothesis established here is that stable isotopic characteristics of contaminants can distinguish the source of PCE contamination. This study hopes to test this hypothesis. In the course of this study the author also gained knowledge about the physical and isotopic properties of PCE and TCE and how they relate to landfill processes. Information about the history and (or) source of a PCE or TCE sample can be obtained by comparing the isotopic ratios of the samples with each other, values in the literature, and known physical properties. Specifically, this study has three objectives: (1) implement procedures for the measurement of carbon and chlorine stable isotopes from liquid PCE and TCE samples, (2) examine how isotopic composition of liquid PCE changes when PCE is successively evaporated, and (3) establish procedures for collecting PCE vapors from a landfill and measuring the isotopic composition of that PCE.

1.1 Basic Concepts of Isotopes

This study deals entirely with stable environmental isotopes. Stable environmental isotopes are isotopes that do not spontaneously disintegrate by any known mode of decay, and are the naturally occurring isotopes of elements found in

abundance in our environment. The specific isotopes of importance to this study are ^{12}C , ^{13}C , ^{35}Cl , and ^{37}Cl .

The molar ratio of the two most abundant isotopes of a given element gives its isotopic ratio (i.e. $^{13}\text{C}/^{12}\text{C}$). Measurement of actual isotope ratios is difficult. In practice, it is easier to measure differences in isotope ratios, under which factors related to instrumental settings and drift cancel. In the laboratory, ratios are measured relative to a laboratory reference material, which has a known relation to an international standard reference material. Thus isotope ratios are almost always reported in relation to this international standard reference material using the delta (δ) notation:

$$\delta \text{ (}\text{‰}\text{)} = \frac{\text{R (sample)} - \text{R (reference)}}{\text{R (reference)}} \times 1000 \quad (1.1)$$

where

R = the molar isotope ratio: $^{13}\text{C}/^{12}\text{C}$ or $^{37}\text{Cl}/^{35}\text{Cl}$.

The international standard reference compounds (reference) used for carbon and chlorine are identified later.

Physical and chemical processes can change the δ values of a species. Evaporation, adsorption, diffusion and chemical reactions are examples of these processes. During these processes typically the lighter isotope reacts faster than heavier isotopes, changing the δ values of both the product and the remaining reactants. For example, when water evaporates, the H_2^{16}O water molecules will evaporate slightly faster than the H_2^{18}O molecules. Thus the $\delta^{18}\text{O}$ value of the evaporated water vapor is lower than the $\delta^{18}\text{O}$ value of the liquid water from which it

evaporated. Since a finite amount of water with a lower $\delta^{18}\text{O}$ value leaves the liquid phase, the residual liquid $\delta^{18}\text{O}$ value increases as a result of the evaporation. Such a process in which the isotopic composition of a substance changes (certain isotopes are preferentially added or removed) is called isotopic fractionation. Fractionation is expressed in this study as a α value, which is an equilibrium or kinetic relationship of the distribution of isotopes between two phases, or as a Δ value, where Δ is equal to $1000\ln(\alpha)$. Equilibrium fractionation occurs when opposing reactions transform equal amounts of a compound between phases, creating a balance or equilibrium. The δ value in each phase remains constant with time, but often the δ values will differ between phases. For example, when a jar that is half full with water is sealed, eventually a condition is reached where the amount of water vapor created by evaporation equals the amount being lost to condensation. A constant 9.8‰ difference is found between the $\delta^{18}\text{O}$ values found in the liquid and vapor phases at 25°C . For kinetic fractionation, it is assumed that once a product is created it can no longer affect the reactants in any way. Thus the isotopic differences between the phases are created because one isotope reacts faster than the others. The Rayleigh model describes kinetic fractionation processes, with the assumption that isotopic homogeneity is maintained in the reactants (they are well mixed), and is defined by the equation:

$$R = R_0 F^{\alpha - 1} \quad (1.2)$$

where α is described above, F is the fraction of the reactants remaining, R_0 is $^{13}\text{C}/^{12}\text{C}$

or $^{35}\text{Cl}/^{37}\text{Cl}$ before fractionation started ($F = 1$), and R is $^{13}\text{C}/^{12}\text{C}$ or $^{37}\text{Cl}/^{35}\text{Cl}$ after the reactants have been reduced to F .

1.2 Chlorine

1.2.1 Chemical behavior

With seven outer electrons, chlorine seeks one more electron to complete its octet. The chloride anion is a form of chlorine with eight outer electrons. Because of the complete octet, the chloride anion has a very conservative chemical behavior (does not participate in most chemical reactions). Its strong ionic character tends to form weak bonds, creating compounds with a high solubilities. Furthermore it is the most abundant naturally occurring form of chlorine, being found in salt deposits, brines and dissolved in water.

Another way in which chlorine exists with a complete octet is by forming a covalent bond. While chlorine in this form is not as abundant in nature, it is commonly found in manufactured organics (solvents, pesticides, etc.).

1.2.2 Chlorine Isotopes in Nature

The two most abundant chlorine isotopes are ^{35}Cl and ^{37}Cl . ^{35}Cl makes up about 75.5% of the chlorine atoms and ^{37}Cl makes up about 24.5%. Chloride in the oceans is homogeneous in isotopic composition (Kaufman et al., 1988). Because of this, ocean chloride is generally used as the international standard isotopic reference material for the determination of $\delta^{37}\text{Cl}$ values. Early chlorine isotope studies showed a small natural range of only 3.5 ‰ (Long et al., 1993). This is perhaps due to the

conservative chemical behavior of chloride. However, owing to the high instrumental analytical precision, meaningful distinctions have been observed within this range among formation waters (Eastoe and Guilbert, 1992; Kaufman et al., 1988) and between chlorine-containing minerals (Eastoe and Guilbert, 1992). Slight fractionation effects have been described during evaporite mineralization (Eggenkamp et al., 1995), HCl volatilization in aerosols (Volpe and Spivack, 1994), upward diffusion of chloride (Desaulniers et al., 1986), and during flow through semi-permeable clay disks (Philips and Bentley, 1987; Campbell, 1985). Later studies of chlorine at geologically active sites greatly extend the $\delta^{37}\text{Cl}$ range to 15.2 ‰. $\delta^{37}\text{Cl}$ values as low as -7.7 ‰ are found in the marine pore waters of a subduction zone (Ransom et al., 1995), and $\delta^{37}\text{Cl}$ values of $+7.5$ ‰ are found in hydrothermal smectite veins (Magenheim et al., 1995). Eggenkamp and Schuiling (1995) also found large $\delta^{37}\text{Cl}$ variations in late stage volcanic (fumarolic) environments.

1.2.3 Chlorine Isotopes in Synthetic Organic Compounds

$\delta^{37}\text{Cl}$ values are found with a larger range in synthetic organics than in most naturally occurring forms of chlorine. Although early studies of organic reactions indicated α values as high as 1.008 (Bartholomew et al., 1954; Hill and Fry, 1962), chlorine isotope variations in organics were ignored for a long time. Tanaka and Rye (1991) reported a range of 9.43 ‰. This variation is likely caused by fractionation during the different manufacturing procedures used to synthesize different chemicals.

1.2.4 Measurement Techniques

While a measurement precision of 1 ‰ (1 σ) or more may be sufficient for systems with isotopic compositions that vary over a range of several tens per mil, it is not sufficient for PCE, with a range of only 2.8 ‰. Earlier measurement techniques required gas mass spectrometry measuring Cl as Cl₂, or thermal ionization of solid materials producing Cl⁻ ions for measurement (Bartholomew et al., 1954; Vengosh et al., 1989). The two most common techniques currently used are gas mass spectrometry of CH₃Cl⁺ and thermal ionization of Cs₂Cl⁺.

1.2.4.1 Thermal Ionization of Cs₂Cl⁺

The chlorine must first be converted to the aqueous chloride form with other anions removed before starting this technique. The chloride sample solution is passed through a cation exchange column to exchange other cations for Cs⁺. This solution is then concentrated by evaporating most of the water, and dried onto a tantalum filament along with a graphite-ethanol ion-enhancer solution. The filament is mounted in the mass spectrometer, where an applied current heats the sample producing the Cs₂Cl⁺ ions. Applying an electric potential accelerates these ions and the isotopes are separated on passing through a magnetic field, and finally measured by a detector. Magenheimer et al. (1994) used a Daly detector, while Xiao and Zhang (1992) used Faraday cup detectors. This technique allows sample sizes as small as 2 μ g as CsCl, and has a precision of 0.25 ‰ (1 σ). The small sample capability of this method has the advantage of greatly increasing the number of substances for which isotope measurement is practical.

1.2.4.2 Gas Mass Spectrometry of CH_3Cl^+

The high precision obtainable by this technique makes it the preferable technique provided that a sample of at least 1.5 mg as AgCl is available. The sample must first be converted to the aqueous chloride form. It is then quantitative precipitated as AgCl, which is collected on a filter and dried. Five to ten milligrams of AgCl are weighed out and sealed in a Pyrex™ tube with methyl iodide. Heating the tube to 100°C for 48 hours produces CH_3Cl . The sealed Pyrex™ tube is cracked open and the vapor contents are extracted. High yields of CH_3Cl are produced for gas mass spectrometry after separation by gas chromatography and cryogenic techniques (Long et al., 1993). The mass spectrometer sequentially switches between the sample and a reference gas having a known isotopic composition. The CH_3Cl is ionized and accelerated at the source. By slightly changing the voltage for acceleration, atomic masses 50 and 52 are sequentially measured. From these measurements the $\delta^{37}\text{Cl}$ values are calculated. The analytical precision of 0.24 ‰ originally reported has been improved to 0.08 ‰ by the University of Arizona environmental isotopes lab (performed the measurements in this study).

1.3 Stable Carbon Isotopes

Carbon atoms make up the backbone of all organic molecules. Both naturally occurring and manufactured organic molecules come in an enormous number of physical variations, chemical compositions and physical properties. Since stable carbon isotopes are necessarily a part of all of these molecules, the potential for

carbon isotope applications is obvious. For example, varying degrees of fractionation during the production of thermocatalytic methane, microbial methane by fermentation, and microbial methane by CO₂ reduction produces three different ranges of δ¹³C values (Grossman et al., 1989). Hydrocarbons tend to be very depleted with respect to ¹³C. Several studies have confirmed that natural (biological or physical) degradation of hydrocarbons occurs at a site by finding lower δ¹³C values in soil CO₂ and (or) aqueous bicarbonate, than could be explained by other (e.g. root respiration) CO₂ production pathways (Aggarwal and Hinchee, 1991; Baedeker et al., 1993; Revesz et al., 1995; Landmeyer et al., 1996; Conrad et al., 1997; Sturchio et al., 1998; Hunkeler et al., 1999a; Hunkeler et al., 1999b). Carbon isotopes have also been used to study ancient atmospheric conditions. For example, past changes in climatic conditions are recognized by δ¹³C changes in soil carbonates (Cerling, 1984), and in carbonate sediments (Magaritz et al., 1983).

The two stable carbon isotopes are ¹²C and ¹³C, with terrestrial abundances of 98.9 % and 1.1 % respectively. PDB, calcite from fossil *Belemnitella americana* in the Pee Dee formation, is the conventional international reference material. The measurement technique of preference is gas source mass spectrometry of CO₂ (Clark and Fritz, 1997). Very small sample sizes down to 50 μg are possible for measurement with high precision (approximately 0.1 ‰ at the 1 σ level).

1.4 Isotopic Fingerprinting

As mentioned earlier, chlorinated hydrocarbons, and PCE and TCE in particular are common contaminants of groundwater. Remediation is costly and time

consuming, and often the parties responsible are difficult to identify. Determining the responsible party on the basis of the isotopic composition of the contaminant molecule is becoming increasingly useable. This determination is called “isotopic fingerprinting”. Recent improvements in the analytical precision of $\delta^{37}\text{Cl}$ value measurements and the large δ value range occurring in organic compounds, allows the measurement of subtle differences between chlorinated hydrocarbons. A key advantage for the isotopic fingerprinting of chlorinated hydrocarbons came with the discovery that the carbon and chlorine isotope compositions of a given chemical (PCE, TCE, and 1,1,1 trichloroethane [TCA]) differ among manufacturers (van Warmerdam et al., 1995). Combined carbon and chlorine δ -value measurements significantly improve the ability to distinguish a source. For example, PCE from two different manufacturers with similar $\delta^{37}\text{Cl}$ values might be distinguished from each other by having different $\delta^{13}\text{C}$ values. Before isotopic fingerprinting can be used in a real world application, several potentially confounding variables must be considered: changes in the isotopic composition of the chemical both at the source and along the path of migration, by sorption, by evaporation, and by microbial activity.

1.5 Remediation Techniques

1.5.1 Physical Remediation

Two common physical remediation techniques for the removal of PCE and TCE from contaminated sites are “pump-and-treat” and soil vapor extraction. The “pump-and-treat” approach is the most commonly used procedure for contaminant removal in the saturated zone, and entails the removal of groundwater through a

network of extraction wells, and above ground treatment. The removal of the water causes the neighboring groundwater to be drawn towards the well. Soil vapor extraction (SVE) is a common technique for unsaturated (vadose) zone clean up. This technique is essentially the same as pump-and-treat, except that soil air is removed rather than aquifer water. Contaminants are evaporated or desorbed, drawn to the extraction wells, and brought to the surface for treatment.

1.5.2 Biological Remediation

A very promising technique to remediate PCE and TCE contaminated sites is through biodegradation. Carbon and chlorine isotopes can possibly play an important role here, since they should help confirm the presence of biological remediation and quantify its rate. The most common biological remediation pathway is dechlorination. Bacteria can successively remove each of the chlorine atoms from a PCE molecule. In this manner, PCE degrades to TCE, then to cis-1,2 dichloroethylene (cis-1,2 DCE), then to vinyl chloride (VC), then finally to ethylene. A significant drawback is that the intermediates (TCE, cis-1,2 DCE, and VC) are equally toxic as PCE. Isotopic fractionation occurs to various degrees at each of these dechlorination steps, as described below.

Bacterial dechlorination occurs under various conditions by different strains of bacteria. Degradation of TCE and its daughter products can take place in an aerobic environment (Wilson and Wilson, 1985; Suchomel et al., 1990; Hopkins et al., 1993; Sturchio et al., 1998). Different additives can stimulate degradation, including natural gas (Wilson and Wilson, 1985) and Phenol (Hopkins et al., 1993). An undetermined

pathway other than dechlorination also degrades TCE (Hopkins et al., 1993). A fractionation effect ($\alpha = 0.999475$) for Cl in the aerobic dechlorination of TCE exists (Sturchio et al., 1998). Numerous studies show that bacteria have the ability to dechlorinate PCE and its degradation products under anaerobic conditions (Holliger et al., 1993; Neumann et al., 1994; Scholz-Muramatsu et al., 1995; Maymo-Gatell et al., 1995; Sharma and McCarty, 1996; Fennell et al., 1997; Aravena et al., 1998; Hunkeler et al., 1999a; Hunkeler et al., 1999b; Lollar et al., 1999). Different bacteria strains use different compounds for the electron donor: H_2 or formate (Holliger et al., 1993), H_2 or pyruvate (Neumann et al., 1994; Scholz-Muramatsu et al., 1995), only H_2 (Maymo-Gatell et al., 1995; Fennell et al., 1997), or 58 compounds including many carbohydrates, short-chain fatty acids, amino acids, purines and pyrimidines (Sharma and McCarty, 1996). No significant isotopic fractionation of chlorine occurred during anaerobic biodegradation of PCE to TCE and TCE to DCE, but a significant fractionation occurred for DCE to VC (Aravena et al., 1998). ^{13}C fractionation followed the same trend, and was small for the first two biodegradation steps, and large for the steps DCE to VC and VC to ethylene (Hunkeler et al., 1999b). The biodegradation of TCE to DCE occurs with a α -value of .9929 (Lollar et al., 1999).

Although previous studies of fractionation during the degradation of PCE to ethylene dramatically demonstrate the presence of isotopic fractionation, they do not mention the specific bacterial strain used. Because some of the different strains use fundamentally different mechanisms (e.g. aerobic verses anaerobic) for dechlorination, it is possible that they produce different fractionation effects. As an

analogy, plants using the C3 physiology have significantly different carbon isotope fractionation from those using the C4 physiology (Ode et al., 1980). If the strain specific fractionations from each of the pure strain biodegradation bacteria were known, the net fractionation effect at a field site containing a mixture of different strains could be calculated.

CHAPTER TWO

FIELD SITE CHARACTERIZATION AND BACKGROUND

2.1 History

Except where noted otherwise, all of the information in this chapter is from a recent study of the Harrison Landfill (Hydro Geo Chem, inc. [HGC], 1999) and (or) from personal observations made while visiting the site. The field site used in this study is the Harrison landfill, located at the northeast corner of Harrison and Irvington roads, Tucson, Arizona. The 48.6-hectare (120 acre) site is owned by the city of Tucson. Directly to the north lies the active B&R materials quarry. Directly to the east are a mobile home park and an inactive Pima County landfill. Undeveloped land lies to the south and west.

Before 1972 the site was a sand and gravel pit, which had been excavated to depths of 15 meters (50 feet). Deposition of refuse of residential, commercially collected, privately collected, and public origin began in 1972. Refuse was initially deposited in the northern part of the site, and progressed southward with time as the total material increased. The refuse was deposited directly on top of the original surface without an intervening liner. Disposal activities ceased on April 1, 1997. The depth of the waste material varies from about 1.1 m (3.5 ft) to approximately 30.5 m (100 ft) below the land surface (bls). The waste footprint of the site is approximately 28 hectares (70 acres). By April 1, 1998 the entire landfill had been buried under a three layer cap, 1.1 to 1.5 m (3.5 to 5 ft) thick comprised of compacted topsoil, silt, and uncompacted topsoil respectively (bottom to top).

Methane concentrations exceeded 5% in the soil air, thus the city of Tucson installed a landfill gas extraction system (August, 1995) to prevent such gases from migrating off the site. 25 extraction wells were drilled along the north and east sides of the site. 32 additional extraction wells were added to the system in September 1998. 12 groundwater monitoring wells were drilled in April 1997, 8 of them within the site, and 4 of them off-site, down gradient. Two additional multi-purpose wells were installed in September 1998. One purpose of the two multipurpose wells was as injection and extraction wells for a soil vapor extraction system. Air injection began August 23, 1999 at well SVI 1 at 118,000 cubic centimeters per second ([ccms], 250 standard cubic feet per minute [scfm]), and extraction began at well SVE 1 at 425,000 ccms (900 scfm).

2.2 Hydrogeology

The water table is approximately 76.2 m (250 feet) bls giving rise to a large vadose zone. Camp Dresser and McKee (CDM), 1996 characterized the aquifer beneath the landfill as comprising three zones: an upper aquifer zone, a low permeability zone, and a lower aquifer zone. The upper and lower aquifer zones consist of coarse-grained sediments, and the low permeability zone consists of fine-grained sediments. Groundwater elevations in deep wells (>100 m or 328 ft bls) were 0.15 to 0.30 m (0.5 to 1 ft) lower than in the shallower wells (<85 m or 280 ft). This indicates a downward vertical hydraulic gradient of approximately 0.006 meter per meter (0.006 ft/ft). The effective porosity is 35%. Hydraulic conductivity is 2.5 m/day (8.2 ft/day) in the lower aquifer zone, and 16.2 m/day (53 ft/day) in the upper

aquifer zone. The average velocity in the lower aquifer zone is 0.043 m/day (0.14 ft/day), and 0.43 m/day (1.4 ft/day) in the upper aquifer zone. Flow is to the northwest with a hydraulic gradient of 0.008 m/m (ft/ft).

2.3 Climate and Vegetation

As a part of the closure requirements at the landfill, vegetative seeding of the topsoil cap layer was completed in October 1998. Since then tumbleweed has proliferated in the semi-arid environment. The average annual precipitation for Tucson, Arizona is 30 cm (12.5 inches). Two distinct rainy seasons are winter (November-March) and summer (July-September). The winter rain is typically by frontal storms, producing low intensity rainfall events with widespread precipitation. The summer rain is by convective storms with high intensity rainfall events that are localized and short duration. Although approximately the same amount of precipitation falls in each of the two seasons, most of the summer precipitation is lost to evapotranspiration before it can infiltrate into the ground. At the Harrison site, one would expect the largest infiltration to occur at the two detention basins, to which the surface water runoff is routed.

2.4 Sampling Location

The author collected all field samples from one of the two multipurpose wells installed in September 1998, SVE1. It is located in the northern portion of the landfill site. Drilling reached a depth of 76.2 m (250 feet) below the land surface. HGC determined that the well passes through refuse from a depth of 1.5 meters (5 ft) and

continues down to a depth of 6.1 meters (20 ft), which they believed to be the bottom of the landfill. The well passes through sediments consisting of mostly sand and gravel at depths greater than 6.1m (20'). Four independent PVC pipes, screened at various intervals, descend to different depths in the well bore. SVE1-80, SVE1-135 and SVE1-245 are made with 12.7 mm (½") PVC tubing, descend to 24.4m (80'), 41.1m (135') and 74.7m (245') respectively, and are screened over the intervals 22.9-24.4m (75'-80'), 39.6-41.1m (130'-135'), and 73.2-74.7m (240'-245') respectively. SVE1-200 is made with 15.2cm (6 inch) PVC piping, descends to 61.0m (200') and is screened over the interval 45.7-61.0m (150'-200'). The remaining space in the drill bore contains medium sand at the screened intervals, fine sand for the 1.5m (5') immediately above the screened interval, 0.9-1.5m (3-5') of bentonite immediately above the fine sand, and concrete filling all other empty spaces left by the borehole. All four PVC pipes have sampling ports and valves above the land surface. Piping for SVE1-200 extends 274m (300 yards) farther east along the surface where it is connected to a vacuum pump. All field samples collected in this study were from SVE1-135.

2.5 Contaminants

HGC operates a groundwater-monitoring program, which samples the groundwater quarterly, and measures contaminants in the groundwater. The contaminants of most concern that HGC found in Harrison groundwater were all volatile organic compounds, and include PCE, TCE, cis-1,2-dichloroethene (cis-1,2-DCE), vinyl chloride (VC), dichloromethane (DCM), trichlorofluoromethane (Freon

11), and dichlorodifluoromethane (Freon 12). Only PCE, TCE, and DCM concentrations exceeded the US Environmental Protection Agency maximum contaminant levels (0.005 mg/L for each), and only in wells screened near the water table. Contaminant concentrations appear to decrease with increasing depth below the water table, and are not present in wells screened at greater than 30.5m (100 ft) below the water surface elevation.

CHAPTER THREE

METHODOLOGY

3.1 Overview

One of the objectives of this study is to develop a technique for extracting tetrachloroethylene (PCE) vapors from a contaminated site and measuring the carbon and chlorine δ values in this PCE. The procedure involves seven steps. (1) Pump the contaminated air from well SVE1-135, out of the ground and through an adsorbent, collecting the PCE vapors (collection step). (2) The PCE is removed from the resin by heating, and transfers to a tube containing copper oxide wire (transfer step). (3) Combust the PCE in the tube (combustion step). Carbon dioxide produced in this combustion contains the carbon from the PCE. (4) Extract the CO_2 and then measure the $\delta^{13}\text{C}$ (CO_2 extraction and measurement step). The chlorine from the PCE crystallizes as copper chloride after the combustion. (5) Dissolve the copper chloride, producing aqueous chloride, then remove chlorine from the aqueous solution by precipitation as silver chloride and collect on a filter (AgCl production step). (6) The silver chloride reacts with methyl iodide to produce methyl chloride (methyl chloride reaction step). (7) Extract the methyl chloride from the reaction products, and then measure its $\delta^{37}\text{Cl}$ value (CH_3Cl extraction and measurement step).

Three types of tests revealed the purity and yield of the products produced in the procedures, and the accuracy of the measurements. (1) The author processes known quantities of solvents. To determine if the combustion, and AgCl production steps (described above) obtain high yields and accurate δ values, the author measures

the δ values of manufactured solvents: Aldrich PCE, ICI TCE and DOW TCE. Several replicate measurements are made of each of these three solvents. The δ values of the DOW and ICI TCE are known (Van Warmerdam et al., 1995). (2) The second test determines if the collection and transfer sections produce high yields and none or minimal fractionation effects. By simulating field samples in the lab, using the Aldrich PCE, the author tests these procedures by measuring yields and $\delta^{13}\text{C}$ values. (3) The purpose of the third test is to insure that the δ values actually come from PCE at the field site, and not some other (chloro) carbon that might have been collected. A GC-MS analysis is performed on one sample collected at the field site to see which organic compounds were collected. The conversion to methyl chloride, carbon dioxide extraction, and methyl chloride extraction procedural steps are not tested in this study, since they are known to produce results with a high degree of precision and accuracy (Long et al., 1993; Eastoe et al., 1999 and others).

In addition, the author performs a laboratory experiment in which the isotopic behavior of PCE during progressive evaporation is measured.

3.2 Extraction and Measurement Procedures

3.2.1 System Design

In June-July, 1999 the author designed the procedure for collecting PCE vapors from the vadose zone at Harrison landfill. Harrison well SVE1-135 had the highest PCE vapor concentration of those wells most recently measured at 570 $\mu\text{g/L}$. The author therefore decided to use SVE1-135 as the sampling location due to these high PCE vapor concentrations and conservatively chose 100 $\mu\text{g/L}$ as the expected

PCE concentration for the purpose of designing the procedures. In addition, the author intended to collect in a single field excursion, two or three samples, each providing enough Cl for multiple $\delta^{37}\text{Cl}$ measurements.

In order to collect samples of several milligrams of PCE, 100 L air sample sizes were required. Typical commercially available organic vapor collection and desorption tubes were inappropriate because the narrow tubes allow maximum flows of only 125mL/min (for 4mm inner diameter [ID] tubes packed with 4cm TenaxTM TA), requiring at least 800 min. sampling times.

EPA (Environmental Protection Agency) methods 0030 and 0031 describe a procedure for collecting 20 L air samples of 22 VOCs (including PCE) from smokestack emissions in 16mm ID adsorbent traps. These VOST (volatile organic sampling train) tubes also contain TenaxTM TA polymer, a “clean” adsorbent resin recommended for PCE use. Since PCE is less volatile than most of the other VOCs in methods 0030 and 0031, and this study only concerns PCE, the author decided that 100 L samples could be collected using VOST traps. To check this, the author determined a safe volume to pump for PCE using published data on breakthrough volumes (Manura, 1997). Manura (1997), defines breakthrough volume as the calculated volume of carrier gas per gram of adsorbent resin which causes the analyte molecules to migrate from the front of the adsorbent bed to the back of the adsorbent bed. The breakthrough volume for PCE, with TenaxTM TA at 0°C as the adsorbent resin, is 1600 L/g. Breakthrough volumes depend highly on the temperature of the resin, as can be seen in Figure 3.1 (data are from Manura, 1997). It is this property that makes the TenaxTM TA resin so useful, since PCE can be either collected on, or

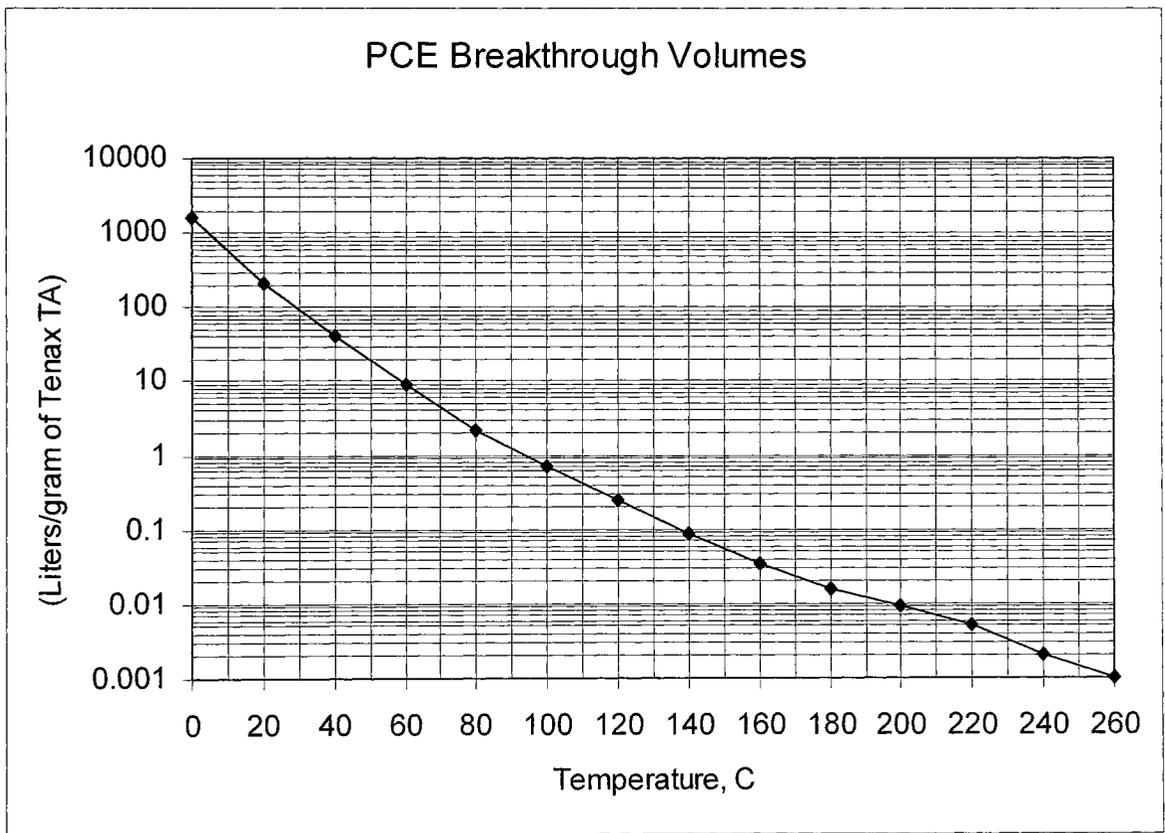


Figure 3.1 The temperature dependence of breakthrough volume for PCE on Tenax™ TA resin (Manura, 1997).

removed from the adsorbent bed with a carrier gas simply by changing the temperature. Manura (1997) calculated breakthrough volumes by measuring the carrier gas volume passed until analyte concentrations peaked. Since the objective is to collect all the PCE passing through the adsorbent column, and not miss any that breaks through at a slightly lower volume (before the peak), the author applied a factor of 0.5, giving a breakthrough volume of 800 L/g for collection purposes. Finally, multiplying by the 1.6g of Tenax™ TA (amount suggested in EPA method 0031) used gives a volume of 1280 L that can be collected on each VOST tube before PCE breakthrough becomes a concern. To be extra cautious, the author decided for each field sample to consist of two VOST tubes with Tenax™ TA resin in parallel and cooled to 0°C. Thus, in each field excursion, to collect 3 samples, a total of 6 VOST tubes are used.

3.2.2 Assembly and Preparation of Adsorbent Columns

The key system component for collecting the PCE is the adsorbent column. The following describes column assembly, removal of organic contaminants, and the use of the columns to collect field samples.

To capture PCE from an air stream, the PCE contaminated air passes through two adsorbent columns (Fig. 3.2, Table 3.1). Figure 3.2 shows the adsorbent column setup used. Table 3.1 gives brief descriptions of the numbered parts in Figures 3.2-3.7. For additional part information see Appendix A. The outside casing of the columns is a glass VOST tube. 1.6 to 1.7 grams of 30/60 mesh Tenax™ TA polymer adsorbent resin is held inside the casing between plugs of pesticide-grade glass wool.

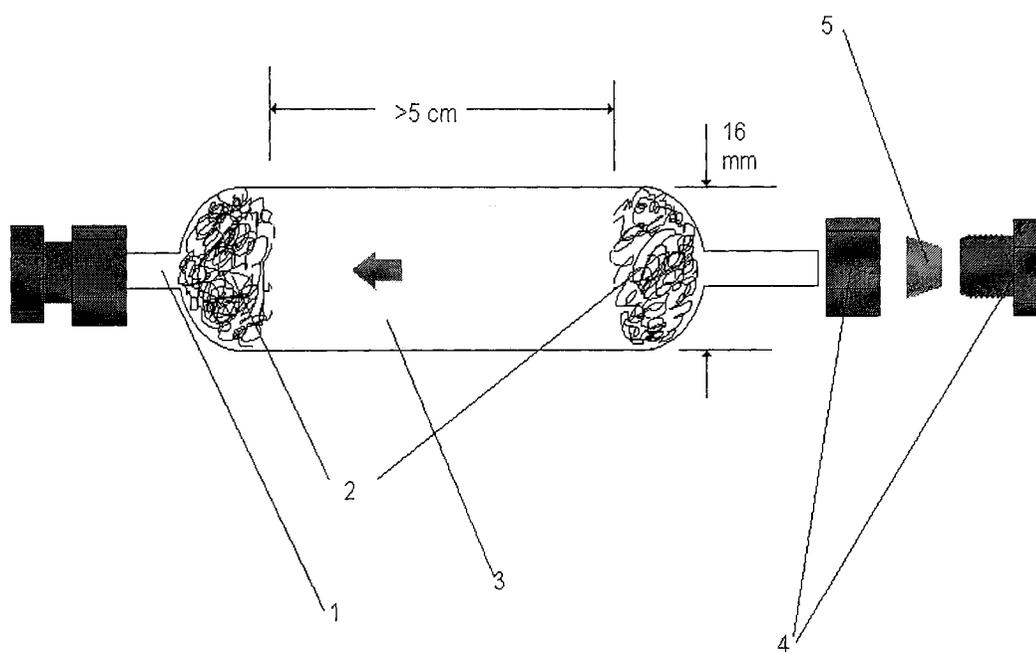


Figure 3.2 VOST adsorbent column setup. Table 3.1 lists, and Appendix A describes the numbered parts.

Key to Figures 3.1 – 3.6

- A-J. Valves**
1. VOST glass tube
 2. Glass wool
 3. Tenax TA[®] adsorbent resin
 4. ¼" nut and cap
 5. Teflon[®]- ceramic ferrule
 6. ¼" OD Teflon[®] FEP tubing
 7. ¼" OD Pyrex[®] tubing
 8. 3/16" ID Tygon[®] tubing
 9. ¼" Swagelok[®] union, graphite ferrules
 10. ¼" Teflon[®] compression unions
 11. Insulation
 12. Adsorbent column(1,2, and 3)
 13. Heating unit element
 14. Voltage controller
 15. Flowmeter stand
 16. Flowmeter
 17. 1/8" NPT male barbed elbows
 18. He line (glass & stainless steel)
 19. Liquid Nitrogen
 20. Stainless steel vacuum dewer
 21. He tank with regulator
 22. Barbed "T" connector
 23. Steel tubing clamp
 25. ¼" gas line filter
 26. Well SVE1-135
 27. Cold packs
 28. Circular Support
 29. Ring Support
 30. ¼" Cajon[®] union
 31. ¼" Teflon[®] compression elbow
 32. 2 styrofoam cups with ¼" holes
 33. ¼" OD Vycor[®] tube
 34. CuO wire on a quartz wool plug
 35. Heating assembly (11,13, and 29)
 36. Pres. transducer & needle display
 37. Pinch clamp
 38. Tube cracker: bellows, gas line filter, regular and reducing Cajon[®] unions
 39. Condensing trap
 40. Vycor[®] sample capsule
 41. 2 styrofoam cups with nitrogen (l)
 42. Digital pressure display
 43. Switch
 44. Pressure transducers
 45. Condensation finger
 46. Glass vacuum dewer with N₂ (l)
 47. Stainless steel vacuum dewer with ethanol at -80 C

Table 3.1 List of numbered parts in Figures 3.2-3.6. See Appendix A for more detail.

The ends are capped with ¼ inch (6.4 mm) Swagelok™ caps with ceramic impregnated Teflon™ ferrules. Pre-assembled columns can also be used.

The adsorption columns can be reused several times, but they must be cleaned (conditioned), of organic contaminants before each use (Figure 3.3). Helium gas free of organic compounds and oxygen from a regulated helium tank passes through a liquid nitrogen trap. The gas passes through glass and stainless steel tubing on an existing line, then through ¼ inch Teflon™ FEP tubing and flexible 3/16 inch (8.5 mm) ID Tygon™ tubing. The gas then passes through an adjustable flow meter maintaining a 1 L/min. flow rate, and then through the VOST column, which one heats to 190 to 230° C, flushing out contaminant vapors in the process. Finally the gas passes through a port back into the pre-existing line, which leads to a vacuum pump.

At each joint between Teflon™ tubing and the Teflon™ union fittings, the author cuts a notch in the tubing ¼ inch from the end with a grooving tool to ensure air tightness. To attach tubing to the flowmeter, the author uses 1/8-inch NPT male elbows with 3/16-inch barbs for the Tygon™ tubing. For a tight seal between the Tygon™ and Teflon™ tubing, the author stretches the flexible Tygon™ tubing around the outside of the FEP tubing. To withstand the high temperatures inside the furnace, short sections of ¼" Pyrex™ tubing on both sides of the VOST tube connected with brass ¼ inch Swagelok™ unions with graphite ferrules are used. Before their first use, and after each subsequent use, the author cleans these brass Swagelok™ unions,

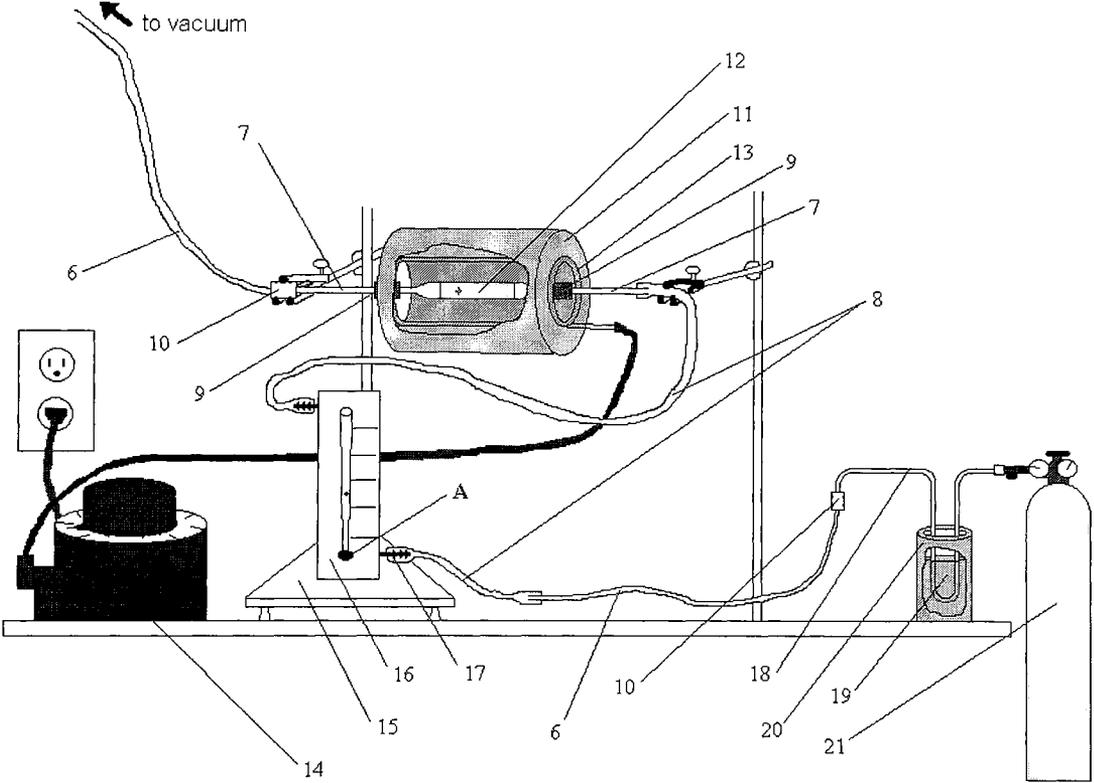


Figure 3.3 Setup for adsorbent column conditioning. Table 3.1 lists the numbered parts.

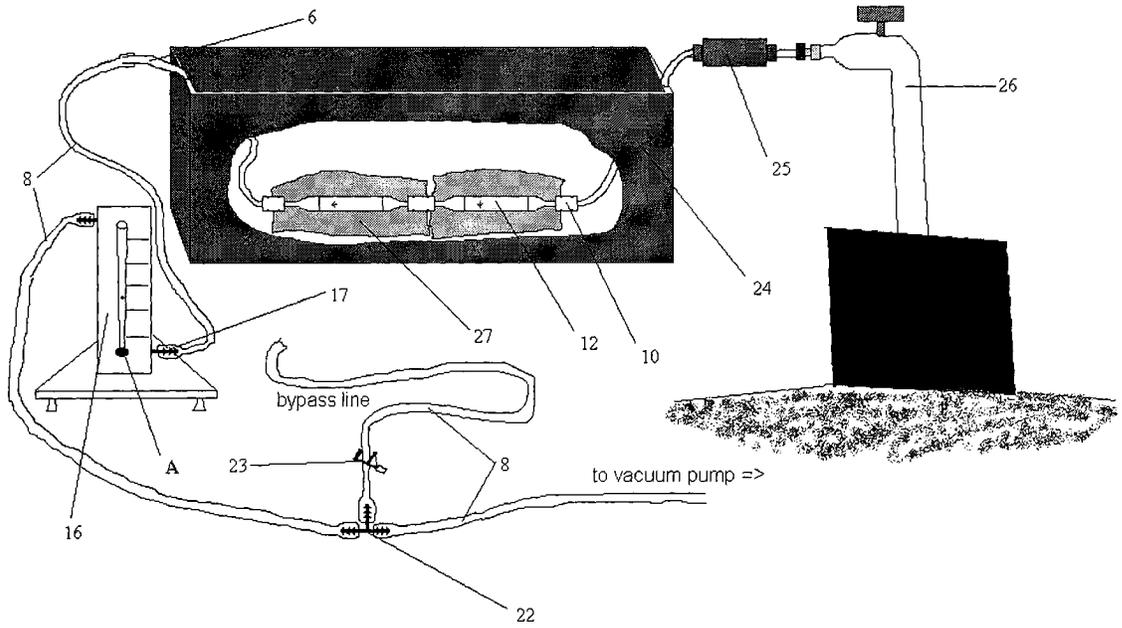


Figure 3.4 Harrison SVE1-135 sampling apparatus. Table 3.1 lists the numbered parts.

and the nuts and caps for the columns by placing them in a tube furnace for an hour at 250° C.

3.2.3 Field Sampling

Figure 3.4 shows the field-sampling apparatus: The gas-line filter removes particles from the air stream. The bypass tube is necessary to pass the excess flow from the fixed rate portable pump. The SVE1-135 well port has a ¼” Swagelok™ thread. The sampling apparatus attaches to this with a ¼” Swagelok™ nut and a Teflon™-ceramic ferrule, fastening the Teflon™ tubing in place. After opening a valve at the top of the wellhead and turning on the vacuum pump, air flows out of the well through the sampling apparatus. While collecting samples, the author maintains a flow rate of 1 L/min. (maximum flow rate for VOST columns in EPA methods 0030 and 0031) by adjusting valve A and the clamp on the bypass line. Each VOST column sample pair is collected for 100 minutes, checking the flow rate every 15 minutes. The cold packs keep the columns close to 0° C. After each 100 L sample collection, the author detaches the columns from the sampling apparatus as a pair, replaces the nuts and caps (see Figure 3.2), and places the sample in a second cooler with cold packs until returning to the lab and storing them at 4°C.

The PCE concentration at the time of sampling is measured by collecting the PCE on Supelco ORBO™ 32s charcoal adsorbent tubes. A single ORBO™ 32s tube (not cooled) substitutes for the pair of VOST tubes (Fig. 3.4), with a flow rate of 0.4 L/min. The author typically collects ORBO™ samples of 1 to 10 L after collecting

the first VOST sample. All ORBO™ samples are analyzed by gas chromatography (GC) at the University of Arizona analytical chemistry lab.

3.2.4 Transfer to Combustion Tube

Before the PCE can be combusted, it must first be transferred to a tube containing an oxidant and capable of withstanding the high temperatures of combustion. However, first one must remove condensed water, adsorbed TCE and other soil air compounds.

HGC measured TCE concentrations up to 240 µg/L at SVE1-135, but are always less than PCE concentrations. Freon concentrations are also almost as high as PCE. These and other VOCs present in the soil air are likely to also be collected on the VOST column. As the objective was to measure isotopes only on the PCE, the author removes as much of these other VOCs as possible. To remove compounds more volatile than PCE, passing an additional 20 L of helium through the columns (cooled to about 0° C by ice packs) allows the more volatile compounds to break through the columns. Helium flows at 1 L/min. for 20 minutes. This step completely removes Freons, methylene chloride, and several other volatile organic compounds present in the landfill.

Next the author concentrates each PCE sample into a single VOST column. Figure 3.5 illustrates the setup for this procedure. Helium passes through the heated (140-180° C) column on the right, and flushes out the PCE vapors to the cold (approximately 0° C) column on the left, trapping the PCE there. A flow of 0.4 L/min. for 15 minutes is used. Afterwards one removes, caps and continues storing

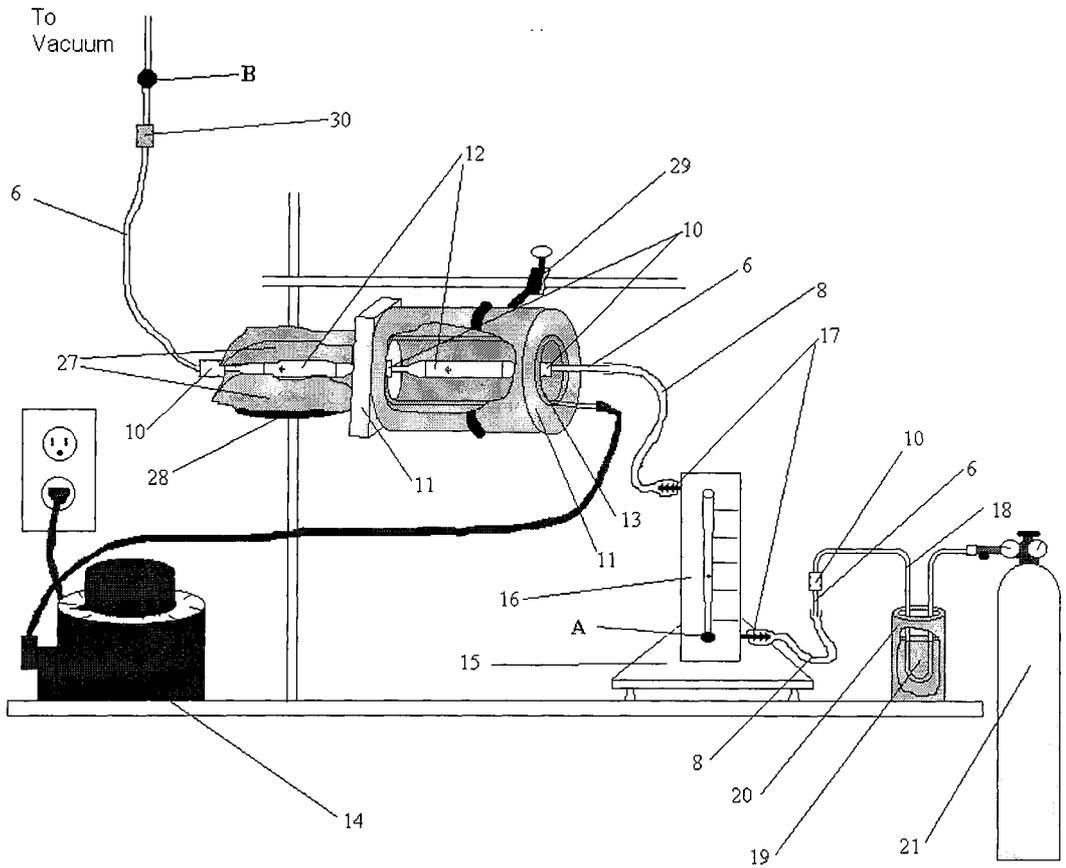


Figure 3.5 Setup for concentrating samples into a single VOST tube. Table 3.1 lists the numbered parts.

the cold VOST column (with the PCE sample) at 4° C. The author removes the heated column from the heater, and allows helium to flow through it until it cools, preventing the Tenax™ resin from combusting.

Here, one removes all but a trace of the condensed water, and as much TCE as possible from the sample. The setup used is the same as that used in Figure 3.5 with two exceptions. The sample column is a single VOST column, the column on the right (inside the heater). The column on the left is a freshly conditioned column kept at room temperature (~23° C, no cold packs). Again, one uses a flow of 0.4 L/min. for 15 minutes, 140-180° C for the heater, and the same storage and cool down procedures described above. Water vapor visibly condenses inside the downstream column within the first 2-3 minutes, and then completely evaporates after 15 minutes. If water is still visibly present after 15 minutes, the author repeats this step. As the downstream column is at room temperature, its capacity to adsorb PCE and TCE is much lower than when cooled. With a breakthrough volume less than PCE, most TCE breaks through the VOST column at room temperature, removing it from the sample. PCE, however, does not break through due to the low volume, and remains in the room temperature column (new sample column).

In this section the author describes the procedure of transferring PCE samples in a VOST tube to a combustion tube with cupric oxide wire, and sealing it in (Figure 3.6). As the arrows indicate, the tube furnace can be moved horizontally. The Vycor™ combustion tube contains about 1 gram of copper oxide wire suspended with a quartz wool plug. Two Styrofoam cups surround the CuO part of the Vycor™ tube. A tight fit between holes in the bottom of the cups and the tube prevents liquids from

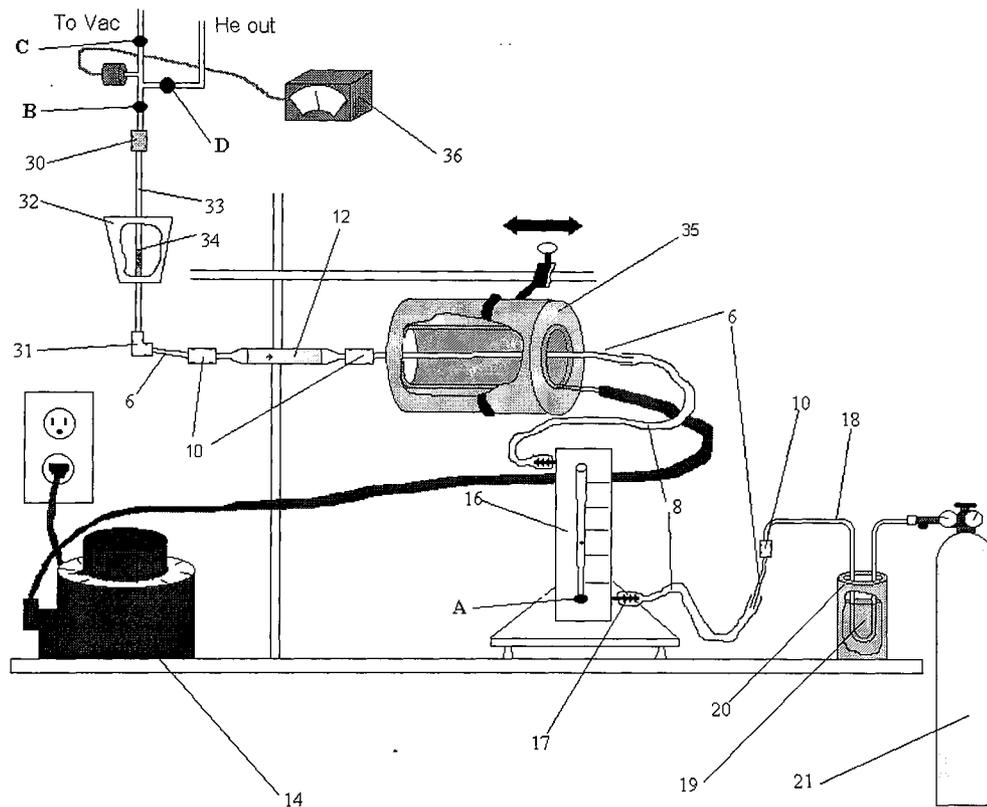


Figure 3.6 Setup for transferring a sample to a combustion tube. Table 3.1 lists the numbered parts.

leaking out of the cups and holds them in place. The He out line leads to a fume hood. The procedures are as follows:

- (1) Preheat the heater to about 175 °C. Flush all lines with helium, and then close all the valves.
- (2) Assemble the apparatus as shown in Figure 3.6, attaching the VOST column last, so that it is still cold at the completion of the assembly.
- (3) Open valves B and C and wait (<1 min.) for a pressure of less than 1 torr, then close valve C.
- (4) Crack open valve A. Add liquid nitrogen (LN₂) to the Styrofoam cups.
- (5) After the pressure rises to above atmospheric, open valve D. Adjust Valve A to a He flow of 0.4 L/min., then move the tube furnace to the left, covering the VOST tube. Wait 15 minutes while the PCE transfers to the combustion tube.
- (6) Close valves A and D, then open valve C. Collapse the Vycor™ combustion tube between the Styrofoam cup and the elbow union with a torch.
- (7) Upon reaching a high vacuum, collapse the other end of the Vycor™ tube between the styrofoam cups and the Cajon™ union, producing a sealed capsule containing copper oxide wire, PCE and an inert quartz wool plug.
- (8) Remove the Vycor™ end piece, open valve A, and remove the VOST tube from the heater. Keep the He flowing until the VOST tube cools.

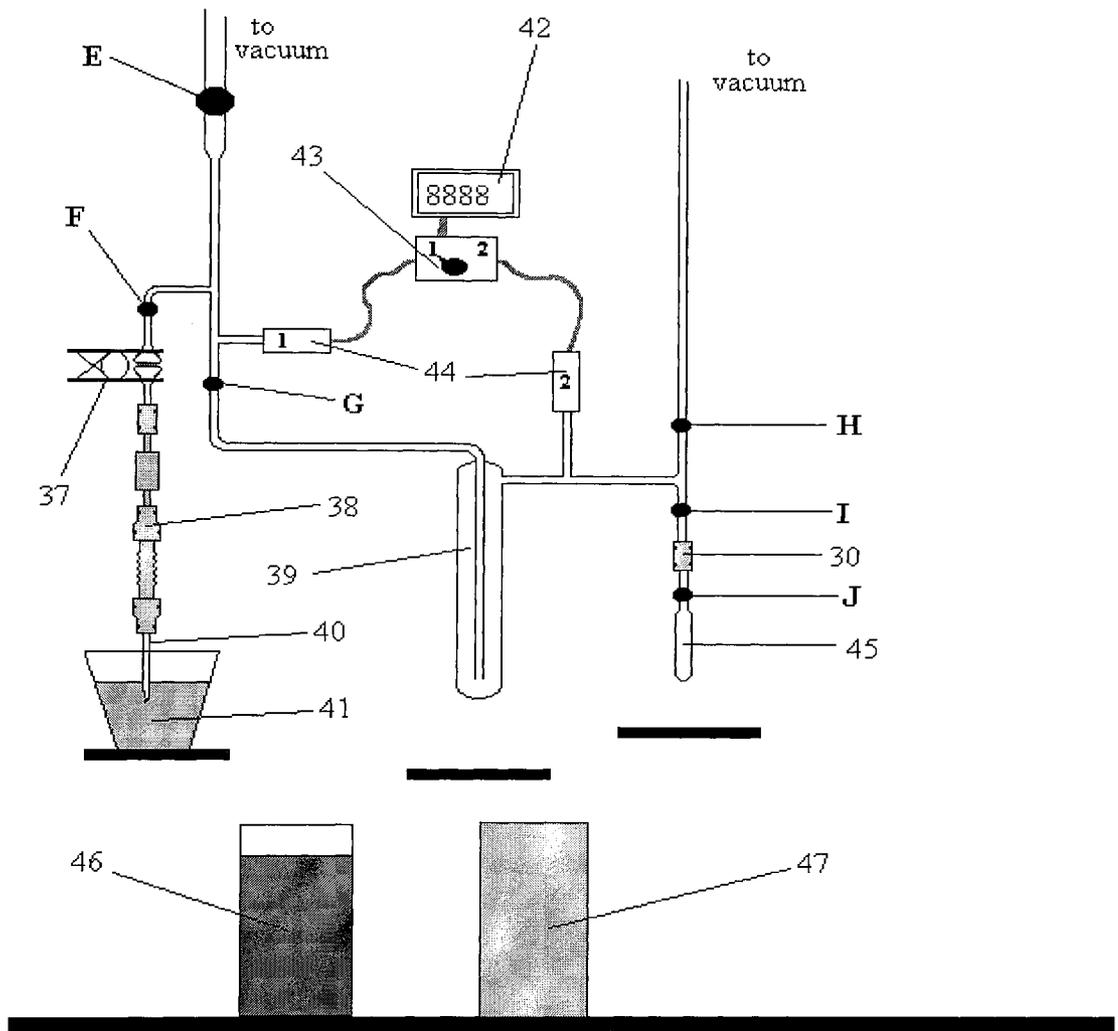


Figure 3.7 Setup for carbon dioxide extraction. Table 3.1 lists the numbered parts.

3.2.5 Combustion

Gently shaking the sealed Vycor™ tube, distributes the CuO wire as evenly as possible inside the capsule for complete combustion. The capsule is carefully placed into the tube furnace for three hours at 700° C. All the PCE carbon is now as gaseous CO₂. The chlorine from the PCE may be visible as colorless to slightly yellow-green copper chloride on the inside wall of the capsule.

3.2.6 Carbon Dioxide Extraction and $\delta^{13}\text{C}$ Measurement

This section describes how the carbon dioxide is cryogenically purified and its $\delta^{13}\text{C}$ value measured on a gas source mass spectrometer. The apparatus used for CO₂ extraction's primary function is for sulfur isotope preparation, and Figure 3.7 shows only the parts used in this procedure. The glass and stainless steel dewers contain LN₂ and ethanol at -80° C, respectively. At the start of the procedure, one closes all the valves, evacuates the spaces between valves to as high a vacuum as possible, and displays the pressure at transducer 1. Before inserting into the tube cracker, the author washes the outside of the capsule with deionized water to remove any chloride that might have deposited there during handling. Opening Valves E and F evacuates the air around the tube cracker. The author cools the capsule end protruding from the tube cracker with LN₂, freezing CO₂ and other condensable gasses inside. The author closes valve E, and cracks open the capsule. An increase in pressure indicates the presence of non-condensable gases in the capsule. Opening valve E removes these gases, and upon reaching the maximum vacuum, the author closes it again. The trap is cooled with LN₂. Opening valve G and removing the LN₂ from the end of the

capsule allows the CO₂ to transfer to the trap. When the pressure stops decreasing, the author closes valves F and G, and switch the pressure display to transducer 2. Opening valve H momentarily, removes the residual gases. The author replaces the LN₂ on the trap with -80° C ethanol, increasing the temperature of the trap and volatilizing CO₂ while less volatile compounds (like water) remain in the trap. The author cools the condensation finger with LN₂, and opens valves I and J. When all the CO₂ condenses, one opens valve H removing the remaining non-condensable gases, then closes I and J, and detaches the condensation finger from the outlet port. The author then introduces the CO₂ sample into the gas source mass spectrometer, and measures the $\delta^{13}\text{C}$ value.

3.2.7 Silver Chloride Production

One of the advantages of this procedure is that it allows both $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ values to be measured from the same sample. The remaining Vycor™ capsule fragments contain solid copper chloride from the combusted PCE, which one converts to silver chloride. The procedures described below are similar those described in Jendrzejewski et al., 1997:

- (1) Carefully remove the capsule pieces from the tube cracker and put them inside an envelope.
- (2) Pour 20-50 mL of chloride free deionized water is into a 300-mL beaker. Break the capsule fragments into small pieces (<3cm), and place them in the beaker. Crush the end pieces with a clean pair of plyers to prevent air pockets.

- (3) Add 5-10 mL of concentrated nitric acid. Place the beaker on a hot plate and heat to just short of boiling.
- (4) Prepare the filtering apparatus (Whatman #2 filters rinsed several times with deionized water, a magnetic filter funnel, and a 1000mL-erlenmeyer vacuum flask.).
- (5) Pour the solution through the filter once all the copper oxide dissolves in the beaker. Rinse the inside of the beaker with deionized water, flushing any solid fragments into the filter, and the fragments inside the filter apparatus until any hint of blue (Cu^{2+} cations give a solution a blue color) disappears.
- (6) Pour the solution back into the beaker, and discard the fragments and filter.
- (7) Add silver nitrate (1 Normal, about 5ml) to the beaker to precipitate white AgCl crystals. Cover the beaker with aluminum foil to keep the light out, and allow the precipitate to settle overnight. Check for complete precipitation by adding a few more drops of AgNO_3 . If more AgCl precipitates, repeat this step.
- (8) On a watch-glass, weigh a Gelman GN-6 metricel (samples with more than 15 mg of AgCl) or glass fiber (samples less than 15 mg of AgCl) filter. Prepare the filtering apparatus with this filter. Filter the sample.
- (9) Remove the sample filter, and place it on the weighed watch glass. Scrape the AgCl together to facilitate removal from the filter after it dries. Wrap the watch glass and filter in foil carefully without any contact between foil

and precipitate, and place them in a drying oven ($\sim 60^\circ\text{C}$) for at least 24 hours.

3.2.8 Reaction to Yield Methyl Chloride

Since the mass spectrometry technique requires methyl chloride gas, the silver chloride must be converted to methyl chloride. One accomplishes this by reacting the silver chloride with liquid methyl iodide. The procedures in this and the next sections are also described in the literature (Long et al., 1993; Kaufman et al., 1984).

- (1) Weigh the dried filter and watch glass together, and determine the silver chloride mass. Calculate the percent yield of AgCl (yield 1). The expected mass of silver chloride can be calculated from the measured PCE concentration at the time of sampling and the sample size. If the yield is less than 70%, the sample may have fractionated, and should be repeated.
- (2) Remove the silver chloride from the filter, and funnel it into a small amber vial.
- (3) Prepare 9 mm PyrexTM tubing for the reaction by baking it at 800°C , then washing it with deionized water. Seal the tubes at one end creating approximately 30cm long sections.
- (4) Weigh 5-10 mg of silver chloride and place it into a PyrexTM tube, then attach the tube to a vacuum pump line with a CajonTM "T" junction. Attach a septum to the unused junction end, and evacuate the tube.

- (5) Cool the end of the finger with LN₂, and shut the valve leading to the vacuum. Inject 25-100 μL of methyl iodide through the septum with a 1cc syringe.
- (6) After a few minutes, open the valve to the vacuum, and collapse the tube with a torch near the Cajon™ junction, creating a sealed reaction capsule.
- (7) Wrap the capsule in foil and place it in an oven at 100 °C for at least 48 hours.

3.2.9 Extraction of Methyl Chloride and δ³⁷Cl Measurement

Before it can be measured on the mass spectrometer, the methyl chloride is extracted from the other products and the excess reactants. The author breaks the reaction capsule open and transfers the contents to a nitrogen trap. An ethanol bath warms the trap to -15 °C. The volatilized gases pass through a gas chromatograph with a helium carrier gas, separate, and one collects the methyl chloride on two nitrogen traps. After transferring to a compartment with a known volume and a pressure transducer, the author calculates the mass of methyl chloride. One calculates the CH₃Cl reaction percent yield (yield 2) using the mass of silver chloride measured in the previous section as the expected value. Finally the author brings the gas down to a finger with a valve and transfers it to the mass spectrometer. A VG 602C mass spectrometer modified electronically for peak hopping makes the δ³⁷Cl measurement with an analytical precision of 0.08 ‰. For more detailed information on the mass spectrometer parameters, see Long et al., 1993.

3.3 Procedure Testing

3.3.1 Manufactured PCE and TCE

In order to test the combustion and silver chloride production sections, several samples are prepared from manufactured liquid PCE and TCE. This study uses TCE from two different manufacturers, Dow and ICI. $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ values are available for both of these in the literature (van Warmerdam et al., 1995). The author also measures various sized samples of liquid Aldrich PCE (lot # 03840 PN). This study determines several replicate $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ values for each of the three solvents.

To measure liquid solvents, one adds ~1g of CuO wire to a Vycor™ tube sealed at one end, then attaches the tube to a vacuum line with a Cajon™ “T” junction that contains a septum. The author injects the sample through the septum with a syringe, freezes it at the end of the tube with LN₂, evacuates any non-condensable gases from the tube, and then collapses it with a torch, producing a combustion capsule. Yield 2, $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ value determinations are as described in section 3.2. For the manufactured solvent samples, one calculates the expected AgCl mass for the yield 1 value from the solvent injection volume of the sample, and the density of the solvent.

3.3.2 Simulated Field Samples

In order to determine the ability to capture and transfer PCE, the author simulates field sampling in the lab. Of particular concern is that the PCE might breakthrough the columns, and that the desorption efficiency might be low, lowering

the recovered yield. Low yields indicate that samples might be fractionating during the procedures.

Starting with the field sampling apparatus (Fig 3.4) minus the bypass valve and gas line filter, the author momentarily opens the Teflon™ union “upstream” of the VOST columns, and injects 10 µL of the Aldrich PCE. Rather than soil air, the author sucks 100 L of helium through the apparatus at 1 L/min. One then processes these simulated field samples as genuine field samples.

3.3.3 GCMS Analysis of a Field Sample

Finally, the author tests the ability of the procedures to separate the PCE from other VOCs. One collects a field sample as described earlier. Rather than to a Vycor™ combustion tube, the author transfers this sample to an ORBO™ 32S charcoal tube, and seals it with plastic caps. The author brings this tube to the University of Arizona analytical chemistry laboratory, for GCMS analysis, indicating which organic molecules are present.

3.4 Successive Evaporation of PCE

The basic procedure is very similar to that of Poulson and Drever, 1999. 12mL (19.74 g) of PCE is put in a weighed 25mL Savillex™ Teflon™ vial with a Teflon™ cap. While the PCE evaporates in the fume hood, at various intervals the author takes 7 liquid PCE samples with a syringe. Before and after removal of each sample, the author caps and weighs the vial. Further analysis of these samples is as described earlier for manufactured PCE and TCE.

CHAPTER 4

PROCEDURAL MOTIVATION

A significant amount of the work in this study is experimental in nature, particularly the procedures for collecting PCE vapors for isotope analysis. Several problems arose during the development of these procedures. It would be useful for future studies wishing to use or improve upon these procedures to know what specifically the problems were, and how this study dealt with them.

4.1 Measurement Precision

The author initially intended for $\delta^{37}\text{Cl}$ values to be measured by the Cs_2Cl^+ thermal ionization technique. The author prepared a CsCl standard solution and measured its isotope composition several times with a VG336 Mass spectrometer with faraday cup detectors. Despite repeated attempts, precision no better than 1 ‰ was obtained. The author decided to switch to the CH_3Cl^+ technique, which was well established in the nearby University of Arizona isotope geochemistry laboratory. The larger amount of chloride required was to be obtained by collecting larger samples.

4.2 Combustion Yield

The author noticed that black soot deposited inside some of the sample capsules after combustion of PCE. Since PCE contains carbon, it was an indication of incomplete combustion. The author further noticed that the soot appeared in the largest samples at the end of the tube furthest away from the copper oxide wire.

Shaking the tube so that the copper oxide wire was spread evenly in the tube, and reducing the sample sizes (20 μ L or less), prevented the formation of soot in later samples.

4.3 PCE: Similarities to Water

With a melting point of -19°C and a boiling point of 121°C, PCE behaves physically similar to water. This was a problem because large amounts of water vapor condensed inside the VOST tubes when collecting the field samples. During the procedure to transfer the PCE from the VOST tube to the combustion tube, the water also transferred, forming an ice plug that blocked the flow of the following PCE vapors. Small amounts of water in the combustion tube was also problematic. After the author sealed the combustion tube and started heating it up, the water vapors built up enough pressure to cause the tube to explode.

It was imperative to remove the water from the samples. The author rejected the use of desiccating pre-filters since they would likely also sorb PCE. Eventually the author developed a technique that took advantage of the ability of PCE to sorb to the Tenax™ TA resin. By transferring the PCE to an “empty” VOST tube with a mild vacuum, the author succeeded in removing most of the water while still retaining the PCE.

4.4 Acetate Filter Contamination

It was impossible to scrape very small (< 15 μ g) AgCl samples off of the filter paper (Gelman GN-6 Metricel). Therefore the author tried the CH₃I reaction without

removing the filter paper. This led to generation of an unknown gas and apparent CH_3I yield much greater than 100% in one field sample, which was highly undesirable. Substituting glass fiber filters (VWR, $0.7\ \mu\text{m}$) for the filter papers solved this problem, as they did not produce gas in the CH_3I reaction.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Manufactured Solvents

The measured δ values of the three manufactured solvents are presented in Table 5.1. The overall one standard deviation precision was 0.07 ‰ for $\delta^{13}\text{C}$ ($n = 13$), and 0.09 ‰ for $\delta^{37}\text{Cl}$ ($n = 12$) using an equation for the standard deviation of grouped data, and not including samples with a yield of less than 70%. For Aldrich PCE, the samples varied in size from 5 to 50 μL , and yield varied from 42.4 to 97.1 %. The two 50 μL samples had the two lowest yields, and showed evidence of incomplete combustion, thus the author excluded them in the following calculations. Although the δ values suggest that one of these did not fractionate, the author decided to categorically exclude all samples with yields less than 70% to remove any selection bias. $\delta^{13}\text{C}$ values had a range from -25.9 ‰ to -25.8 ‰ and $\delta^{37}\text{Cl}$ values had a range from -0.2 ‰ to $+0.1$ ‰. $\delta^{13}\text{C}$ values were at -25.9 ± 0.02 ‰ ($n=4$) and $\delta^{37}\text{Cl}$ values were at 0.0 ± 0.13 ‰ ($n=4$). Figure 5.1 plots the mean Aldrich PCE $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ values along with previous manufactured PCE δ values from van Warmerdam et al., 1995 and Beneteau et al., 1999. As Figure 5.1 shows, the $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ values for Aldrich PCE fall within the range of previous measurements.

Aldrich PCE $\delta^{37}\text{Cl}$ is within one standard deviation of the Dow and ICI $\delta^{37}\text{Cl}$ values previously reported. Thus Aldrich PCE may be mistaken for ICI or Dow if

Table 5.1
Carbon and Chlorine Isotope Compositions of Manufactured Chlorocarbons

Sample	Solvent volume (uL)	Yield 1 (%) ^a	delta ¹³ C vs PDB	Yield 2 (%) ^b	delta ³⁷ Cl vs SMOC
Aldrich PCE					
1	50	62.8	-26.38	82.3	-0.28
2	50	42.4	-25.91	98.0	-0.02
3	20	90.5	-25.89	99.4	-0.16
4	10	86.6	-25.84	96.7	-0.15
5	5	97.1	-25.87	92.2	+0.01
6	5	96.1	-25.84	94.7	+0.12
Mean, STD*		92.6, 4.9	-25.9, 0.02	95.8, 3.0	0.0, 0.13
ICI TCE					
1	5	90.8	-31.00	94.4	+3.30
2	5	113.3	-31.09	101.1	+3.34
4	5	104.6	-31.22	98.4	+3.24
5	5	124.2	-31.14	N/A	N/A
6	5	115.0	-31.18	97.0	+3.18
7	5	106.7	-30.96	N/A	N/A
Mean, STD*		109.1, 11.3	-31.1, 0.10	97.7, 2.8	3.3, 0.07
DOW TCE					
1	5	109.6	N/A	74.1	+3.99
2	5	97.1	-31.67	99.1	+4.16
3	5	99.2	-31.62	100.3	+4.08
4	5	120.8	-31.66	103.8	+4.04
5	5	60.4	N/A	97.2	+4.77
Mean, STD*		106.7, 10.9	-31.7, 0.03	94.3, 13.6	4.1, 0.07
All Solvents, STD			0.07	0.09	

* - Mean and Standard Deviation (STD) not including rejected samples (Aldrich PCE 1,2; Dow TCE 5)

a - Yield 1 = measured AgCl mass (see 3.2.7 and 3.2.8) / expected AgCl mass. Expected AgCl mass = solvent volume * solvent density (1.623 g/mL for PCE and 1.464 g/mL for TCE) * 1.157 (correcting factor for change in molecular mass)

b - Yield 2 = CH₃Cl pressure * 0.123 (conversion factor that takes the CH₃Cl gas volume and differences between the molecular masses of AgCl and CH₃Cl into account) / mass of AgCl reacted (see 3.2.8 step 4)

N/A - Not Measured

Table 5.1 Carbon and chlorine isotope compositions and yields of manufactured chlorocarbons.

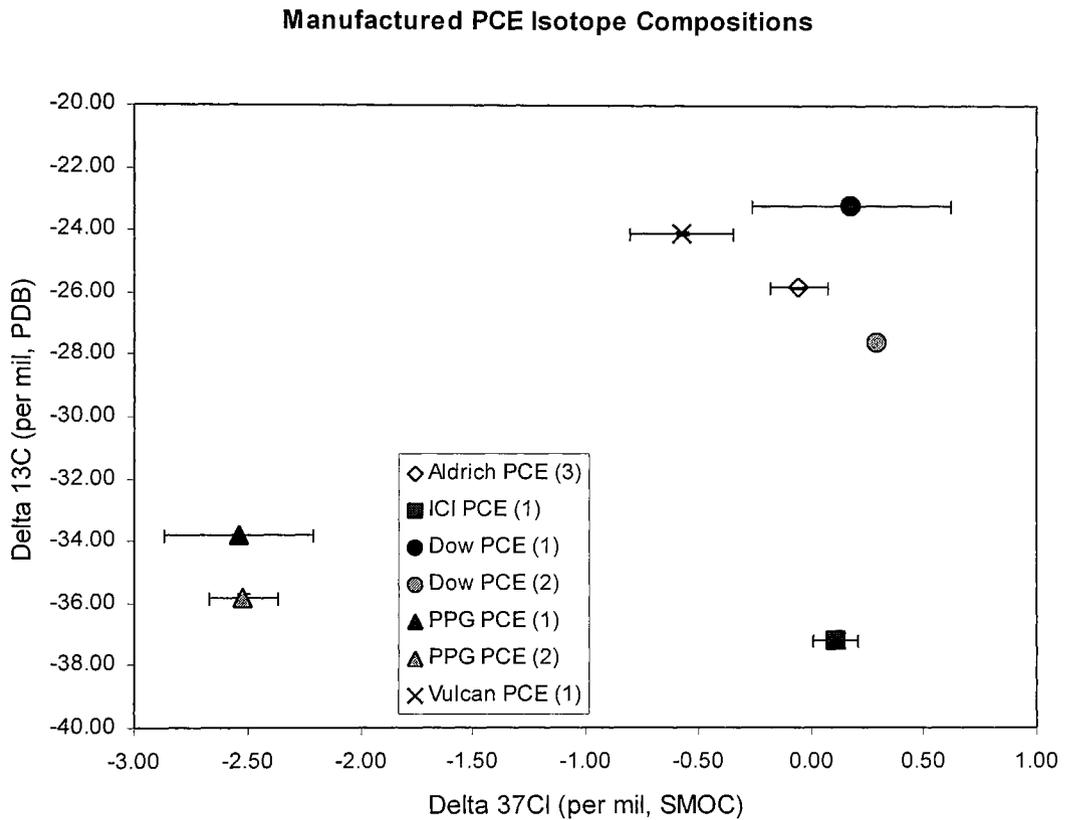


Figure 5.1 $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ values for Aldrich PCE and a comparison with previously measured isotope compositions of PCE. (1) van Warmerdam et al., 1995. (2) Beneteau et al., 1999. (3) This study.

$\delta^{37}\text{Cl}$ values are the sole distinguishing criteria. Evidence from Beneteau et al., 1999 questions the use of $\delta^{13}\text{C}$ values as a secondary distinguishing characteristic. They notice that although $\delta^{37}\text{Cl}$ values remained approximately the same between two different batches of PCE produced two years apart by PPG and Dow, $\delta^{13}\text{C}$ values differ. However, the extent of these differences is poorly defined, and if they are small, it may still be possible to use $\delta^{13}\text{C}$ values as a secondary distinguishing characteristic, possibly for distinguishing between Dow and ICI PCE since their $\delta^{13}\text{C}$ values are 11.2‰ apart. Aldrich and Dow PCE, however, are isotopically too similar to separate even if the batch variation is small.

All ICI TCE and DOW TCE samples used $5\mu\text{L}$ of solvent. Both solvents were obtained from the University of Waterloo, from the same production batches as the corresponding samples measured by van Warmerdam et al., 1995. ICI TCE $\delta^{13}\text{C}$ values had a range from -31.2‰ to -31.0‰ and $\delta^{37}\text{Cl}$ values had a range from $+3.2\text{‰}$ to $+3.3\text{‰}$. $\delta^{13}\text{C}$ values were at $-31.1 \pm 0.10\text{‰}$ ($n=6$) and $\delta^{37}\text{Cl}$ values were at $+3.3 \pm 0.07\text{‰}$ ($n=4$).

The author rejected one Dow TCE sample with a yield of 60.4% based on its low yield. Dow TCE $\delta^{13}\text{C}$ values had a range from -31.6‰ to -31.7‰ and $\delta^{37}\text{Cl}$ values had a range from $+4.0\text{‰}$ to $+4.2\text{‰}$. $\delta^{13}\text{C}$ values were at $-31.7 \pm 0.03\text{‰}$ ($n=3$) and $\delta^{37}\text{Cl}$ values were at $+4.1 \pm 0.07\text{‰}$ ($n=4$).

Both the Dow and the ICI TCE isotope measurements fell within the range of values for manufactured TCE previously measured. Essentially the two manufactured TCE isotope compositions measured in this study were replicates of those measured

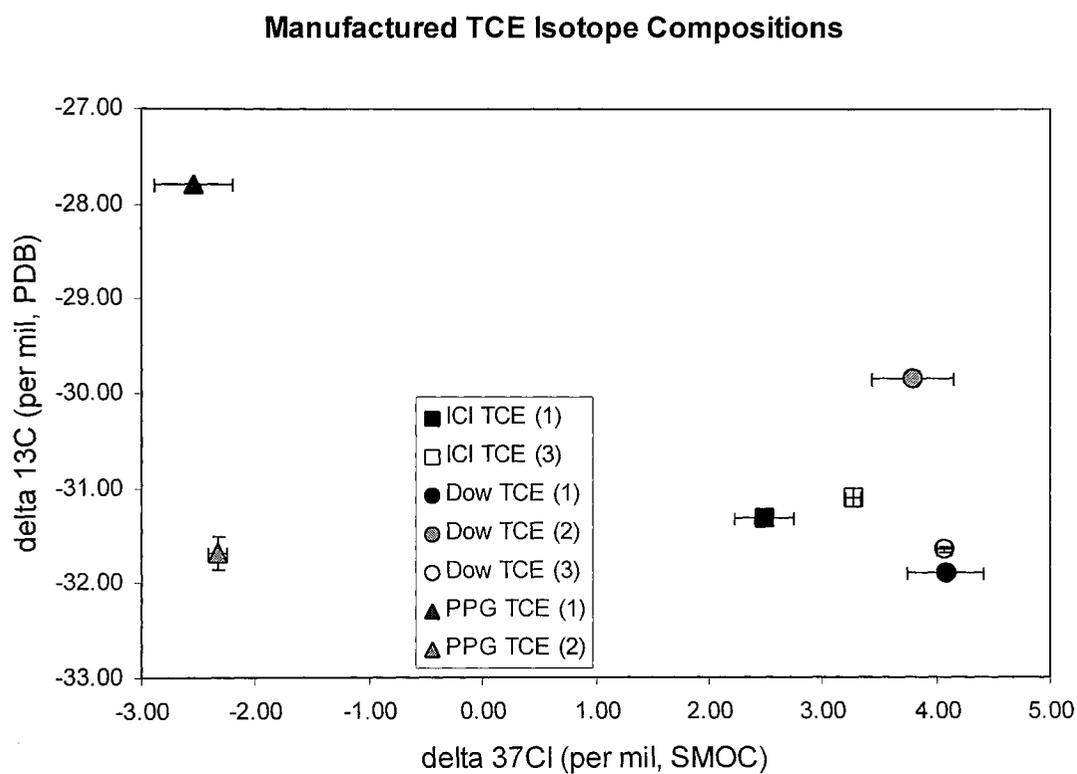


Figure 5.2 $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ values for ICI TCE and Dow TCE, and a comparison with previously measured isotope compositions of TCE. (1) van Warmerdam et al., 1995. (2) Beneteau et al., 1999. (3) This study.

in van Warmerdam et al., 1995. The main difference between their procedure and this study's is that they combusted their solvents in a Parr Oxygen Bomb, while the author combusted samples in Vycor™ tubes at 700° C with copper oxide as the oxidant.

Results are presented in Table 5.1 and Figure 5.2. $\delta^{13}\text{C}$ values for both TCE samples measured in this study were slightly higher than those measured previously, both by 0.2 ‰. Although these differences are equivalent to at least 2 standard deviations, they were systematic since they are both about the same value and in the same direction (higher than the previous $\delta^{13}\text{C}$ values). This kind of effect is common when comparing isotope values measured in different laboratories.

$\delta^{37}\text{Cl}$ value differences were not systematic, however. While the Dow TCE $\delta^{37}\text{Cl}$ value was the same as the previous measurement, the ICI TCE $\delta^{37}\text{Cl}$ value was 0.8 ‰ higher. This represents at least a three standard deviation difference, which is unlikely to have occurred simply by chance. About five years passed between the initial isotope measurements by van Warmerdam et al. (1995) and this study's measurements. Because of its low boiling point (87 °C), TCE is volatile, and evaporates quickly. It is possible that at some time during the intervening years, some TCE in the ICI sample evaporated, slightly fractionating the remaining liquid. Previous studies describe TCE evaporation (Poulson and Drever, 1999; Huang et al., 1999). Plotting their $\delta^{13}\text{C}$ values and $\delta^{37}\text{Cl}$ values, measured after varying degrees of evaporation of liquid TCE, gives a straight-line relationship (Figure 5.5). The average slope of this line, based on the three data sets presented in the two studies gives a line

with the equation:

$$\delta^{13}\text{C}_{\text{final} - \text{initial}} = -0.18 \delta^{37}\text{Cl}_{\text{final} - \text{initial}} \quad (5.1)$$

Substituting a value of -0.8 ‰ for $\delta^{37}\text{Cl}_{\text{final} - \text{initial}}$ into Equation 5.1 gives a $\delta^{13}\text{C}_{\text{final} - \text{initial}}$ value of $+0.1 \text{ ‰}$. Thus evaporating TCE with a $\delta^{13}\text{C}$ value of -31.0 ‰ and a $\delta^{37}\text{Cl}$ value of $+2.5 \text{ ‰}$ down to 65% of the initial solvent volume should produce this study's measured ICI TCE $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ values of -31.1 ‰ and $+3.3 \text{ ‰}$ respectively. In other words, attributing the high ICI TCE $\delta^{37}\text{Cl}$ value to fractionation effects during evaporation is an explanation that is consistent with the data and studies on TCE evaporation because a 0.1 ‰ difference in $\delta^{13}\text{C}$ is statistically more probable than a 0.8 ‰ difference in $\delta^{37}\text{Cl}$.

Van Warmerdam et al. (1995) reported combustion yields between 65% and 75%. Although they report that no isotopic differences were present at slightly higher or lower yields, Jendrzewski et al. (1997) asserts that yields closer to 100% would give confidence that the chlorine isotopic data is accurate, then introduces the CuO wire combustion technique which is used in this study's procedures. Of the 15 manufactured solvent samples of 20 μL or less, only one had a yield 1 of less than 85%, and was likely the result of a laboratory measurement error. The other 14 had yield 1 values from 86.6% to 124.2%, with the mean at $103.7 \pm 11.7\%$. The large standard deviation can most likely be attributed to low precision in the measurement of solvent volumes (from markings on the syringe). Since the mean value was over 100%, this might warrant some concern that contamination might have been present. Possible sources of contamination were from chloride residue on the outside of the

combustion tube that might have been deposited during handling, and dust accumulation during AgCl preparation. Even if the high yield is due to contamination, it is still very close to 100%, thus such contamination would not significantly affect the $\delta^{37}\text{Cl}$ measurements, unless the contaminant was isotopically very different from the chloride in the sample, which is unlikely. The closeness of the mean yield to 100% gives confidence that the $\delta^{37}\text{Cl}$ values measured are accurate. Furthermore, it indicates that the combustion and aqueous chemistry procedures described in chapter 3 are capable of producing accurate results.

Yield 2 percentages are also presented in Table 5.1. The author determined that all were acceptable. Yields above 100% were due to balance imprecision. Otherwise, Dow TCE sample #1 was the only measurement outside the acceptable range of 85-100%. The low yield of this sample was likely due to an incomplete transfer of AgCl from a leaky Pyrex™ tube that was replaced without reweighing the AgCl. Sample being lost in this manner does not cause the remainder, which was measured for $\delta^{37}\text{Cl}$, to fractionate.

5.2 Progressive Evaporation of PCE

The results of the progressive evaporation experiment are in Table 5.2 and Figures 5.3-5.6. Appendix B shows how the author determined the values for $\ln(F)$ in Table 5.2. As evaporation progressed, the remaining liquid PCE increased 3.6 ‰ in $\delta^{37}\text{Cl}$ and decreased 2.8 ‰ in $\delta^{13}\text{C}$ as the liquid fraction decreased from 1 to 0.0076.

δ -values can be substituted into The Raleigh fractionation equation, which can be rearranged giving the equation (Poulson and Drever, 1999):

$$\ln[(\delta + 1000)/(\delta_1 + 1000)] = (\alpha - 1)\ln(F) \quad (5.2)$$

δ_1 is the δ -value of the initial liquid before fractionation, and δ is the δ -value in the liquid for a fraction F of liquid remaining. Equation 5.2 is also in the form of a straight line with a slope of $(\alpha - 1)$. Thus if evaporation does follow a Raleigh fractionation trend, it should plot as a straight line. A good linear least squares fit is seen in Figure 5.3 between $\ln[(\delta^{13}\text{C} + 1000)/(\delta^{13}\text{C}_1 + 1000)]$ and $\ln(F)$ ($R^2 = .993$). The slope of the regression gives a α -value of 1.00062 ($\Delta^{13}\text{C}_{\text{vapor-liquid}} = +0.6 \text{ ‰}$) for carbon.

Fractionation of chlorine isotopes also follows a Raleigh fractionation trend. Figure 5.4 shows a good linear least squares fit between $\ln[(\delta^{37}\text{Cl} + 1000)/(\delta^{37}\text{Cl}_1 + 1000)]$ and $\ln(F)$ ($R^2 = .981$). The slope of the regression gives a α -value of 0.99923 ($\Delta^{37}\text{Cl}_{\text{vapor-liquid}} = -0.8 \text{ ‰}$) for chlorine.

The positive Δ -value for chlorine is expected and consistent with previous studies of other chlorinated VOCs, however the negative Δ -value for carbon is unexpected according to current theories on fractionation effects during evaporation, but still consistent with previous measurements of chlorinated VOCs. Generally it is believed that molecules with lower molecular weights (made up of light isotope atoms) will behave as if they have a slightly lower boiling point than molecules of the same type with higher molecular weights. Thus low molecular weight molecules would be expected to evaporate faster than heavier molecules, such that evaporation

Carbon and chlorine isotopic compositions in PCE successive evaporation experiment

Sample Name	ln (F)	delta 13C (per mil, PDB)	ln[(delta 13C+ 1000)/974.01]	delta 13C (final - initial)
Carbon				
S1	0.00	-25.99	0.0000	0.00
S2	-1.15	-26.49	-0.0005	-0.50
S3	-1.70	-26.98	-0.0010	-0.99
S4	-2.38	-27.26	-0.0013	-1.27
S5	-3.13	-27.90	-0.0020	-1.91
S6	-3.96	-28.34	-0.0024	-2.35
S7	-4.87	-28.81	-0.0029	-2.82
Sample Name	ln (F)	delta 37Cl (per mil, SMOC)	ln[(delta 37Cl + 1000)/1000.32]	delta 37Cl (final - initial)
Chlorine				
S1	0.00	0.32	0.00000	0.00
S2	-1.15	1.07	0.00075	0.75
S3	-1.70	1.12	0.00080	0.80
S4	-2.38	2.03	0.00171	1.71
S5	-3.13	2.79	0.00247	2.47
S6	-3.96	3.19	0.00286	2.87
S7	-4.87	3.95	0.00362	3.63

Table 5.2 Successive evaporation of Aldrich PCE experiment. Appendix B describes the ln(F) calculations.

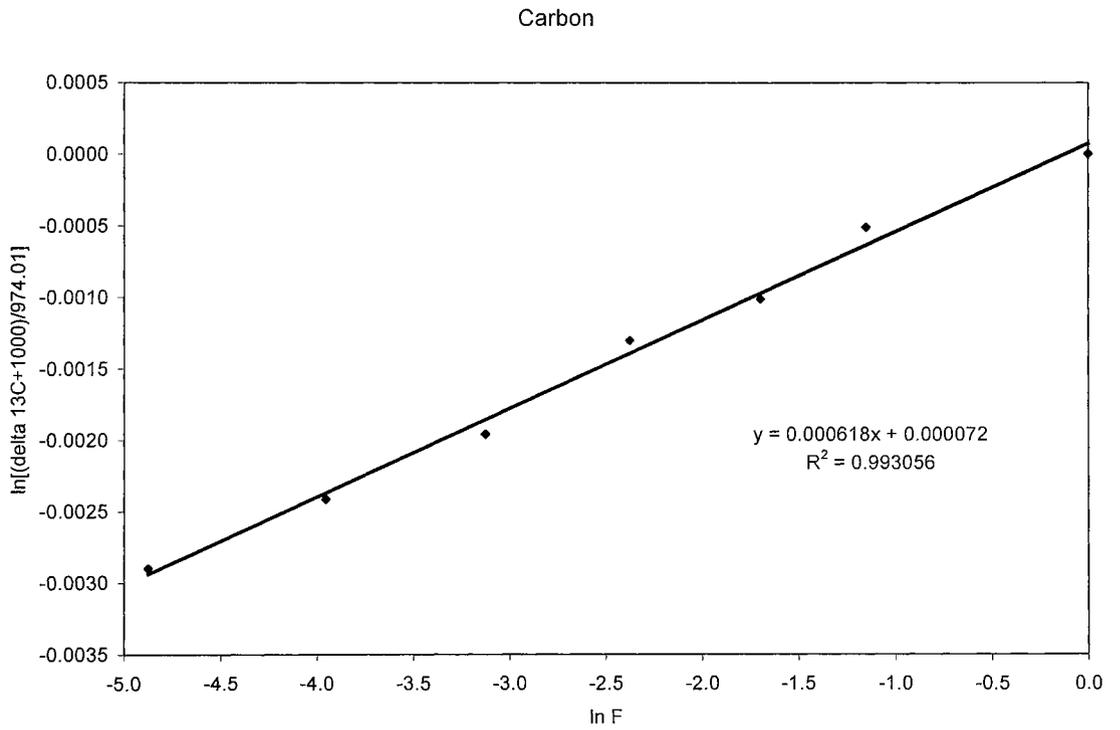


Figure 5.3 Straight line regression of $\ln[(\delta 13C + 1000) / 974.01]$ against $\ln(F)$, indicating an α value of 1.00062.

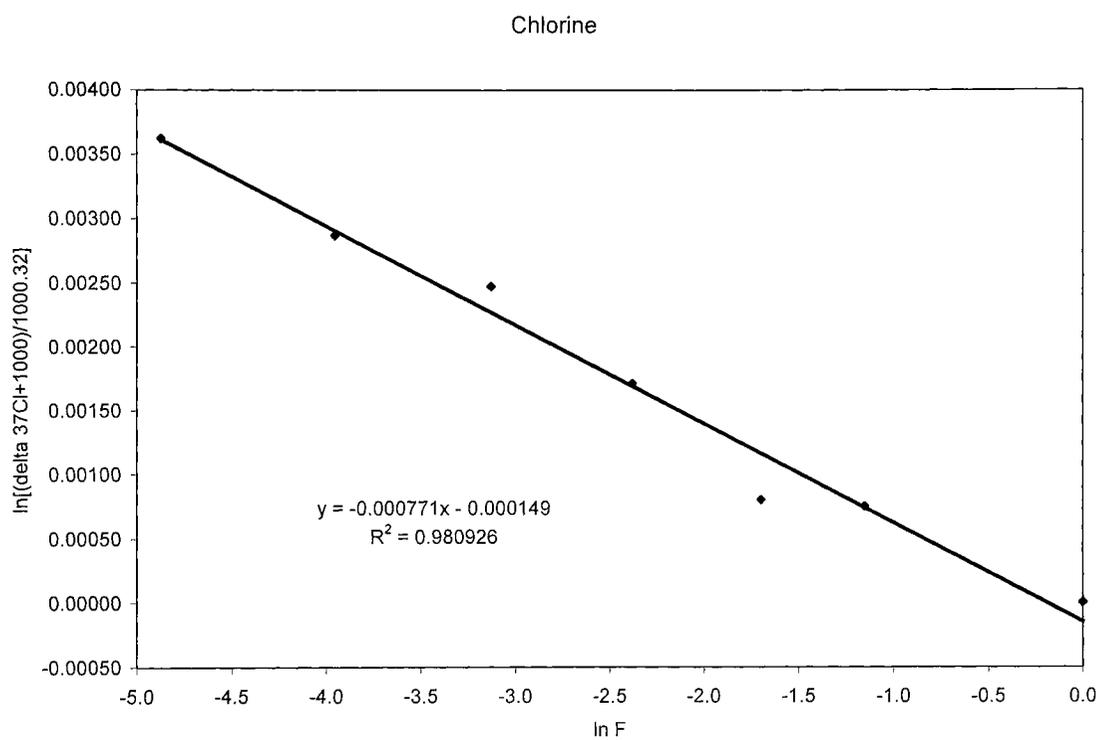


Figure 5.4 Straight line regression of $\ln[(\delta 37\text{Cl} + 1000) / 1000.32]$ against $\ln(F)$, indicating an α value of 0.99923.

would tend to increase the concentration of high molecular weight molecules in the residual liquid. The negative Δ -value for chlorine during PCE evaporation indicates that as evaporation progresses, the residual liquid becomes more concentrated with ^{37}Cl rich PCE molecules, which is consistent with what would be expected as explained above. The positive Δ -value for carbon isotopes, however, indicates that as evaporation proceeds, the ^{12}C concentration increases in the residual liquid molecules, which is contrary to what would be expected as explained above. The reason for this apparent contradiction has yet to be determined, but similar effects are noticed in evaporation studies of other chlorinated VOCs. TCE also has a positive $\Delta^{13}\text{C}_{\text{vapor-liquid}}$ value of + 0.24 ‰, + 0.35 ‰ (Poulson and Drever, 1999) or +0.31 ‰ (Huang et al., 1999). Dichloromethane (DCM) has a $\Delta^{13}\text{C}_{\text{vapor-liquid}}$ value of +0.65 ‰ (Huang et al., 1999). This study's value of +0.6 ‰ is within the range of these previous measurements. For chlorine fractionation during evaporation, the negative sign of the $\Delta^{37}\text{Cl}_{\text{vapor-liquid}}$ value for PCE is also consistent with previously measured values of -1.64 ‰, and -1.81 ‰ for TCE (Poulson and Drever, 1999, and Huang et al., 1999, respectively) and -1.48 ‰ for DCM (Huang et al., 1999). Although this study's value of -0.8 ‰ is not within the range of these previous measurements, this is not unreasonable, as so few previous measurements of evaporative fractionation of chlorinated VOCs exist, and none of them for PCE.

Figure 5.5 displays $\delta^{13}\text{C}$ versus $\delta^{37}\text{Cl}$ values measured from the residual liquid after various degrees of evaporation of chlorinated VOCs from this study and others. Since the starting liquid isotopic compositions differed between studies, the author

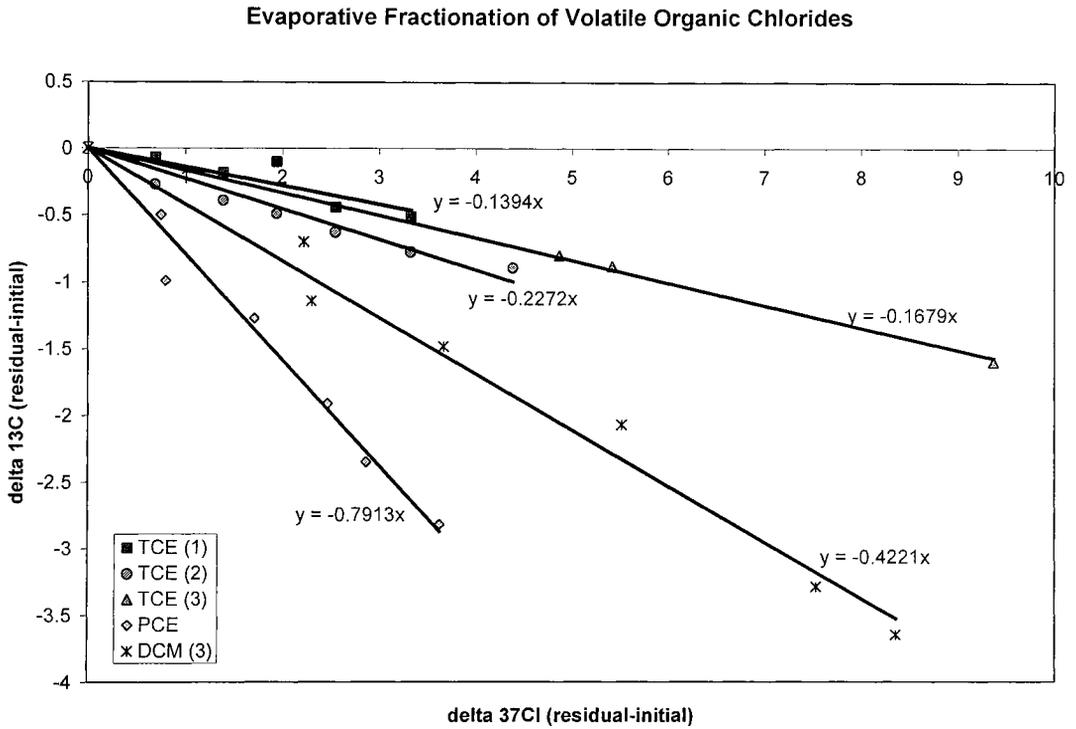


Figure 5.5 Normalized $\delta^{13}\text{C}$ versus $\delta^{37}\text{Cl}$ for evaporative fractionation of PCE, and comparison with previous studies of TCE and DCM. (1) TCE isotope data from Poulson and Drever, 1999, experiment 2; (2) TCE isotope data calculated from Poulson and Drever, 1999, experiment 1; (3) TCE and DCM isotope data from Huang et al., 1999.

subtracted out the initial δ values, so that all the studies would appear to start with the same carbon and chlorine δ values. Two trends are plotted for TCE from Poulson and Drever (1999) since they report $\delta^{13}\text{C}$ values from two different laboratories. They report just one set of $\delta^{37}\text{Cl}$ values, measured at the same fractions as only one of the two $\delta^{13}\text{C}$ sets. The author interpolated additional $\delta^{37}\text{Cl}$ values from the Poulson and Drever (1999) $\delta^{37}\text{Cl}$ values, for their other set of $\delta^{13}\text{C}$ values, in order to plot the second trend in Figure 5.5. As can be seen in Figure 5.5, the progressive evaporation of PCE produces a fractionation effect significantly different from that for TCE and DCM. In comparison to DCM and especially to TCE, $\delta^{13}\text{C}$ values in PCE increase much more significantly for a given decrease in $\delta^{37}\text{Cl}$ values (the slope is much more negative).

5.3 PCE Field Samples

5.3.1 PCE Concentration History

PCE concentrations measured at various times are shown in Table 5.3 and Figure 5.6. Prior to 12/13/99, Hydro Geo Chem, Inc., a private consulting firm, measured all PCE concentrations. The author measured PCE concentrations on 12/13/99 and afterwards using the procedures described earlier.

In the four month period between 9/16/98 and 1/21/99 the PCE concentration increased by over 2000% from 27 $\mu\text{g/L}$ to 570 $\mu\text{g/L}$ for unknown reasons. On August 23, 1999 the soil vapor extraction system began operation, with extraction-pumping from well SVE1-200. SVE1-200 is a 6" (15.2 cm) diameter well, screened on the

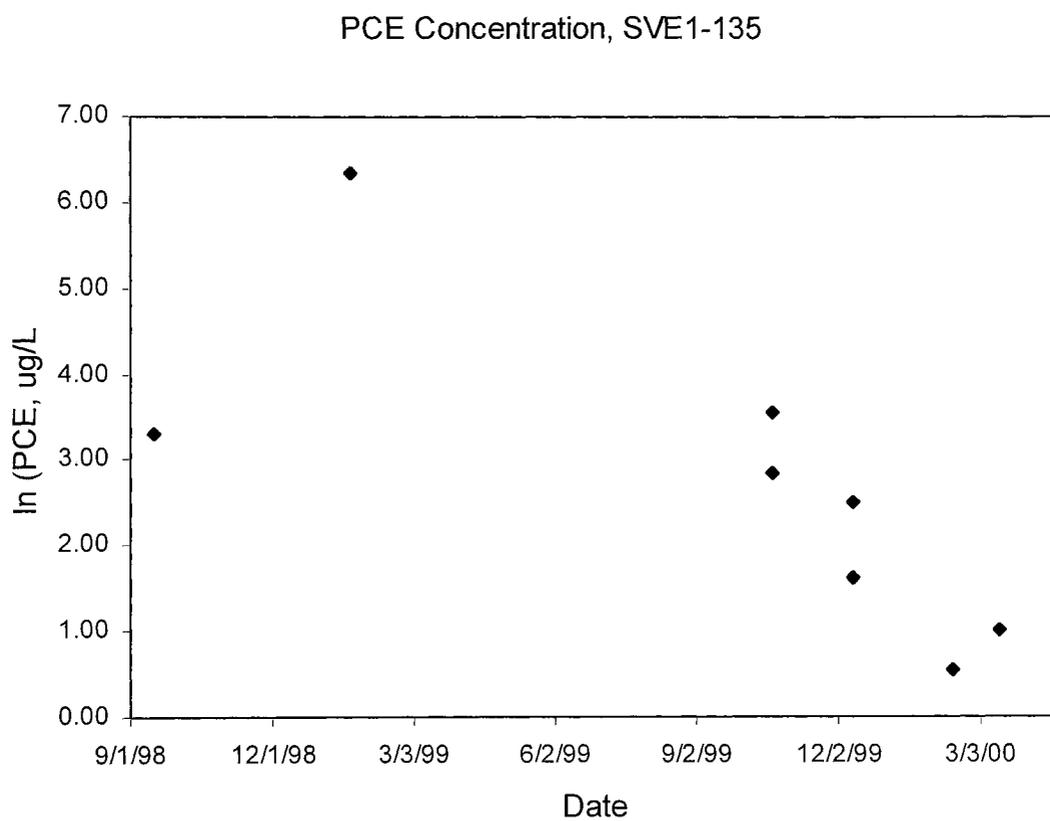


Figure 5.6 PCE soil air concentration from Harrison landfill, well SVE1-135.

Table 5.3 PCE soil air concentration from Harrison landfill, well SVE1-135

Date	PCE, $\mu\text{g/L}$	Comments
9/16/98	27	a,b
1/21/99	570	a,b
10/21/99	35	a,b
10/21/99	17	a,b
12/13/99	12	c
12/13/99	5	c
2/15/00	1.7	c
3/16/00	2.7	c

a – Used Summa canister method

b – Measured by Hydro Geo Chem, Inc.

c – Used carbon filter/GC method (this study)

interval of 45.7 – 61.0 m (150 to 200 feet) below the surface. PCE concentrations measured after August 23, 1999 decrease with time. This indicates that the soil vapor extraction system is reducing PCE concentrations at SVE1-135. On 2/28/00 the City of Tucson shut off the soil vapor extraction system for a period of three weeks. Perhaps as a result of this, the PCE concentration shows a slight, however statistically insignificant (GC measurement precision is 1 $\mu\text{g/L}$) increase on 3/16/00.

5.3.2 Simulated Field Samples

The results of the three test field samples are presented in Table 5.4. The range from 91.1% to 108.5% in the yield 1 values and was within the range for combustion and precipitation of manufactured solvents (as expected for so many

Table 5.4 Results of three simulated field samples, which tested the sorption and de-sorption procedures.

Sample Name	$\delta^{13}\text{C}$ ($^{\circ}/_{00}$, PDB)	Yield 1 (%) ^a
TFS1	-25.8	102.5
TFS2	-	108.5
TFS3	-25.5	91.1

a- Yield 1 is the percent recovery of sample processed through the simulated field sampling, transfer, combustion and AgCl production procedures

fewer samples). The similarities of the yield 1 values with manufactured solvent yield 1 values, suggests that the additional procedures beyond those used for measuring manufactured solvents (trapping and de-sorbing PCE) used in the simulated field sampling test were highly efficient. Differences from 100% in the yield are likely caused by the same factors that prevented 100% yields in the manufactured solvents.

$\delta^{13}\text{C}$ measurements also indicate that the collection and de-sorption procedures are acceptable. Since Aldrich PCE was used in these samples, the expected $\delta^{13}\text{C}$ value is $-25.9^{\circ}/_{00}$. TFS 1 is very close to this value. This indicates that the procedures are capable of making $\delta^{13}\text{C}$ value measurements from PCE in simulated field samples. The $\delta^{13}\text{C}$ value measured for TFS 3, however, was not as close to $-25.9^{\circ}/_{00}$, being $0.3^{\circ}/_{00}$ higher. It is possible that some carbon dioxide from the laboratory atmosphere leaked into the combustion tube, producing a slight contamination. Whatever the cause, $0.3^{\circ}/_{00}$ is a small difference in comparison to the large range ($14^{\circ}/_{00}$) of $\delta^{13}\text{C}$ values found in manufactured PCE.

5.3.3 GCMS Analysis of a Processed Sample

The purpose of this analysis was to determine how effective the procedures were at removing VOCs other than PCE from the sample. GCMS analyses qualitatively determine which compounds are present in a sample. The sample submitted for GCMS analysis went through the exact same collection and PCE purification procedures as the genuine field samples, thus one expects the compounds identified in this GCMS analysis were the same as those found in the genuine field samples. It is important to know which compounds were present in the sample since they supplied the carbon and chlorine isotopes that determined the δ -values. The result of the GCMS analysis is presented in Figure 5.7. The GCMS analysis identified 21 separate compounds. The University of Arizona analytical chemistry lab (performed the GCMS analysis) explained that peaks 11 and 14 were not from the sample. (They represent dichlorobenzene impurities in the solvent used to extract the ORBO™ 32S charcoal cartridge.)

This GCMS analysis was purely qualitative. Peak height and area responses to concentration differed between compounds. This was due to differing detector responses between compounds, and an inherent non-linear display of that response used to exaggerate the small peaks. Once the author identified the potential sample contaminants and looked up their soil air concentrations (previously measured by HGC, see Appendix C), most had concentrations less than 5 percent of the PCE concentration. Thus these compounds could not contribute significantly to the measured δ values. The only compounds both identified by GCMS analysis and with high soil air concentrations were TCE and PCE (peaks 1 and 3, respectively).

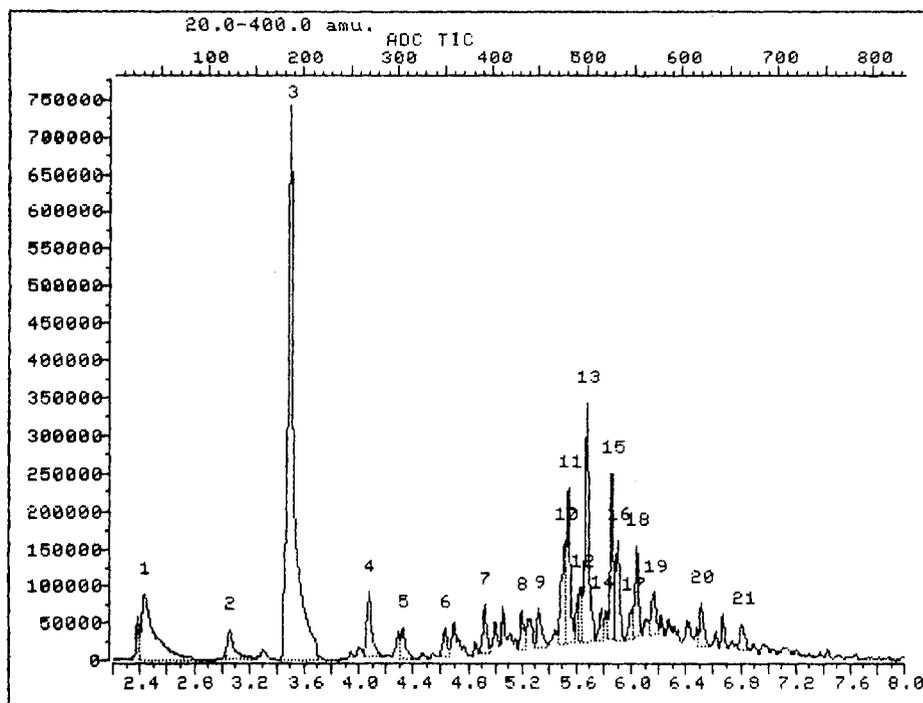


Figure 5.7 Gas chromatograph mass spectrometry analysis of a processed soil air sample from Harrison landfill well SVE1-135. The most likely compounds determined for each peak were: (1) TCE, (2) Benzene, methyl-, (3) PCE, (4) Benzene, 1,3-dimethyl-, (5) Benzene, 1,2-dimethyl-, (6) Benzene, (1-methylethyl)-, (7) Hexane, 2,2,5,5-tetramethyl-, (8) Cyclohexane, 1-methyl-2-propyl-, (9) Benzene, 1-ethyl-4-methyl-, (10) Octane, 2,5,6-trimethyl-, (11) Artifact from extraction solvent, (12) Benzene, 1-ethyl-4-methyl-, (13) 1,1-Dimethylpropyl 2-ethylhexnone, (14) Artifact from extraction solvent, (15) Hexane, 2,2,5,5-tetramethyl-, (16) Octane, 2,5,6-trimethyl-, (17) Naphthalene, decahydro-, (18) Nonane, 3-methyl-5-propyl-, (19) 2-Undecane, 4-methyl-, (20) 2H-Inden-2-one, octahydro-3a-methyl-, trans-, (21) Cyclopropane, 1-(2-methylbutyl)-1-(1-methylpropyl)-.

Although some TCE was present in the processed sample, the author believes that the procedures reduced its concentration to an insignificant level, however there is no evidence to support or deny this assertion.

5.3.4 Harrison PCE δ -Values

The measured $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ values of the Harrison SVE1-135 PCE field samples are presented in Table 5.5. $\delta^{13}\text{C}$ values ranged from -27.3 ‰ to -25.1 ‰ with the mean at -26.1 ± 0.7 ‰. If one assumes a fractionation effect similar to PCE evaporation occurs in the landfill when PCE volatilizes, one would expect that the liquid PCE from which this study's samples evaporated had a $\delta^{13}\text{C}$ value 0.6 ‰ lower ($\Delta^{13}\text{C}_{\text{vapor-liquid}} = +0.6$ ‰), giving a range of -27.9 ‰ to -25.7 ‰ and a mean of -26.7 ± 0.7 ‰ for the liquid PCE from which the samples evaporated. This range of $\delta^{13}\text{C}$ values falls entirely within the range previously reported for manufactured PCE, and includes Dow (Beneteau et al., 1999) and Aldrich (this study) PCE. One explanation for the large range and standard deviation is that the PCE isotope composition remained constant in SVE1-135 soil air, and variations in PCE $\delta^{13}\text{C}$ values resulted from the overall precision of the procedures. Another explanation is that the ^{13}C composition of PCE in SVE1-135 soil air was not constant with time. Since samples were collected over a four-month time period, it is possible that the large range and standard deviation were due to gradual changes of the PCE isotopic composition with time. Figure 5.8 displays how the $\delta^{13}\text{C}$ values changed with time. $\delta^{13}\text{C}$ values decreased from 11/9/99 until 12/13/99, after which they increased back

Sample Name	delta 13C (per mil, PDB)	Yield 1 (%) ^a	Yield 2 (%) ^b	delta 37Cl (per mil, SMOC)
SVE1-135-3	-25.99	-	186.9	+6.29
SVE1-135-4	-25.57			
SVE1-135-5	-26.80	0.0	-	-
SVE1-135-6	-27.32			
SVE1-135-8	-25.09	98.3	88.8	+2.59
SVE1-135-9	-26.00			
SVE1-135-10	-26.11			
SVE1-135-11	-25.92	80.2	85.3	+3.66
SVE1-135-12	-25.67			

a – Yield 1 = measured AgCl mass (see 3.2.7 and 3.2.8) / expected AgCl mass.

Expected AgCl mass = PCE concentration * sample volume * 1.157 (correcting factor for change in molecular mass)

b – Yield 2 = CH₃Cl pressure * 0.123 (conversion factor that takes the CH₃Cl volume and differences between the molecular masses of AgCl and CH₃Cl into account) / mass of AgCl reacted (see 3.2.8 step 4)

Table 5.5 δ values and yields of Harrison landfill soil air samples collected 11/9/99 to 3/16/00. To measure $\delta^{37}\text{Cl}$ values, we combined all samples collected on the same day.

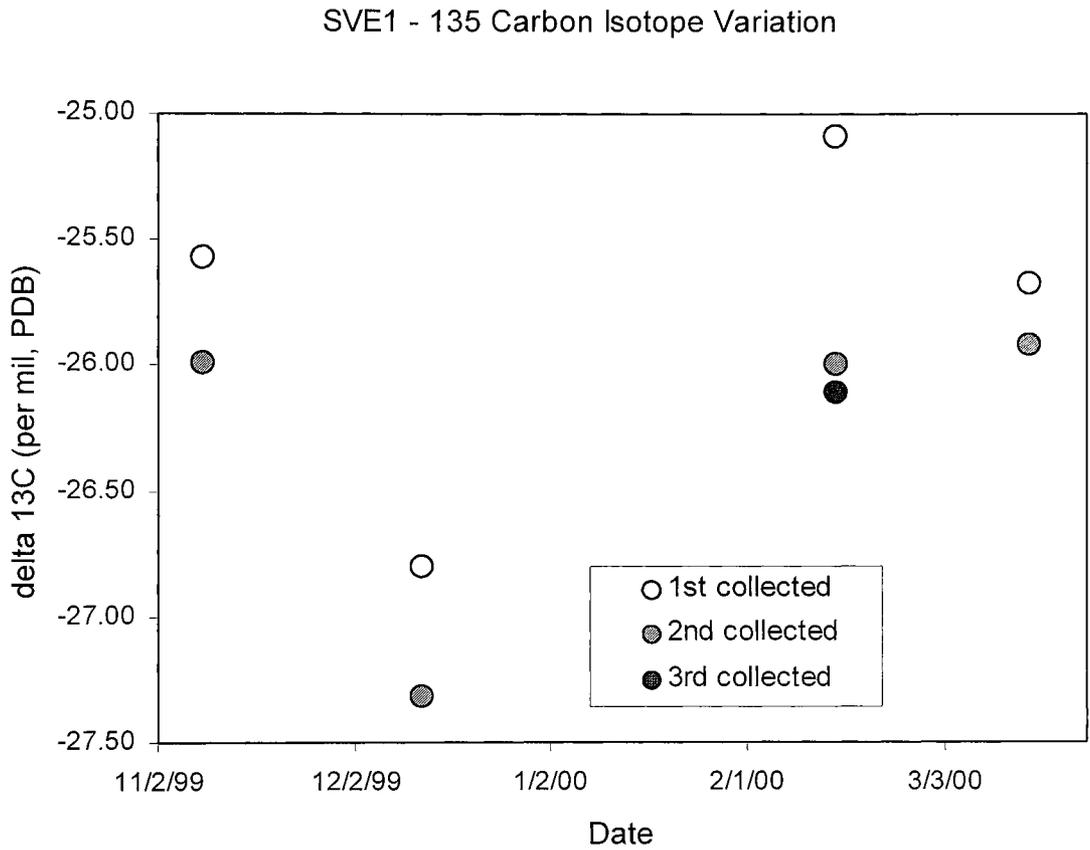


Figure 5.8 $\delta^{13}\text{C}$ variations with time for Harrison landfill SVE1-135 soil air samples collected 11/9/99 to 3/16/00.

up to around the same level as on 11/9/99. It is hard to attribute a physical process that would be capable of producing such a trend. Perhaps a high degree of isotopic heterogeneity was present in the landfill PCE. For samples collected on the same day a $\delta^{13}\text{C}$ decrease is evident from the samples collected first to those collected later in the day. $\delta^{13}\text{C}$ values decreased by as much as 1 ‰.

The author made three $\delta^{37}\text{Cl}$ measurements of PCE from Harrison SVE1-135 (Table 5.5). $\delta^{37}\text{Cl}$ measurements of +6.3 ‰, +2.6 ‰, and +3.7 ‰ are from samples collected on 11/9/99, 2/14/00 and 3/16/00 respectively. Thus the $\delta^{37}\text{Cl}$ value of the liquid from which this study's vapor samples evaporated was at +7.1 ‰, +3.4 ‰, and +4.5 ‰ ($\Delta^{37}\text{Cl}_{\text{vapor-liquid}} = -0.8$ ‰). All three of these $\delta^{37}\text{Cl}$ values are significantly higher (≥ 3.1 ‰) than the highest previously reported $\delta^{37}\text{Cl}$ value for liquid PCE, +0.3 ‰. Because of the unexpectedly low PCE concentration, the author combined two or three samples together for each measurement. The author has very little confidence in the value of +6.3 for samples collected on 11/9/99, as it was made before perfection of the laboratory and field techniques.

Yield 1 values were 98.3% and 80.2% for the 2/15/00 and 3/16/00 samples respectively. These were high yields, and similar to those obtained from manufactured solvents and the simulated field samples, despite the increased uncertainty associated with the PCE concentrations (used as the expected value for yield 1). Because of the high yields, one has confidence that these two samples did not fractionate during the analytical procedures, and are good measurements of the PCE vapors collected. Thus one would expect typical $\delta^{37}\text{Cl}$ values in the range of

+2.6 ‰ to +3.7 ‰ versus SMOC for PCE vapors from Harrison SVE1-135, and with less certainty, chlorine isotope ratios might be present all the way up to + 6.3 ‰ versus SMOC.

CHAPTER SIX

IMPLICATIONS OF THE δ -VALUES

In this chapter the author suggests theories explaining the measured Harrison SVE1-135 soil air δ -values. There are several possible explanations for the $\delta^{37}\text{Cl}$ values being higher than any previously measured, which the author particularly explores in this chapter. Additionally, the author conjectures about possible future studies and applications related to this work.

6.1 $\delta^{13}\text{C}$ Values

Since the sample $\delta^{13}\text{C}$ values are within the range previously reported for manufactured solvents, a mixture of solvents, or Dow or Aldrich PCE alone in the landfill could produce the measured $\delta^{13}\text{C}$ values. Such a theory, however, completely ignores the measured $\delta^{37}\text{Cl}$ values, which are outside the range of previous measurements, thus cannot by itself completely explain both the $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ values measured.

6.2 $\delta^{37}\text{Cl}$ Values

$\delta^{37}\text{Cl}$ values of the liquid from which this study's samples evaporated, were at least 3.1 ‰ higher than any previously reported PCE $\delta^{37}\text{Cl}$ value. It is highly unlikely that fractionation during the collecting and processing procedures could be so

great without lower yields. Two kinds of explanations remain for the high $\delta^{37}\text{Cl}$ values. The $\delta^{37}\text{Cl}$ value of the PCE when it was put into the landfill could have been much higher than is currently found in manufactured PCE (source effects), or naturally occurring processes within the landfill could have fractionated the PCE (in-situ fractionation).

6.2.1 Source Effects

The isotope composition of the PCE when it was dumped in the landfill is unknown, and may have differed significantly from recently manufactured PCE. The oldest PCE measured for $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$, was manufactured in 1993. Harrison Landfill opened for operation in 1972. Although Beneteau et al. (1999) suggest that PCE $\delta^{37}\text{Cl}$ values do not vary among batches from a single manufacturer, more studies need to be done to confirm this, and this may not have been the case before 1993. It is quite possible that manufacturing procedures may have changed within the period of 1972-1993. Manufactured PCE possibly had $\delta^{37}\text{Cl}$ values of + 3.4 ‰ to +4.5 ‰ or even as high as +7.1 ‰ then.

Furthermore, the assumption that the PCE when it was dumped had the same isotope composition as it did when purchased from the manufacturer may be invalid. The δ -values of PCE may have fractionated before the PCE was dumped in the landfill. For example, PCE was often used in the dry cleaning business. If PCE were recycled in order to reduce the cost of purchasing more of the solvent, a large amount may have evaporated, enriching the residual liquid in ^{37}Cl and ^{12}C . If fresh

(unfractionated) PCE were constantly being added to replace the PCE that evaporated, it is possible to create a liquid that is highly enriched in ^{37}Cl and ^{12}C .

6.2.2 In-Situ Fractionation Effects

Three kinds of in-situ fractionation affects might have occurred in the Harrison landfill. These include evaporation, sorption and biodegradation. Some of the liquid PCE in the refuse likely evaporated into the air spaces present. Naturally occurring or artificially induced movement of the vapor out of these air spaces allowed more PCE to evaporate. If one assumes that the high $\delta^{37}\text{Cl}$ values were due solely to evaporative fractionation, this indicates that a large fraction of the PCE had already evaporated and left the landfill. In order to increase the $\delta^{37}\text{Cl}$ values in a residual liquid PCE by 3.1‰ (decrease $\delta^{13}\text{C}$ values by 2.5‰), over 98% of the initially dumped PCE must have evaporated, and moved off the site. If this were true, it suggests that the landfill gas extraction system, which was in operation for five years before collecting this study's samples, or naturally occurring evaporation processes, were effective in removing large amounts of PCE from the landfill. The isotope composition of the pre-evaporated liquid PCE ($\delta^{13}\text{C} = -24.2\text{‰}$, $\delta^{37}\text{Cl} = +0.3\text{‰}$) would fall within the range reported for Dow PCE ($\delta^{13}\text{C} = -27.6$ to -23.2‰ , $\delta^{37}\text{Cl} = +0.2$ to $+0.3\text{‰}$ [Beneteau et al., 1999]).

Very little is known about the isotope effects of sorption on PCE. Sorption of PCE is more likely to occur in soils containing a high organic content. The solid waste in a landfill contains a very high organic fraction. Also, PCE exists in two mobile phases: vapor and aqueous. Different fractionation effects may occur due to

sorption in each of these phases. At a PCE-contaminated site in Angus, Ontario, Beneteau et al. (1999) reasoned that sorption of aqueous PCE and other fractionating effects were insignificant over the 220m length of the contaminant plume, however conditions there differ significantly from those in Tucson (PCE was transported in the aqueous phase, not the vapor phase). In order to get an increase in the $\delta^{37}\text{Cl}$ values, sorption would have to be greater for PCE molecules with more ^{35}Cl isotopes than average, which seems to be the opposite of what would be expected.

Although numerous previous studies have been done on the isotopic effects of biodegradation of TCE to DCE, only one examines the isotopic effects of biodegrading PCE to TCE. Aravena et al. (1998) detected no isotope fractionation when PCE was biologically degraded to TCE in a field study. Although Aravena et al. (1998) tend to indicate otherwise, the high degree of isotope selectivity possible by biological organisms might be capable of producing a large fractionation effect. Such a large fractionation effect might explain the high $\delta^{37}\text{Cl}$ values noticed in the field samples, without requiring that a very high percentage of the PCE be already degraded.

6.3 Possible Future Studies and Applications

For Harrison landfill, the ultimate goal would be use $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ values to determine the parties that are guilty of the PCE contamination. Achieving such a goal will be difficult, if not impossible. It will be necessary to identify all the potential PCE contamination sources over the 25 years in which disposal activities occurred, and assign $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ values for each. In-situ fractionation effects need to be

better determined at the site. Spatial and temporal variations in PCE isotopic compositions need to be better defined at the site. Such measurements might also prove useful should PCE contaminated groundwater be found down gradient. It might be possible to determine if Harrison landfill were the source of such a contamination, or rule it out as a possible source, based on a comparison of the isotopic compositions of the PCE contaminants at both sites.

The procedures developed for the sampling of PCE vapors from soil air for $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ analysis could prove to be useful in future applications. They are particularly applicable in semi-arid to arid regions, such as the western and southwestern United States, where depths to the water table are large, giving rise to a large unsaturated zone. At this point, applications are limited to situations where possible contamination sources are well defined isotopically, and where in-situ fractionation effects can be ruled out. For example, responsibility for the remediation of a contaminated site may be determinable, if contaminant samples from the potential guilty parties could be obtained. Future studies may use the procedures developed in this study to better understand biodegradation and sorption fractionation effects, and to determine fraction factors for these effects. Once these fractionation factors are determined, more complicated sites can be studied by accounting for these effects. Fractionation effects due to evaporation can now be determined using the fractionation factors measured for PCE in this study. Whether two PCE samples could be related by evaporation as well as determining the degree of evaporation are now possible.

CHAPTER SEVEN

SUMMARY AND CONCLUSIONS

- Following the high yield technique of Jendrzewski et al. (1997), the author measured $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ values from liquid PCE and TCE samples in the laboratory. The author measured high precision ($1\sigma < 0.1 \text{ ‰}$) δ -values when liquid solvent samples sizes were less than 20 μL . Aldrich PCE (not previously measured) had δ -values similar to Dow PCE. $\delta^{13}\text{C}$ values of manufactured TCE were consistently 0.2-0.3 ‰ higher than previously reported. $\delta^{37}\text{Cl}$ values were the same (Dow) or 0.7 ‰ higher (ICI, perhaps due to evaporative fractionation) than previously reported values. High yields suggested that the measurements were accurate.
- This study followed the procedure of Poulson and Drever (1999) in an experiment that examined fractionation of PCE during evaporation. Evaporation followed a Rayleigh distillation trend with a α value of 1.00062 ($\Delta^{13}\text{C}_{\text{vapor-liquid}} = +0.6 \text{ ‰}$) for ^{13}C fractionation, and a α value of 0.99923 ($\Delta^{37}\text{Cl}_{\text{vapor-liquid}} = -0.8 \text{ ‰}$) for ^{37}Cl fractionation
- The author designed a custom procedure for collecting PCE vapors from a landfill and measuring the $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ values of that PCE. The author collected PCE vapors by pumping the contaminated soil air through VOST tubes containing Tenax™ TA adsorbent resin, trapping the PCE vapors. Back in the laboratory, the author transferred the PCE to a combustion tube by heating the VOST tubes while

simultaneously passing a He carrier gas through the tubes, such that samples could then be processed like liquid solvent samples. Simulating the field sampling in the laboratory tested the $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ accuracy. Yields close to 100% and $\delta^{13}\text{C}$ values close to the test PCE's $\delta^{13}\text{C}$ value suggested that this study obtained a high degree of accuracy in the simulated field samples. A GCMS analysis of one field sample suggested that except for possibly TCE, the procedures successfully remove VOCs other than PCE from the samples.

- $\delta^{13}\text{C}$ values from field samples collected on four different dates ranged from -27.3 to -25.1 ‰ with a mean of -26.1 ± 0.7 ‰ ($n = 9$). $\delta^{13}\text{C}$ values varied by as much as 1.0 ‰ in samples collected on the same day.
- $\delta^{37}\text{Cl}$ values were $+2.6$ and $+3.7$ ‰. Low PCE concentrations of 1.7 $\mu\text{g/L}$ and 2.7 $\mu\text{g/L}$ in the soil air necessitated the combination of two or more samples for each $\delta^{37}\text{Cl}$ measurement. The liquid PCE from which this study's samples evaporated was at least 3.1 ‰ higher than any previous reported $\delta^{37}\text{Cl}$ measurement of PCE.
- One explanation for the high $\delta^{37}\text{Cl}$ values is that the PCE dumped in the landfill was isotopically dissimilar to the more recently manufactured PCE $\delta^{37}\text{Cl}$ values reported in the literature. Other theories suggest that evaporative, isotopically selective sorption, or biodegradative fractionation produced the high $\delta^{37}\text{Cl}$ values.

APPENDIX A
EQUIPMENT DETAILS

Equipment description	Supplier	Catalog #
1. VOST glass tube	Supelco	2-1993
2. Glass wool	Supelco	2-0409
3. Tenax™ TA adsorbant resin (35/60 mesh)	Alltech	01495
4. 1/4" nut and cap (400-C 1/4")	Supelco	2-2008
5. Teflon™-Ceramic Ferrule (M-1)	Supelco	2-2086-U
6. 1/4" Teflon™ FEP tubing	Cole - Parmer	P6406-66
7. 1/4" Pyrex™ tubing		
8. Flexible Tygon™ tubing (R3603)	Aldrich	T8788
9. 1/4" unions with graphite ferrules (unions)	U of Arizona Stores	0801 0380
(ferrules, M-4)	Supelco	2-2492
10. 1/4" Teflon™ compression unions (PFA)	Cole - Parmer	P06374-22
11. Insulation		
12. Adsorbant column (see figure 3.2)		
13. Heating element, 2x 1 5/8" inner diameter tubular h	Mellen	12-200
14. Voltage controller		
15. Flowmeter stand (tripod stand)	Cole - Parmer	P32462-55
16. Flowmeter (100 mm scale, 0.4-5 LPM)	Cole - Parmer	P32461-50
17. 1/8" NPT thread male barbed elbows (HDPE)	Cole - Parmer	P06451-10
18. He line (Pyrex and stainless steel)	Custom built	
19. Liquid nitrogen		
20. Staines steel vacuum dewer		
21. He tank with regulator		
22. Barbed T connector	Cole - Parmer	P06462-10
23. Steel tubing clamp	Cole - Parmer	P06404-10
24. Insulated cooler	Target	
25. 1/4" gas line filter	Supelco	2-0621
26. Well SVE1-135 (see HGC, 1998)		
27. Cold packs (get soft bag type instead)	Safeway	frozen peas
28. Support stand		
29. Ring support		
30. 1/4" Cajon™ union (ultra torr 316)	Cajon	
31. 1/4" Teflon™ compression elbow	Cole - Parmer	P06374-32
32. 2 styrofoam cups with a 1/4" radius hole	Safeway	styro cups
33. 6mm Vycor™ tube	Corning	743170
34. CuO wire on a quartz wool plug (CuO)		
35. Heating assembly (11,13 and 29)		
36. Pressure transducer and needle gauge		
37. Metal pinch clamp	Kontes	675000-0028
38. Tube cracker with bellows, gas line filter, and regular and reducing cajon unions		

Equipment description	Supplier	Catalog #
39. Condensing trap		
40. Vycor™ sample capsule		
41. 2 styrofoam cups with liquid nitrogen (19 and 32)		
42. Digital pressure display		
43. Switch		
44. Pressure transducers		
45. Condensation finger (with high vacuum valve)	Kontes	
46. Glass vacuum dewer with liquid nitrogen	Cole - Parmer	P-03766-20
	Cole - Parmer	P-03763-40
47. Stainless steel vacuum dewer with ethanol at -80C		
ORBO™ 32s charcoal tubes	Supelco	
Grooving Tool	Cole - Parmer	P06374-72
9mm Pyrex™ tubing	Corning	234090
Magnetic Filter funnel, 47mm, Gelman	VWR	28144-832
Kimax™ Filtering Flask	VWR	29415-143
Whatman filters, #2, Wh# 1002-055	VWR	88455-041
Gelman filters, GN-6 Metrice	VWR	28148-697
Glass fiber filters	VWR	28496-132
Nitric acid		
Silver nitrate, ACS grade		
25ml Savillex™ Teflon™ vial		

APPENDIX B

CALCULATING THE FRACTION OF PCE REMAINING FOR SAMPLES
COLLECTED DURING THE SUCCESSIVE EVAPORATION EXPERIMENT

Table B1
Calculating ln (F) from vial and sample weights

Sample Name	Vial wt. (g)	PCE in Vial (g)	Sample PCE (g)	Fraction (F)	ln (F)	Corresponding Initial PCE (g)
S1	65.3835	19.7224		1.0000	0.00	19.7224
S2	51.9081	6.2470	0.0188	0.3167	-1.15	19.6630
S3	49.2687	3.6076	0.0262	0.1835	-1.70	19.5202
S4	47.4736	1.8125	0.0208	0.0929	-2.38	19.2962
S5	46.5077	0.8466	0.0154	0.0439	-3.13	18.9452
S6	46.0240	0.3629	0.0165	0.0192	-3.96	18.0838
S7	45.7994	0.1383	0.0130	0.0076	-4.87	16.3840

In this appendix the author describe how he calculated the values for ln (F) in Table 5.2. Table B1 displays the relevant data. The empty vial weighed 45.6611 g. Immediately after adding PCE, the author collected sample S1 in order to characterize the initial isotopic composition of the PCE before evaporation. Weighing the vial again gave the initial mass of PCE before evaporation (19.7224 g). After various amounts of evaporation, the author collected additional samples (S2-S7). Before collecting each of these, the author capped and weighed the vial, giving the values in the second column of Table B1. The third column shows the PCE weight in the vial, which was obtained by subtracting the weight of the empty vial from the second column. Immediately after removing each sample the author weighed the vial again. Subtracting this weight from the pre sample weights (second column) gives the weight of the sample, which the fourth column shows. The author calculated the fraction of PCE remaining (F, 0.3167) represented in sample S2 by dividing the PCE in the vial (6.2470) by the pre evaporation PCE mass (19.7224). PCE fractions remaining for samples S3 – S7, however, are not calculated in such a simple manner because in addition to evaporation of PCE, some of the weight loss is due to the

removal of PCE collected for sample S2. To correct for this, one conceptually removes the PCE collected in sample S2 from the system. By dividing the S2 sample size (0.0188) by F for S2 (0.3167), the pre-evaporated mass of PCE represented by the sample is calculated. Subtracting this value from the pre-evaporation PCE mass gives a corresponding initial PCE mass (final column). Conceptually, this is the initial mass of PCE present in an equivalent system with no earlier sample collections. One calculates the fraction for S3 by dividing the PCE weight (3.6076) by the corresponding initial PCE weight for S2 (19.6630). For samples S4–S7, use the same process to calculate the F values displayed in Table B1.

APPENDIX C

SUMMA CANISTER VOC CONCENTRATION DATA FROM HARRISON
LANDFILL SOIL AIR

Constituent	SVE-1-135'	SVE-1-135'	SVE-1-135'	SVE-1-135'	SVE-1-135'	SVE-1-135'	Maximum Fraction of PCE	Present in GCMS Analysis
	9/15/98 (ug/L)	1/21/99 (ug/L)	10/21/99 A (ug/L)	10/21/99 B (ug/L)	10/21/99 A (ug/L)	10/21/99 B (ug/L)		
Benzene	3.1	19	1.6	0.93			0.11	no
Chlorobenzene	0.43	ND (0.070)	ND (0.66)	ND (0.21)			0.02	no
Chloroethane (Ethyl Chloride)	ND (0.13)	ND (0.081)	ND (0.76)	ND (0.24)			0.00	no
Chloroform	0.4	ND (0.15)	0.2	ND (0.44)			0.01	no
1,2-Dichlorobenzene (o)	0.37	1.6	0.97	0.37			0.03	undetermined
1,3-Dichlorobenzene (m)	0.26	ND (0.092)	ND (0.86)	ND (0.27)			0.01	undetermined
1,4-Dichlorobenzene (p)	2.1	17	7.3	3.8			0.24	undetermined
1,1-Dichloroethane (1,1-DCA)	7.2	77	7.1	4.2			0.27	no
1,1-Dichloroethene (1,1-DCE)	0.55	4.1	0.62	0.37			0.02	no
cis-1,2-Dichloroethene (cis-1,2-DCE)	4.2	35	4.1	2.4			0.16	no
Dichloromethane (Methylene Chloride)	63	460	29	19			2.33	no
Ethylbenzene	3.9	19	5.9	2.3			0.19	no
Freon 11 (Trichlorofluoromethane)	3.3	43	12	5.2			0.39	no
Freon12 (Dichlorodifluoromethane)	160	280	110	68			5.93	no
Freon113 (1,1,2-Trichlorotrifluoroethane)	550	2.6	1.7	0.72			20.37	no
Freon114(1,2-Dichlorotetrafluoroethane)	17	240	12	8.1			0.63	no
Styrene	0.38	ND (0.13)	ND (1.2)	ND (0.38)			0.01	no
Tetrachloroethene (PCE)	27	570	31	17			1.00	yes
Toluene	19	94	1.8	9.9			0.70	no
1,1,1-Trichloroethane (1,1,1-TCA)	ND (0.26)	ND (0.17)	ND (1.6)	ND (0.49)			0.00	no
Trichloroethene (TCE)	16	240	17	11			0.65	yes
1,2,4-Trimethylbenzene (Pseudocumene)	2	8.4	2.6	1.3			0.08	no
1,3,5-Trimethylbenzene (Mesitylene)	1.1	11	1.6	0.84			0.05	no
*m,p-Xylenes	7.9	36	11	6.6			0.39	no
o-Xylene	2.8	26	4.4	2.7			0.16	no
Vinyl chloride (VC)	4.1	68	1.4	1			0.15	no

ND (0.21) = Not detected (Practical Quantitation Limit [PQL])

Table C1 Organic compounds found in Harrison SVE1-135 (HGC, personal communication) and comparison with GCMS identified compounds

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