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Chemical and Isotopic Characterization of Organic Natural Gas Plant Emissions in Alberta

by

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled " Chemical and Isotopic Characterization of Organic Natural Gas Plant Emissions in Alberta " submitted by Tracy L. Comis in partial fulfilment of the requirements of the degree of Master of Science in Chemistry.

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Abstract

This thesis investigates the isotopic and chemical characteristics of volatile organic compounds (VOCs), and quantifies particulate-form n-alkanes and polycyclic aromatic hydrocarbons emitted from natural gas processing facilities, with the goal of identifying compounds suitable for source apportionment. Sampling methods and analytical techniques appropriate for isotopic analysis were developed, and used to examine receptor site, control site, and natural gas plant samples. VOCs emitted from natural gas plants were tentatively identified and isotopically characterized. Specific VOCs were found that differed in $\delta^{13}C$ value by up to 8‰ between natural gas plants, and are potentially suitable source apportionment compounds. Toluene was present in samples from all natural gas plants, but not at quantities sufficient to provide isotopic information. Increases in aerosol concentrations at the receptor site during the winter months were likely the result of increased anthropogenic activities.

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Dedication

To my parents who taught me all of the life skills I know, including the value of hard work and pursuing an education. Thank you for supporting me emotionally and financially while I finished my degrees.

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List of Abbreviations

CF-IRMS	Continuous Flow – Isotope Ratio Mass Spectrometer
CF-MS-IRMS	Continuous Flow – Mass Spectrometer – Isotope Ratio Mass Spectrometer
CIA	Cumulative Impact Assessment
CPI	Carbon Preference Index
GC	Gas Chromatograph
FID	Flame Ionization Detector
IRMS	Isotope Ratio Mass Spectrometer
KIE	Kinetic Isotope Effect
MS	Mass Spectrometer
MSC	Meteorological Service of Canada
PAH	Polycyclic Aromatic Hydrocarbon
SPT	Sample Preconcentration Trap
VOC	Volatile Organic Compound
VPDB	Vienna Pee Dee Belemnite

CHAPTER 1: INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction

Environmental issues have become a focus for the media in recent years, applying increased pressure on industry and government to demonstrate accountability for environmental problems that exist. As a result, source apportionment of pollutants has become the common goal of many governments, industries, and researchers. Frequently, multiple sources of the same pollutants exist within a geographic region, therefore the tracing of pollutants to one source is often difficult. This is the situation with petroleum emissions in Alberta.

If source apportionment of petroleum pollutants is possible, regulators could undertake air quality monitoring to ensure that mitigative measures developed to reduce emissions are effective, which is currently very difficult to do when fugitive emissions are considered in addition to stack emissions. Pollutant source apportionment could be used to verify pollutant dispersion models, a task that is challenging where multiple sources contribute to pollutant loads. This technique could also benefit regulatory agencies because it would provide a method of tracing pollutants to their sources in order to determine liability. This could serve to increase compliance with emissions guidelines. Source apportionment could become extremely useful in the future as Canada strives to meet its commitments to the Kyoto Protocol, which will require the ability to distinguish between biogenic and anthropogenic sources. Source apportionment could also be of assistance to government and industry with respect to cumulative impact assessments (CIAs), which are among the newest forms of environmental impact assessments. Currently the effectiveness and quality of CIAs are often reduced because industry and

government have problems attributing current pollutant levels to specific sources due to lack of government authority, cooperation from industries, and knowledge regarding the relative contribution from biogenic versus anthropogenic emissions. Source apportionment could help alleviate these problems, and improve the quality of select environmental impact assessments.

Source apportionment would be particularly useful if it can be applied to emissions from the petroleum industry in Alberta, given that multiple sources of airborne petroleum pollutants are present, both from petroleum processing and use. In Alberta, the petroleum industry is a huge contributor to the economy, while potentially causing environmental and human health concerns. The ability to distinguish different pollutant sources from one another at various receptor locations is becoming more important, while becoming increasingly complex because of continued development. Due to suspected health and environmental problems associated with pollutants emitted from petroleum production, including natural gas processing facilities, the ability to apportion sources of these pollutants would be extremely valuable by providing policymakers with the information necessary to regulate reductions in emissions.

The goal of this thesis is to develop methods appropriate for isotopic analysis of volatile organic compounds (VOCs), and particulate-form n-alkanes and polycyclic aromatic hydrocarbons (PAHs). This thesis will also investigate whether there are specific VOCs and particulate-form n-alkanes and PAHs emitted from natural gas processing facilities in Alberta that may be useful for source apportionment using stable isotopes of carbon.

1.2 Natural Gas

1.2.1 Formation

Alberta is a province rich in fossil fuels including natural gas, which is composed primarily of methane (CH_4). Methane is often found in association with water, hydrogen sulphide, carbon dioxide, and other petroleum products. Alberta is the source of approximately eighty percent of the natural gas consumed in Canada, and roughly one third of these reservoirs are sour, meaning that they contain greater than one percent hydrogen sulphide (Government of Alberta, 2002).

Oil and gas are formed by the burial and bacterial degradation of marine sediments rich in organic matter, followed by later high-temperature stages of thermal metamorphosis (Evans *et al.,* 1971). The isotopic character of fossil fuels from different reservoirs can vary depending on a number of factors, beginning with isotopic variations in the source of organic matter (which can include bacteria, plankton, animals, fish, and vegetation). Other variables that may cause isotopic fractionations contributing to isotopic variation in natural gas reservoirs include differences in temperature and pressure encountered during formation (Speight, 1998), and reactions with inorganic compounds, including calcium sulphate.

1.2.2 Processing

Natural gas processing removes heavier hydrocarbons (hydrocarbons other than methane), hydrogen sulphide, carbon dioxide, and water from methane mixtures. Water causes corrosion and hydrate formation, carbon dioxide reduces the heating value of the gas and can solidify under pressures and temperatures used for transport, and hydrogen sulphide is extremely toxic and corrodes metal surfaces by forming sulphuric acid (Matar

and Hatch, 1994). Hydrogen sulphide recovered from input gas may be vented, flared, incinerated, or used in the production of sulphur-containing compounds (e.g. elemental sulphur and sulphuric acid) (Environmental Protection Agency, 1995). Removal of carbon dioxide and hydrogen sulphide occurs through adsorption and absorption processes including chemical absorption, which typically uses amines (Matar and Hatch, 1994). Water can be removed using molecular sieves, and heavier hydrocarbons are typically removed by washing the gas mixture with a solvent that dissolves condensable hydrocarbons (Matar and Hatch, 1994), or through the use of a knockout tank. The natural gas product is then transported through pipelines. Currently, it is not known whether the processing of natural gas introduces isotopic fractionations.

1.2.3.1 Emissions Sources

The main sources of emissions from natural gas processing are acid gas wastes, fugitive emissions from leaking process equipment, glycol dehydrator vent streams, and incomplete combustion sources, including compressor engines, incinerators, heaters, and the flare itself (Environmental Protection Agency, 1995). Glycol dehydrator vent streams may release benzene, toluene, xylenes, and ethyl benzene (Environmental Protection Agency, 1995), and combustion sources may emit partially combusted hydrocarbons as a result of incomplete fuel combustion. Older plants using waste gas flares to combust hydrogen sulphide and hydrocarbons may operate at conditions that are less optimal for complete combustion, emitting larger amounts of soot and partially combusted hydrocarbons than more modern processing facilities. The relative importance of emissions from these sources varies between facilities, depending on the inlet composition of the gas and current operating conditions of the gas plant.

1.2.3.2 Emissions Fate

Volatile organic compounds emitted from natural gas processing facilities are problematic for many reasons: they may cause adverse health effects (World Health Organization, 1999), lead to secondary aerosol formation, and/or contribute to ground-level ozone formation (Atkinson, 2000).

Although typical atmospheric levels of VOCs surrounding natural gas processing facilities are not acutely toxic, long-term health effects of chronic exposure to low level pollutants are largely unknown. For example, benzene, ethyl benzene, and many PAHs are suspected to be human carcinogens. While exposure to ambient emissions associated with natural gas processing facilities is not toxic over the short-term, there is no consensus in the literature to disprove chronic effects of exposure.

Airborne particulate matter is classified as being 0.0002 μm to 500 μm in diameter (Wark *et al.*, 1998), and can be sorted into three aerosol size categories: Aitken nuclei, accumulation range particulate matter, and coarse particulate matter. Aitken nuclei are the smallest category of particulate matter at less than 0.1 μm in diameter, and have lifetimes of only a few minutes. They are pollutants formed by condensation and coagulation of hot stack gases from high-temperature combustion sources, including natural gas processing facilities. Aitken nuclei subsequently aggregate to form larger particles in the accumulation range. This size range of particulate matter is approximately 0.1 to 2 μm in diameter, and has lifetimes on the order of a few weeks or more. Coarse particles ranging between 2 and 500 μm are the largest size of particulate matter, and are mainly of primary origin from natural sources. Sources of coarse particulate matter include volcanic emissions, dust, and sea spray.

Particulate matter is a concern due to its potential human health effects after inhalation. PM 10 (particulate matter less than 10 μm in diameter) may be brought into the respiratory tract by breath taken in through the mouth, depositing in the conducting airways and gas-exchange areas of the respiratory system (Miller *et al.*, 1979). PM 2.5 (particulate matter less than 2.5 μm in diameter) is more dangerous to human health because it is capable of being deposited deeper into the respiratory system (Miller *et al.*, 1979). Particulate matter inhaled deeper into the respiratory system is less likely to be removed by the body (e.g. by coughing), and is more likely to be absorbed into surrounding tissue.

VOCs can be altered within the atmosphere by reaction with NO_x radicals, ground-level ozone, and photolysis, however the dominant removal mechanism for VOCs is by reaction with the hydroxyl radical (Atkinson, 2000). VOCs contribute to ground-level ozone formation, which is important to tropospheric chemistry. Degradation of VOCs, mainly by hydroxyl radical oxidation, can result in the formation of organic peroxy radicals ($RO_2^{\cdot}$) (Atkinson, 2000). Organic peroxy radicals can allow ground-level ozone to accumulate by reacting with nitrogen oxide, a compound that removes ground-level ozone when VOCs are not present. Ground-level ozone contributes to photochemical smog formation and may cause respiratory irritations for sensitive individuals. Ground-level ozone is also capable of oxidizing hydrocarbons, resulting in the production of carbon dioxide, a greenhouse gas.

Aerosols are removed from the troposphere through deposition processes, with lifetimes that last from several days to weeks, depending on their size. Aerosols approximately 0.3 μm in diameter are typically removed by deposition after

approximately one month, and aerosols larger than that typically last between 0.5 and 10 days in the troposphere (Pandis *et al.*, 1995). Coarse particles tend to last less time in the atmosphere than those in the accumulation range.

1.3 Stable Isotopes

1.3.1 Isotope Basics

The use of carbon isotopes is one technique currently being applied to source apportionment studies of organic pollutants in water sediments (e.g. McRae *et al.*, 2000), but atmospheric source apportionment studies are still relatively new. Isotopes can reveal information about sources of compounds, as well as physical, chemical, and biological processes that compounds have undergone. Radioactive isotopes decay into different nuclides at statistically reproducible rates, whereas stable isotopes do not decay (Criss, 1999). Of the stable isotopes, carbon is of particular interest due to its presence in all biotic and many abiotic components of the environment. Carbon has two stable isotopes, ^{12}C and ^{13}C, and one radioactive isotope, ^{14}C. ^{12}C is the most abundant stable isotope of carbon, occurring at a natural abundance of 98.90%, with the balance of stable carbon existing as ^{13}C, present at 1.10% natural abundance (Anders and Grevesse, 1989). This thesis focuses on the stable carbon isotope ratio ($^{13}C/^{12}C$) of organic emissions from natural gas processing facilities.

Measurement of the $^{13}C/^{12}C$ ratio is challenging because small differences in isotopic compositions between samples must be resolved. For this reason, the $^{13}C/^{12}C$ ratio is always measured relative to the international standard, Vienna Pee Dee Belemnite (VPDB). The $^{13}C/^{12}C$ isotopic ratio of a sample is expressed as $\delta^{13}C$, in units of ‰,

which is equivalent to parts per thousand difference from the standard, and is calculated using the following formula:

$$\delta^{13}C = \{(^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{standard} - 1\} \times 10^3$$

For carbon isotope analysis, samples are combusted to produce carbon dioxide, and the mass/charge (*m/z*) ratio of carbon dioxide is measured using an isotope ratio mass spectrometer (IRMS) to obtain the isotopic composition of the sample relative to the standard. Care must be taken to avoid isobaric interferences, which are systematic errors caused by the production of a same-*m/z* compound as that of interest as a result of the presence of another non-major isotope species. This occurs with ^{17}O and ^{18}O in the case of carbon dioxide. Production of $^{12}C^{16}O_2$ will result in *m/z* 44, production of $^{12}C^{16}O^{17}O$ and $^{13}C^{16}O_2$ will result in *m/z* 45, and production of $^{13}C^{16}O^{17}O$, $^{12}C^{17}O_2$ and $^{12}C^{16}O^{18}O$ will produce *m/z* 46. By knowing the relative natural abundances of interfering isotopes, isobaric interferences can be corrected for using a calculation. In the case of carbon isotopes, it is the convention to use the Craig correction factor (1957).

1.3.2 Isotopic Fractionations

Deviations from natural isotope abundances are the result of isotopic fractionations. Isotopic fractionations occur during physical, chemical, and biological processes because different isotopes undergo these processes at different rates. Isotope ratios of compounds in nature deviate from natural abundances, often in a predictable manner, and isotopic fractionations can lend information regarding the sources and processes that the compounds have undergone.

Equilibrium isotope fractionations occur during chemical equilibrium and in systems that are comprised of two or more phases containing a common element (Criss,

1999). Non-equilibrium isotope effects take place during processes that are incomplete (approaching equilibrium) or unidirectional (kinetic) (Criss, 1999), and in systems containing two or more phases but where one phase may be lost (open system). Similar to equilibrium fractionation processes, light isotopes often react faster due to less energy being required to break light isotope bonds. Non-equilibrium isotope effects are often important in biological processes because the breaking of bonds needs energy provided by the organism. In this case, the heavier isotope tends to remain as the reactant, as the light isotope bond is preferentially broken. A classic example of this type of fractionation is with bacterial sulphate reduction, which is the conversion of sulphate (SO_4^{2-}) to hydrogen sulphide (H_2S) by bacteria (Harrison and Thode, 1958). This results in an accumulation of the light isotope in the product (H_2S), leaving an enrichment of the heavy isotope in the reactant (SO_4^{2-}).

1.3.3 Fractionations During Natural Gas Formation

Fuex (1977) measured $\delta^{13}C$ values of the abundant components of natural gas and found that the $\delta^{13}C$ values for methane ranged from –55.5‰ to –68.1‰, ethane ranged from –32.2‰ to –37.0‰, propane ranged from –26.7‰ to –30.5‰, and butane ranged from –29.2‰ to –30.4‰. The negative $\delta^{13}C$ values indicate that all of these compounds are enriched in the light isotope of carbon (^{12}C) relative to the international standard (VPDB). Fuex (1977) attributed differences in the isotopic compositions of natural gas components to differences in the isotopic composition of source materials, fractionation incurred during formation, and fractionation subsequent to formation. More specifically, the carbon isotope composition of wet natural gas components (natural gas containing significant quantities of condensable hydrocarbons) depends on the level of maturity at

which the gas was generated, the carbon isotope composition of the organic material from which the gas was derived, and the extent to which kerogen structure (a solid, waxy, organic substance produced by partial decay of organic matter that when heated can produce coal, oil, and gas) influences the gaseous products (James, 1990). Typically, more highly structured kerogen petroleum products (e.g. coal) tend to show more source correlation than those which are less highly structured (e.g. natural gas) (James, 1990). Methane is typically the isotopically lightest component of natural gas, followed by ethane, propane, butane, pentane, etc. (Fuex, 1977; James, 1990; Stahl and Carey, 1975), and with increasing molecular weight, the carbon isotope composition typically approaches that of the source material (James, 1990). Depletion of light isotopes can be the result of thermal cracking (James, 1983) or biological degradation (James and Burns, 1984). Chlorinated compounds produced from biomass burning have also been found to be isotopically light (Czapiewski *et al.*, 2002). These researchers have demonstrated that the isotopic composition of natural gas products often differs between sources, and thus may be a valid tool for source apportionment.

Crude oil is also formed in underground reservoirs through similar processes, and is commonly associated with natural gas. Whiticar and Snowdon (1999) have investigated the gasoline-range fraction of crude oils, which are liquid at room temperature. It was found that oils from the same sources produce isotopic signatures that are highly correlated, and that non-straight-chained hydrocarbons often show better correlation than straight-chained alkanes (Whiticar and Snowdon, 1999). Whiticar and Snowdon (1999) further state that "the carbon isotope ratios of individual hydrocarbons in the C_5-C_8 range provide reliable and unique information for oil correlation".

1.3.4 Fractionations during Atmospheric Transport

The potential for isotopic fractionation of VOCs during exposure to oxidizing compounds in the atmosphere is present due to kinetic isotope effects. The most important atmospheric removal mechanism for VOCs is reaction with the hydroxyl radical ($HO^{\cdot}$), although other reactions may contribute to a small extent (e.g. photolysis, reaction with $NO_3^{\cdot}$, and reaction with ground-level ozone). As with other kinetic isotopic fractionations, the ^{12}C-^{12}C bond reacts faster than ^{12}C-^{13}C and ^{13}C-^{13}C bonds. Reactions of VOCs by oxidation with hydroxyl radicals, particularly unsaturated hydrocarbons, are sufficient to have a significant impact on the carbon isotopic composition of the remaining reactant (Rudolph *et al.*, 2000). Differences in isotopic compositions due to reactions with the hydroxyl radical at different rates are described using KIE (kinetic isotope effect), which is the isotopic enrichment factor that compares $\delta^{13}C$ values of remaining reactants to the products for a given reaction (Anderson *et al.*, 2003). Alkenes tend to react faster with hydroxyl radicals than alkanes, resulting in higher KIEs than alkanes with the same number of carbon atoms. Increasing the number of double bonds, as is the case with benzene, also creates higher KIEs. Consequently, reactions of alkanes with hydroxyl radicals cause relatively small isotopic fractionations, and source isotopic composition dominates ambient isotopic ratios (Rudolph *et al.*, 2000). Therefore, alkanes may be particularly useful for source apportionment of volatile organic compounds.

Quantification and isotopic measurements of VOCs can be combined to study atmospheric removal mechanisms, mixing, and dilution processes (Rudolph *et al.*, 2000). Unsaturated hydrocarbons are particularly useful for this purpose due to relatively large kinetic isotope effects (Rudolph *et al.*, 2000). As a result, isotopic measurements of

VOCs have been used to determine the photochemical ages of air masses (Rudolph and Czuba, 2000; Saito *et al.*, 2002). Unsaturated hydrocarbons have KIEs of up to 10‰ (Rudolph *et al.*, 2000) which may limit their use in source apportionment studies, however KIEs are dependent on the lifetime of the compound in the atmosphere, which can range from a few minutes to several hours.

1.4 Source Apportionment

A variety of techniques have been used in the past to apportion sources of organic pollutants. In many cases, distinguishing between biogenic and anthropogenic sources is a challenge, let alone distinguishing between multiple similar anthropogenic sources. In the past, chemical profiles of different combustion sources of atmospheric pollutants have been examined (Khalili *et al.*, 1995), and combined with chemical mass balance receptor models (Zheng *et al.*, 2002), as well as biomarkers (Simoneit, 1999).

In the 1970s, source apportionment of natural gas components to different reservoirs was successful using isotopic methods (Fuex, 1977; Stahl and Carey, 1975), but was limited to a few compounds present in relatively large quantities in the source reservoirs (including methane, ethane, propane, and butane). With the improvement of compound specific isotopic analysis, isotopes have been recognized as a novel tool that may assist to apportion complex mixtures of trace organic pollutants from industrial sources. The ability to separate compounds chromatographically and analyze isotopic compositions of trace individual components has proven to be much more valuable than bulk carbon isotopic characteristics.

Compound specific isotopic analysis has been used for many petroleum fractions, including source rocks and petroleum fluids (Odden *et al.*, 2002), oils (Rooney *et al.*,

1998; Whiticar and Snowden, 1999), coal (McRae *et al.*, 1998), and even individual gasoline samples (Smallwood *et al.*, 2002). Different petroleum processing practices have been shown to produce isotopically unique signatures (McRae *et al.*, 1999), and degradation of environmental samples has been shown to not significantly change the isotopic composition of heavier hydrocarbons (Mansuy *et al.*, 1997; O'Malley *et al.*, 1994). The use of stable carbon isotopes to apportion pollution sources of contaminants accumulated in water sediments is becoming more common (McRae *et al.*, 2000; O'Malley *et al.*, 1996; Stark *et al.*, 2003). More recently, researchers have begun source apportionment of organic pollutants associated with living organisms, as is the case with oil spill residue adsorbed to bird feathers (Mazeas and Budzinski, 2002) and polychlorinated biphenyls accumulated in living organisms (Yanik *et al.*, 2003).

Stable isotope source apportionment of trace atmospheric pollutants is still relatively new. This technique has been employed to differentiate between combustion sources forming particulate-form polycyclic aromatic hydrocarbons (Norman *et al.*, 1999), and to analyze downtown and suburban isotopic compositions of VOCs in Toronto, where fossil fuel combustion is the dominant source (Rudolph *et al.*, 2002). Emissions from sour gas flaring have been described in detail previously (Strosher, 1996), but not yet characterized isotopically.

1.5 Thesis Introduction

This thesis will focus on volatile organic compounds and particulate-form n-alkanes and polycyclic aromatic hydrocarbons emitted from natural gas processing facilities. Polycyclic aromatic hydrocarbons and n-alkanes were chosen based upon their

predicted isotopic stability with atmospheric transport, suspected presence in source reservoirs, and anticipated formation associated with secondary aerosols.

This is a pilot study, intended to test sampling methods and analytical techniques. This study will examine whether source apportionment of natural gas pollutants using these methods may be a viable tool in the future. Attempts will be made to determine which volatile organic compounds are formed by natural gas processing facilities, and what is present in the aerosol fraction downwind of these facilities. This thesis investigated background levels of these compounds in an "unaffected" region of Alberta, and levels of these pollutants in an "affected" region downwind of the sources. Here it has been examined whether the carbon isotope values of specific organic pollutants emitted from natural gas processing facilities are unique, similar to what has been previously found with natural gas reservoirs. Attempts will also be made to determine which compounds may be useful for source apportionment of natural gas processing emissions in the future.

CHAPTER 2: FIELD METHODS

2.1 Site Description

Alberta is an ideal location to attempt petroleum source apportionment studies, given that multiple major petroleum emitters exist, often within small geographic regions. Seven natural gas processing facilities were chosen in central Alberta, and one receptor site was chosen downwind of the facilities. The presence of many other sources of petroleum pollution (highways, well sites, residences, etc.) facilitated the need for a control site, located upwind of all plants.

The receptor site for this study was located approximately twenty kilometres west of Innisfail, Alberta (Figure 2.1). Sampling was situated approximately four meters above ground.

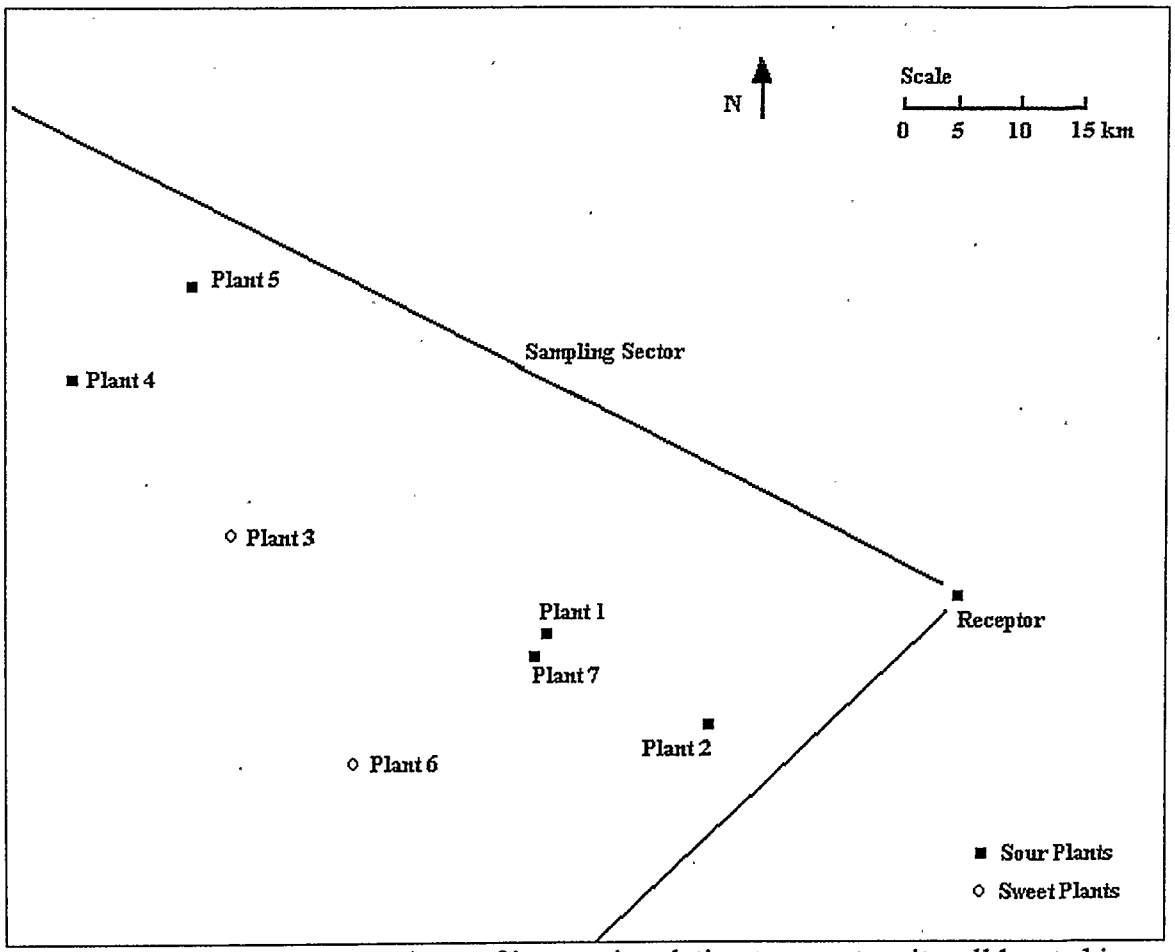

Figure 2.1: Seven natural gas plants of interest in relation to receptor site, all located in central Alberta. Control site was located further to the west. Plant 3 and Plant 6 are sweet plants, while Plants 1, 2, 4, 5, and 7 are sour.

The control site was located less than one kilometre from Highway 11, approximately fifty kilometres west of Nordegg, Alberta. This site was located in rural Alberta, just east of Banff National Park, which allowed for a site relatively un-impacted by petroleum emissions. Given the abundance of petroleum processing and use that occurs in Alberta, it is virtually impossible to find a true "control" site not impacted by petroleum processing and use.

There were seven natural gas plants within the sampling sector (Figure 2.1), located between twenty and seventy kilometres from the receptor site. All plants except

Plant 3 and Plant 6 were sour, meaning that they process natural gas with enough hydrogen sulphide to require sulphur recovery processes.

In addition, Plant 1, Plant 2, Plant 4, and Plant 5 have received grandfather status from the Alberta Energy and Utilities Board. They were not required to meet current sulphur recovery guidelines, and instead were required to meet guidelines from 1988 (Alberta Energy and Utilities Board, 2001). In 1988, new sulphur recovery guidelines were created and existing gas processing facilities were exempt due to the perceived limited environmental benefits relative to the high economic costs that would have been required to implement new technologies to existing plants. It was believed in 1988 that these "grandfathered" gas plants would have limited lifetimes, however they have since exceeded their expected lifetimes, motivating the Alberta Energy and Utilities Board to implement a sunset clause requiring the grandfathering of plants to end by 2017 (Alberta Energy and Utilities Board, 2001). Plant sulphur recovery guidelines vary based upon the quantity of sulphur processed (in tonnes per day). According to the 1988 sulphur recovery guidelines, Plant 1 must have sulphur recovery of 92% (compared to the current guideline of 96%), Plant 2 must recover 82% (compared to the current guideline of 90%), Plant 4 must recover 99% (compared to the current guideline of 99.8%), and Plant 5 must recover 98.5% (compared to the current guideline of 98.8%).

2.2 Aerosols

2.2.1 Sampling

Two types of Sierra Misco high volume samplers were available for aerosol sampling: an AC high volume sampler for sites where constant AC power was available, and a high volume sampler adapted for 24 volt DC power, for sites that had no constant

AC power source. Flow rates were measured using a high volume sampler portable calibration unit (Kurz Instruments). Changes in air flow were particularly important when using the DC high volume sampler due to loss of battery power over time, and a linear relationship was established between battery power and air flow. High volume samplers were either set up to sample directionally, or non-directionally. High volume samplers using directional sampling were connected to a computer, which was connected to a real-time weather station (Peet Bros. Company, Inc.), complete with an anemometer, outdoor humidity sensor, and temperature sensor (Figure 2.2). Weather conditions were recorded every sixty seconds. With each weather reading, parameters were evaluated for acceptability, and if parameters were acceptable, the high volume sampler was turned on. Parameters tested were wind speed (must be > 1 km/h to ensure that the wind was blowing consistently from the desired direction), humidity (must be < 99% to prevent loss of water soluble species), and wind direction. Temperature was also measured, but was not a condition of the on/off status of the high volume sampler.

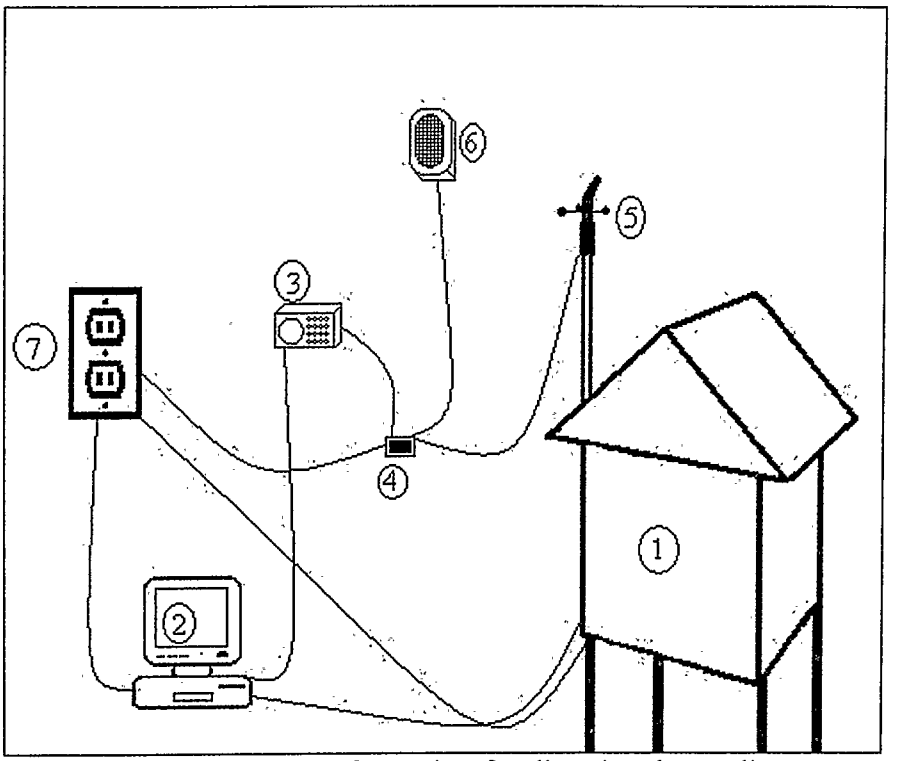

Figure 2.2: High volume sampler configuration for directional sampling.
1. High volume sampler 2. Laptop computer 3. Weather station computer 4. Junction cable box for weather station 5. Weather station anemometer 6. Humidity sensor complete with temperature sensor 7. AC power source

At the receptor site, the AC high volume sampler was set up to sample directionally, only when the wind was blowing from within the sector of interest (between 235 and 302 degrees true north), which was set to encompass emissions from the seven natural gas processing facilities. Sampling occurred at the receptor site between September 2001 and October 2002. Originally, the sampling sector was smaller, set to encompass emissions from only 3 plants. Due to small sample sizes because of infrequent winds from this sector, the sampling sector was increased to include seven natural gas plants.

At the control site, the AC high volume sampler was set up to sample non-directionally, and sampled 24-hour continuous samples to gain an understanding of the

typical background levels of a rural area in Alberta relatively un-impacted by petroleum processing. Sampling occurred at the control site in November 2001 and October 2002.

At the seven natural gas processing facilities, samples were taken from the ground using the DC high volume sampler. Samples were typically between 60 and 90 minutes in length, due to limitations imposed by battery lifetimes. Aerosol sampling of all plants took place in July 2002 and September 2002, with additional samples taken at Plant 4 in December 2002 and March 2003. All aerosol samples taken at plants were not directionally controlled with a computer but were downwind of the plant at the time of sampling. One exception to this was for the sample taken at Plant 4 in March 2003, when a weeklong directional sample was taken using the AC high volume sampler, sampling a ninety-degree sampling sector encompassing plant emissions.

Over eighteen months, twenty-one samples were collected at the receptor site, although four samples were not processed due to initial sampling difficulties. Two aerosol samples were collected at the control site, and a total of seventeen samples were collected at the seven natural gas processing facilities. A complete timeline of aerosol samples is presented in Table 2.1.

Table 2.1: Timeline of aerosol samples collected at plant, control, and receptor sites

Sampling Location	Samples Collected
Receptor Site	Directional sampling September 2001 – October 2002 (n = 21)
Control Site	Sampling events November 2001 and October 2002 (n = 2)
Plant Sites	Sampling events at all plants July 2002 and September 2002 Sampling event at Plant 4 in December 2002 Directional sampling at Plant 4 in March 2003 (n = 17 total)

Aerosol sampling employed high volume samplers equipped with quartz fibre filters (Whatman Grade QM-A, 20.3 cm x 25.4 cm). These filters collected particulate matter greater than or equal to 0.8 μm in diameter (Whatman Technical Support, personal communication, 26 August 2003). All quartz filters were annealed at 550°C for 8 hours to combust organic contaminants prior to taking them into the field, and filters were stored in aluminum foil, inside sealed plastic bags, before and after sampling. All handling of filters was done wearing polyethylene gloves (VWR) to minimize contaminants from skin contact.

2.2.2 QA/QC

Travel blanks were taken during extended field sampling trips. Travel blanks were annealed filters taken into the field along with sample filters, remaining unopened until return to the laboratory for analysis. Travel blanks account for any contamination as a result of filter annealing, travel, handling, storage, and extraction.

Field blanks were also taken at each site, and a subset analyzed. Field blanks were annealed filters taken into the field with sample filters, removed from their packaging, placed onto the high volume sampler for one minute without turning the sampler on, then removed and stored in the same way as sample filters. Field blanks account for all contamination sources monitored in travel blanks, as well as high volume sampler contact (e.g. gasket), filter handling, and air exposure while in the field.

2.3 VOCs

2.3.1 Sampling

VOC samples were stored in stainless steel, fused silica-lined canisters (Restek Silco-Can). VOC samples were collected using a vacuum pump (Gast Manufacturing

Inc., standard diaphragm model) and pressure gauge (Figure 2.3). All tubing and connections were stainless steel and Teflon, to minimize adsorption of analytes onto sample transfer lines. Once in the field, the transfer line was rinsed a minimum of three times with the air being sampled. Following that, the canister was pressurized three times to two atmospheres overpressure, and the sample released each time to rinse the canister with sample. Finally, the air sample was collected by pressurizing the canister again to two atmospheres overpressure, and sealing the canister valve to store the VOC sample prior to turning off the pump.

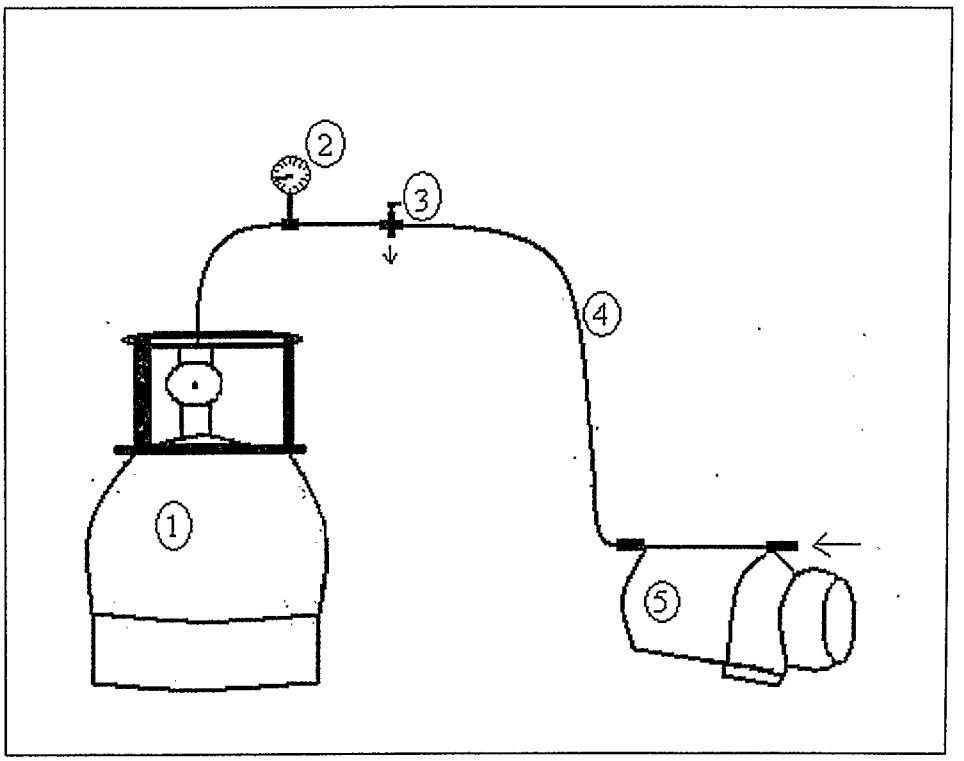

Figure 2.3: VOC sampling equipment.
1. Stainless steel fused silica-lined canister 2. Vacuum pressure gauge 3. Three-way toggle valve 4. Stainless steel and/or teflon transfer tubing 5. Vacuum pump

Helicopter VOC sampling of several natural gas processing facilities initially took place in April 2001. These samples were analyzed in a different manner from those described here, and subsequently are not a part of this thesis. VOC sampling of the seven

natural gas processing facilities of interest took place from a helicopter in December 2002, with additional VOC samples taken from the ground downwind of Plant 4 in July 2002 (during the day) and December 2002 (after sunset). One "upwind" sample was also taken from inside the helicopter, away from the natural gas plants, to provide an alternate upwind control and to verify that the helicopter was not introducing VOCs into samples.

VOC samples were collected at the receptor site between September 2001 and October 2002. The number of samples collected was greatly restricted by the low frequency of the wind being from the desired direction during site visits, despite nearly forty site visits over a period of eighteen months. Receptor site samples were collected in April 2001 (Receptor 1), November 2001 (Receptor 2), August 2002 (Receptor 3), and December 2002 (Receptor 4). One sample was lost due to a leaking canister valve (collected December 2001). Two VOC samples were collected at the control site in October 2002. A complete sampling timeline of VOC samples is presented in Table 2.2.

Table 2.2: Timeline of VOC samples collected at plant, control, and receptor sites

Sampling Location	Samples Collected
Receptor Site	April 2001 (Receptor 1) November 2001 (Receptor 2) August 2002 (Receptor 3) December 2002 (Receptor 4) (n = 4)
Control Site	October 2002 (n = 2)
Plant Sites	July 2002: Ground sample from Plant 4 December 2002: Ground sample from Plant 4 December 2002: Helicopter sampling of all plants and "upwind" sample collected (n = 10)

2.3.2 Canister Cleaning

Canisters were cleaned by wrapping them with heating tape, and heating to a minimum of 100°C for three hours under constant vacuum conditions (10^{-3} torr). Following this, canisters were rinsed a minimum of three times with ultra-pure nitrogen

(Praxair continuous emission monitoring zero gas). This procedure was repeated two more times, and found to clean canisters below the detection limits of the gas chromatograph coupled with a flame ionization detector (GC-FID) when analyzing the entire canister volume (either 3 or 6 L, which corresponded to $> 7 \times 10^5$ times less ppbv than the lowest concentration of measured analyte detected). All canisters were analyzed using the GC-FID prior to field sampling to ensure cleanliness. Canisters were stored pressurized with ultra-pure nitrogen, but prior to sampling the canisters were evacuated to 10^{-3} torr.

The original method of canister cleaning was to immerse sealed canisters into boiling water and heat for extended periods. Canisters were then rinsed with ultra-pure nitrogen. This method was found not to clean canisters thoroughly, and problems were encountered with canisters rusting and floating during heating. This method is not advised for future canister cleaning.

New canisters shipped from the manufacturer were pressurized with nitrogen, and two samples were taken at the receptor site prior to canister cleaning protocol development, due to the time required to test the cleaning method sufficiently. To verify that new canisters were indeed clean and not contaminated with VOCs, two new canisters from the manufacturer were saved and analyzed.

CHAPTER 3: VOLATILE ORGANIC COMPOUNDS

3.1 Methods

Although the study of isotopes has been around for many decades, isotopic analysis of individual hydrocarbons in complex mixtures is relatively new, and as such, method development is still in its early stages. Continuous-flow isotope ratio mass spectrometry (CF-IRMS) involves the coupling of a gas chromatograph (GC) with an isotope ratio mass spectrometer.

Only recently has CF-IRMS been used for analysis of volatile environmental samples, and method evaluation is ongoing to determine whether it is preferable to remove water and carbon dioxide from the samples prior to analysis. Water could be present in significant quantities, causing GC column degradation or isobaric interferences through the formation of CO_2H^+. Carbon dioxide can also be problematic due to the selectivity of the CF-IRMS detector to carbon dioxide, as the detector collects ions at *m/z* 44, 45, and 46. With parts per million levels of carbon dioxide in atmospheric samples (perhaps parts per thousand levels in the plumes), there was concern that the response from ambient carbon dioxide would saturate the detector, overshadowing the $\delta^{13}C$ response from trace organic pollutants (present at parts per billion levels). Because of this, methods were tested to remove water and carbon dioxide.

3.1.1 Water Removal

Attempts to remove water involved using a cryogenic trap. This method has been previously employed by Rudolph *et al.* (2002), although that trap was maintained at –20°C. The cryogenic water trap used in this study consisted of a portion of the stainless steel sample transfer line passing through a bath of ethylene glycol (antifreeze) and ice,

with the temperature maintained at approximately –8°C. The cryogenic trap was placed between the sample and the sample preconcentration trap (SPT), such that water removal would occur prior to contact with the GC column.

With a cryogenic trap, concurrent removal of VOCs and water is possible, particularly with analytes that are less volatile. Removal of VOCs was tested by injecting a known volume of standard gas mixture (propene, 1-butene, 1-pentene, 1-hexene, benzene, toluene, ethyl benzene, o-xylene, m-xylene, and p-xylene) into the GC-FID (gas chromatograph coupled with a flame ionization detector) without the cryogenic trap. The same volume and concentration of standard was subsequently pre-treated by the cryogenic trap for water removal prior to GC-FID analysis. The cryogenic trap was found to remove VOCs from the standard mixture injection based primarily on boiling point, resulting in substantial loss of compounds with boiling points above that of water (Table 3.1). In addition, it was concluded that water was probably not being effectively removed from the samples using this method, on the basis that it would likely be removed at levels similar to that of benzene and toluene (with some error in this estimation due to the different properties of water and hydrocarbons). However, a large decrease in response from less volatile VOCs was observed (Table 3.1). Isotopic fractionation is expected during phase changes, therefore any loss of analyte due to condensation would likely change the isotopic composition of the analytes, hence this technique was subsequently abandoned.

Table 3.1: Results of Cryogenic Trapping of Water from VOC samples (n = 1)

Compound of Interest	% Loss through Cryogenic Trap	Boiling Point (°C)
Propene	< 2	-47.4
1-Butene	< 2	-6.1
1-Pentene	< 2	30
1-Hexene	< 2	63
Benzene	< 2	80.1
Toluene	5	110.6
o-Xylene	16	144
m-Xylene	20	138.3
p-Xylene	20	139.1
Ethyl benzene	24	136.1

These results agree with the prediction given by Klouda *et al.* (2002), who anticipated that any attempt to remove moisture from VOC samples would result in removal of some VOCs. Future attempts to remove water could involve selective complexing agents, such as magnesium perchlorate [$Mg(ClO_4)_2$] (Saito *et al.*, 2002). Nafion could be particularly useful for CF-IRMS analyses, as it is recommended by the Environmental Protection Agency for mass spectrometry (1999), and has been found to be effective for water removal in CF-IRMS analyses (Leckrone and Hayes, 1998). Nafion dryers have been found to remove up to 99.96% of water from saturated carrier gas streams with the dryer operated at 25°C, and up to 99.997% when operated at 0°C (Leckrone and Hayes, 1997). Future attempts to remove water must be examined to determine whether quantitative losses or isotopic fractionations of analytes are occurring. With CF-IRMS analysis, if the Nafion trap is placed after sample combustion but prior to reaching the detector, loss of sample due to interaction with the Nafion is unlikely, as the sample has been combusted to carbon dioxide.

3.1.2 Carbon Dioxide Removal

Ascarite (sodium hydroxide-coated silica) was chosen to selectively remove carbon dioxide through the following reaction (Saito *et al.*, 2002):

$$2NaOH_{(s)} + CO_{2(g)} \rightarrow H_2O_{(l)} + Na_2CO_{3(s)}$$

Others have used potassium carbonate (Rudolph *et al.*, 2002) and lithium hydroxide (Rasmussen *et al.*, 1996). During preliminary testing at the Meteorological Service of Canada, it was suspected that the ascarite trap caused isotopic fractionation of VOCs in a standard mixture, either as a result of reaction of the VOCs with the ascarite or other reactions with the trap (e.g. quartz tube, quartz wool, and associated connections). Due to this, attempts to remove carbon dioxide were abandoned to maintain the isotopic integrity of the data.

These findings compare well with those of Rasmussen *et al.* (1996), who found that carbon dioxide removal using lithium hydroxide resulted in an average twenty percent loss of volatile organic compounds from samples. The production of extra water due to the removal of carbon dioxide also amplifies any problems that would result from water in the samples. It was concluded that the separation of compounds based on volatility using gas chromatography (carbon dioxide sublimes at –78.4°C) would minimize interference from carbon dioxide as it would elute through the GC prior to compounds of interest, and venting of carbon dioxide post-column (prior to reaching the IRMS detector) would be the best method under the circumstances to prevent carbon dioxide from reaching the detector.

3.1.3 Flow Rate Tests

The sample preconcentration trap (SPT) manufacturer recommends that volatile samples be loaded onto the SPT at rates between 10 and 40 ml/min. An intermediate value of 17.5 ml/min was chosen for quantitative analysis, and compared to a lower flow rate of 5 ml/min (Table 3.2). We suspect that if a flow rate of 17.5 ml/min was too fast to quantitatively load the sample onto the SPT, the quantity of sample loaded onto the preconcentration trap would be higher when the flow rate was 5 ml/min. During isotopic analysis at the Meteorological Service of Canada (MSC) in Toronto, a flow rate of 50 ml/min was required to load sufficient material for analysis and thus required the same testing to compare with a flow rate of 20 ml/min (Table 3.2). As can be seen in Table 3.2, large differences between the sample quantity loaded onto the preconcentration trap at the flow rates tested were absent, indicating that 17.5 ml/min and 50 ml/min are likely suitable flow rates for sample loading onto the SPT. Differences that do exist may be attributed to variation in GC-FID and mass flow controller performance ($\pm$ 0.5 ml/min), as well as the manual closing of the valve on the canister by the author. It is likely that an increase in response with higher flow rates is seen because the canister valve was manually closed, and at higher flow rates, more sample would proceed through the with same amount of time required to close the canister, when compared to lower flow rates. GC-FID reproducibility for duplicate runs was better than twelve percent (Table 3.2).

Table 3.2: Quantitative Loading of SPT Using Varying Flow Rates (Note: Runs A and B used a standard of different concentration than Runs C and D)

Compound	A: Peak area at 5 ml/min	B: Peak area at 17.5 ml/min	% difference between A and B	C: Peak area at 20 ml/min	D: Peak area at 50 ml/min	% difference between C and D
Propene	40419	41024	1.50	23196	25158	7.80
1-Butene	54482	55086	1.11	31027	33580	7.60
1-Pentene	66403	67095	1.04	37944	41058	7.46
1-Hexene	77661	78481	1.06	44442	47994	7.40
Benzene	40180	40625	1.11	22843	24724	7.20
Toluene	42347	42979	1.50	24164	26092	7.39
o-Xylene	32994	33590	1.80	18495	20088	7.93
m-Xylene	38777	38463	0.81	21312	22638	6.22
p- Xylene	32199	33266	3.31	18257	20296	11.17
Ethyl benzene	38876	39260	0.99	21672	23565	8.03

3.1.4 GC-FID Quantification

Quantification of volatile organic compounds was performed using a Varian 3800 GC, equipped with an FID and SPT. The column was a Varian CP-Sil5-CB WCOT (wall coated open tubular) column with a dimethylpolysiloxane non-polar stationary phase. The column was 60 meters in length, with an inside diameter of 0.32 mm, and 1 μm stationary phase thickness. Samples were manually injected through two high temperature valves on the side of the GC (Figure 3.1), to allow for the use of a mass flow controller. The mass flow controller was a Tylan Corp. Model FC-260, and was able to control flow between 1 and 100 ml/min, with fluctuations typically +/- 0.5 ml. The initial SPT temperature was –160°C, and it was held at this temperature with the valves in injection position for 60 minutes (Figure 3.1A), in order to allow for enough time to load a large amount of sample so that variable volumes of sample could be added without needing to change the parameters of the temperature program (thus rendering the calibration useless). After sample injection into the SPT, the valves were switched to

allow for helium to flow through the SPT for ten minutes, with the temperature of the SPT remaining at –160°C (Figure 3.1B). This removed nitrogen and oxygen from the sample, which enter the gaseous phase at –196°C and –183°C respectively. At 70 minutes, the valves were switched such that the SPT and helium flow through it were in line with the GC column (Figure 3.1C). Immediately after this point, the SPT was heated rapidly to 200°C, and held at that temperature for the remainder of the run (52 minutes) to ensure that the SPT would be flushed before the next sample injection. This allowed all compounds cryogenically held in the SPT to be transferred for seven minutes through flow of helium, cryo-focussing the analytes onto the head of the column (maintained at –30°C). At 77 minutes, the SPT was switched out of line with the column (Figure 3.1B), although helium flow through it continued. At this point, the column was heated to 240°C at a rate of 7°C per minute, and held at 240°C for an additional 7 minutes. The total run time was 122 minutes.

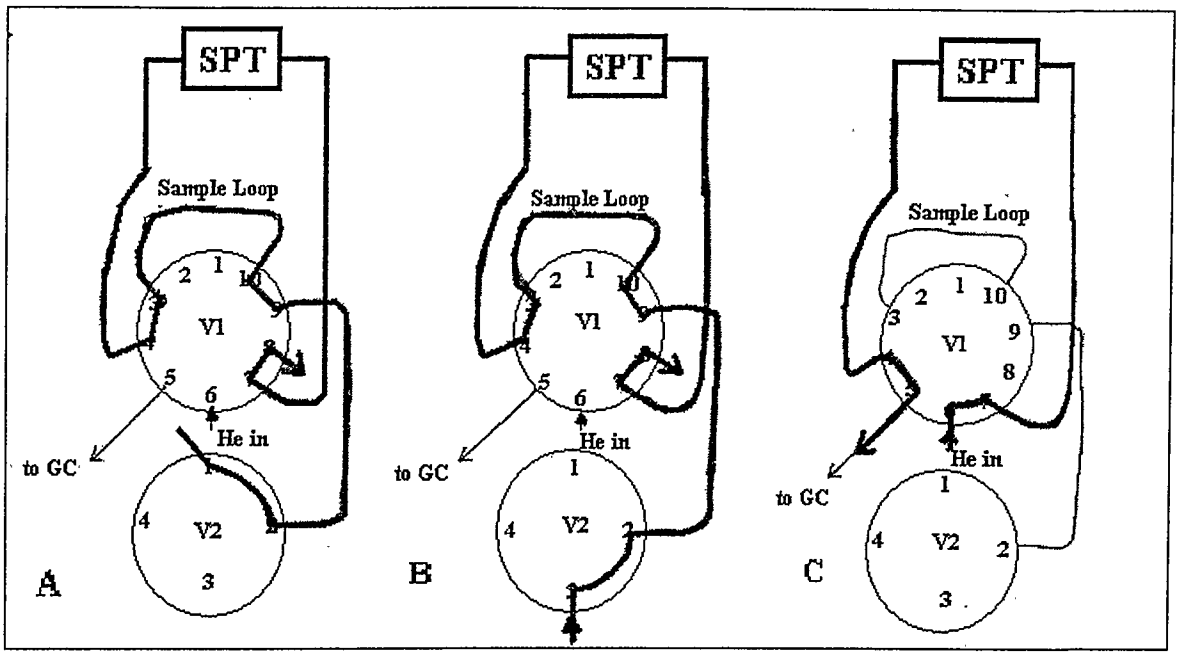

Figure 3.1: Schematic diagram of injection values on the GC-FID, manipulated to control sample injection. V1 = Valve 1, with 10 ports. V2 = Valve 2, with 4 ports.
3.1A: loading of sample onto SPT, 3.1B: rinsing of SPT with carrier gas, 3.1C: loading of sample contained in SPT onto GC column.

Two gas standards for quantification of selected volatile organic compounds were purchased from Supelco. The first was an aromatic mixture containing benzene, toluene, ethyl benzene, m-xylene, o-xylene, and p-xylene, each 10 ppm in a balance of nitrogen. The second was an olefin mixture, containing 100 ppm each of ethene, propene, 1-butene, 1-pentene, and 1-hexene in a balance of nitrogen. These standards were much too concentrated for the work being done in this study, and were diluted to concentrations between 25 and 150 ppbv (parts per billion by volume) in ultra-pure nitrogen using a glass mixing line in the Stable Isotope Laboratory at the University of Calgary. Following multiple runs of standard mixtures on the GC-FID, the response of ethene varied greatly between runs (> 100%), and attempts to quantify ethene were subsequently abandoned. For the remaining analytes, calibration results are displayed in Table 3.3. Different concentration levels for the calibration curve were controlled by manipulating

volumes of the dilute standard mixture injected into the instrument. The concentration of prepared standard used for calibration was approximately 32 ppbv benzene, toluene, ethyl benzene, o-xylene, m-xylene, and p-xylene, and approximately 102 ppbv propene, 1-butene, 1-pentene, and 1-hexene. Calibration levels of approximately 0.01, 0.08, 0.20, and 0.35 nanomoles of standard were used for propene, 1-butene, 1-pentene, and 1-hexene, while levels of approximately 0.004, 0.03, 0.07, and 0.11 nanomoles of standard were used for benzene, toluene, ethyl benzene, o-xylene, m-xylene, and p-xylene.

Table 3.3: Calibration results for VOCs using the GC-FID
[a] The correlation coefficient (r^2) is a measure of the linear association between two variables, and identifies how well the linear calibration curve fits the data.
[b] Relative response factor standard deviation is the standard deviation of the response factors used in the calibration curve (where response factor = area of FID peak/concentration of analyte). Response factor identifies the reproducibility of the response in peak area counts relative to a change in analyte concentration, and is a measure of instrument sensitivity.

Compound	Coefficient of Determination of Calibration Curve (r^2)[a]	Response Factor Relative Standard Deviation (%)[b]	Lowest Calibration Concentration (nanomoles)
Propene	0.9999	2.1	0.011
1-Butene	0.9999	8.8	0.011
1-Pentene	0.9999	10.1	0.011
1-Hexene	0.9999	6.8	0.011
Benzene	0.9999	9.0	0.0039
Toluene	0.9999	6.3	0.0039
Ethyl benzene	0.9999	5.3	0.0037
o-Xylene	0.9999	6.1	0.0037
m-Xylene	0.9999	14.5	0.0037
p-Xylene	0.9999	2.0	0.0036

3.1.5 CF-IRMS Analysis at the Meteorological Service of Canada (MSC)

Isotopic analysis of VOCs took place at the MSC at Environment Canada, in Toronto, Ontario, using an online CF-MS-IRMS system. This analysis was conducted in January 2003, over a time period of approximately 4 weeks, which proved to be a limiting amount of time to change instrument configurations, develop methods, test

methods, and run samples. Instrument description and methodology are previously described by Rudolph *et al.* (1997). The majority of the samples were analyzed by Dr. Norman and the author, with the remaining samples analyzed by Darrell Ernst (MSC). A Saturn ion trap mass spectrometer simultaneously analyzed a portion of samples, scanning in total ion collection (TIC) mode for ions above *m/z* 44. The reason not to scan below *m/z* 45 was due to the relatively large amount of carbon dioxide present in samples. Despite backflush procedures, large ion intensities at *m/z* 44 may have resulted in large data files that were too large to import into the software for data analysis. Water and carbon dioxide removal prior to analysis were not performed due to problems described earlier.

The CF-MS-IRMS system is displayed in Figure 3.2. Samples were cryogenically preconcentrated on the SPT. The column used was an Agilent DB-1MS column with a dimethylpolysiloxane stationary phase. The column was 60 meters in length, with an internal diameter of 0.25 mm and a film thickness of 0.25 μm. The total column flow was 1 ml/minute, with two-thirds of the column flow diverted to the IRMS detector, and one-third sent to the ion trap MS. The column effluent that proceeded to the IRMS detector entered the combustion oven, where VOCs were oxidized to carbon dioxide using a 25 cm long ceramic tube containing oxygenated copper, nickel, and platinum wires held at a temperature of 960°C. The sample was then passed through the reduction oven, which eliminated common species that cause isobaric interferences using a ceramic reactor with copper operated at 600°C (i.e. NO_2 is converted to N_2 and O_2). The sample then entered the Nafion trap, to remove water that was formed in the sample

stream and present in carrier gas. Faraday collector cups simultaneously monitored for *m/z* 44, 45, and 46.

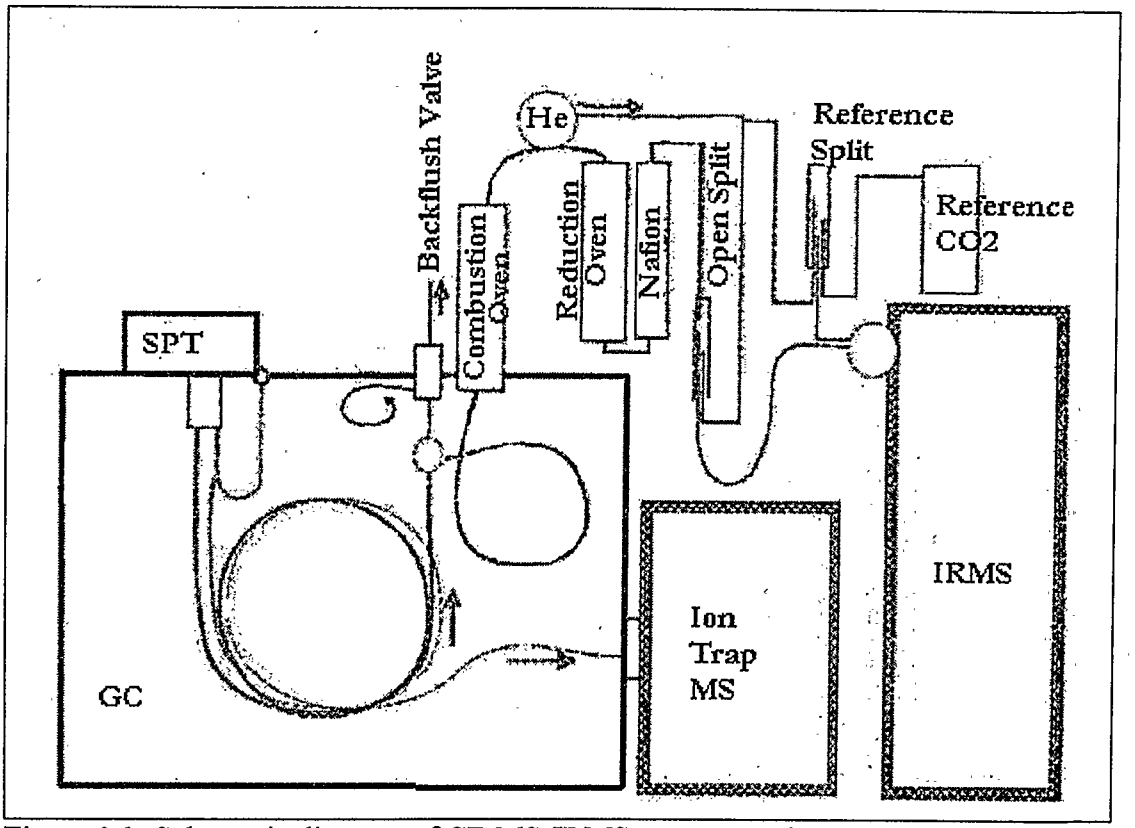

Figure 3.2: Schematic diagram of CF-MS-IRMS system used to analyze VOC samples at MSC in Toronto

Compound identification using mass spectra was attempted for compounds with adequate IRMS response (area $\geq$ 0.5 Volt seconds, Vs), as compounds with sufficient peak areas could provide accurate $\delta^{13}C$ data (Huang, L., MSC, personal communication, 17 February 2003). The limit of linearity of the CF-IRMS was tested briefly by Dr. Norman and the author at MSC, where standard mixtures containing n-pentane, n-hexane, n-heptane, iso-octane, n-decane, benzene, and toluene were repeatedly analyzed using the CF-IRMS (Figure 3.3). When smaller volumes of the standard mixture were injected, resulting in peak areas < 0.5 Vs, it was often not possible to detect the peaks from the standard mixture (in > 50% of cases). When peaks were detected, they often did not

correspond well with the more precise $\delta^{13}C$ values obtained by repeated analyses of larger standard volumes resulting in peak areas > 0.5 Vs (Figure 3.3). Average $\delta^{13}C$ values of peaks with areas > 0.5 Vs differed from $\delta^{13}C$ values of peaks with areas of < 0.5 Vs by 1.2‰, 2.4‰, 2.5‰, and 2.1‰ for n-pentane, n-hexane, benzene, and n-heptane respectively. In the case of n-decane and iso-octane, the $\delta^{13}C$ values of the peaks with areas < 0.5 Vs agreed well with those > 0.5 Vs. More testing would have been required to determine if a lower detection limit is possible given the set-up and procedures described here, and what the lowest possible detection limit would be, therefore the recommendations of the lab manager were followed. Loss of linearity at low concentrations may be due to differential non-linear Faraday collector response at low ion intensities, adsorption/desorption effects, isobaric interference from CO_2H^+, or isotopic fractionations introduced by combustion efficiencies of less than one hundred percent.

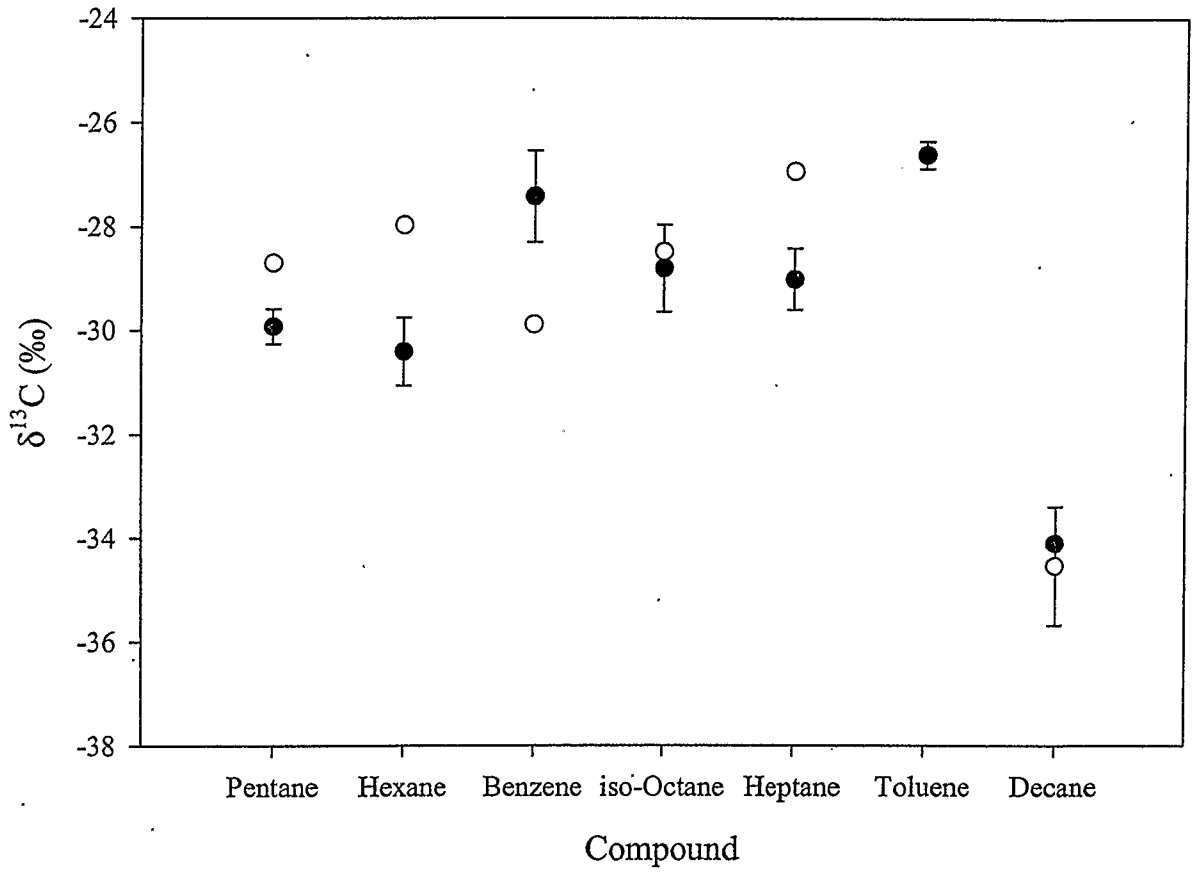

Figure 3.3: $\delta^{13}C$ values from repeated injections (n = 5) of standard containing n-pentane, n-hexane, n-heptane, iso-octane, n-decane, toluene, and benzene (± standard deviation). Solid dots are $\delta^{13}C$ values of standard peaks integrated with areas > 0.5 Vs. White dots are $\delta^{13}C$ values of standard peaks integrated with areas < 0.5 Vs.

Standard mixtures containing n-pentane, n-hexane, benzene, iso-octane, n-heptane, toluene, and n-decane at parts per billion levels were analyzed to compare off-line analyses with on-line analyses (Table 3.4). n-Butane was also present in the mixture, but responses on both the ion trap MS and IRMS were not adequate due to limited ion intensity of the n-butane peak because of the high *m/z* range scanned for, and relatively few carbon atoms present in n-butane resulting in less carbon dioxide produced per mole than for the remaining VOCs. The VOC isotope values were compared to "known off-line" $\delta^{13}C$ values from stock solutions of individual compounds used to prepare the

volatile standards, with the stock solutions analyzed on a different system at the University of Calgary. The "known off-line" standards were prepared by placing approximately 0.1 ml solvent into a glass capillary tube and then placing the capillary into quartz ampules sealed at one end, containing approximately 1 gram cupric oxide. The ampules containing the capillary were placed onto the sealed vacuum line (at atmospheric pressure), cooled in liquid nitrogen to minimize solvent volatilization, and then evacuated to remove laboratory air. The ampules were then sealed off using a CH_4/O_2 torch, and baked at 550°C overnight to combust all solvent to carbon dioxide.

Two volatile mixtures were prepared from the stock solutions: 45 ppbv and 25 pptv (parts per trillion by volume). These mixtures were prepared by injecting known volumes of solvent into the evacuated glass mixing line at the University of Calgary, and gently heating the vacuum line to volatilize all of the solvents. The vacuum line was then flushed with ultapure nitrogen, using known volumes and pressures in the vacuum line and canister to calculate final concentrations. This method assumed that all solvents were completely volatile after heating, and that all solvents had been transferred from the vacuum line into the canister. As can be seen in Table 3.4, the difference in isotopic compositions between the volatile standard mixture and stock solutions ranges from < 0.1‰ to 2.3‰. The solutions have since been re-prepared for isotopic analysis, and are currently awaiting isotopic analysis at MSC using the same instrument as was used for the analysis of the volatile standards. $\delta^{13}C$ data from the standard mixture runs at MSC (Table 3.4) had an average difference between runs of 0.7‰ (standard deviation = 0.3‰, n = 2). Table 3.4 also shows good agreement between standards prepared at different concentrations, demonstrating that the dilution process and possible interactions between

the canister and the sample inside it likely did not significantly impact the isotopic composition of the VOCs at either concentration.

Table 3.4: Comparison of on-line and off-line standards at the Meteorological Service of Canada, and at the University of Calgary, Stable Isotope Laboratory ("Known" $\delta^{13}C$)

Compound	$\delta^{13}C$ (‰) from 45 ppbv standard (n = 1, Area > 0.5 Vs)	$\delta^{13}C$ (‰) from 25 pptv standard (n = 1, Area > 0.5 Vs)	"Known" $\delta^{13}C$ (‰)	$\Delta\ \delta^{13}C$ (‰) between "known off-line" $\delta^{13}C$ and average of all runs > 0.5 Vs area
n-Pentane	-29.7	-30.2	-27.6	2.3
n-Hexane	-30.0	-30.9	-28.2	2.2
Benzene	-27.7	-28.1	-27.0	0.4
iso-Octane	-28.9	-29.6	-27.9	0.9
n-Heptane	-28.6	-29.4	-27.2	1.9
Toluene	-26.8	-26.3	-26.6	< 0.1
n-Decane	-34.1	-34.1	-33.5	0.6

Reproducibility of isotopic analysis was also evaluated by injecting two VOC samples twice, to serve as analytical duplicates (Table 3.5). Standard deviations of all $\delta^{13}C$ values have been calculated from multiple manual integrations of the same isotopic peak, therefore this uncertainty represents that associated with reproducibility of manual peak and baseline definition.

Table 3.5: Analytical duplicates of two VOC samples analyzed at MSC (mean ± standard deviation)

Compound Name	Plant 6 $\delta^{13}C$ (‰)	Plant 6R $\delta^{13}C$ (‰)	$\Delta\ \delta^{13}C$ (‰)	Compound Name	Receptor 4 $\delta^{13}C$ (‰)	Receptor 4R $\delta^{13}C$ (‰)	$\Delta\ \delta^{13}C$ (‰)
Compound 3	-31.3 ± 0.4	-34.4 ± 0.3	3.1	Compound 4	-28.4 ± 1.5	-27.1 ± 0.1	1.3
Compound 11	-38.2 ± 0.3	-39.7 ± 0.1	1.5	Compound 12	-29.4 ± 0.9	-29.9 ± 0.4	0.5
Compound 17	-34.2 ± 0.5	-33.5	0.7	Compound 13c	-25.8 ± 0.1	-22.9 ± 0.4	3.0
Compound 20	-28.9 ± 0.6	-30.9	1.9	Compound 14	-36.8 ± 0.5	-37.2 ± 0.2	0.4

For the analytical duplicates, the average difference in $\delta^{13}C$ between runs was 1.5‰ (standard deviation 1.1‰) (Table 3.5). This variability may be attributed to a number of factors: uneven heating of sample transfer lines, human error associated with manual definition of isotope peaks and baseline, and variability in instrument performance between runs. Due to the fact that the differences show no predictable trend, this leads us to believe that the errors associated with these measurements are related to human error associated with manual integrations, and instrument variability from day to day. All $\delta^{13}C$ values from Plant 6 and Receptor 4 from herein are compilations of analytical duplicate runs.

Mass spectra were evaluated using Saturn GC-MS Workstation Version 5.4 software. Compounds with isotopic information were tentatively identified using fragmentation information, as opposed to comparisons of retention times and fragmentation patterns of standards. Identification was made particularly difficult because of the lack of mass spectral data below *m/z* 45, as commonly the base peak and other major fragments of volatile hydrocarbons fall below this range. Identification was attempted using two print libraries (ASTM Committee, 1969; Mass Spectrometry Data Centre, 1986), the newest version of the NIST computer library (FairCom Corporation, 2002), and comparison of previous natural gas plant samples analyzed on the same instrument in 1998 by York University researchers, yet many compounds were still left unidentified. Identifications established were tentative at best, although as an additional confirmation, boiling points ensured that tentative identifications appeared reasonable with the elution order presented. A total of twenty-seven different compounds were present in adequate quantities to provide isotopic data. A complete list of these

compounds, major mass spectrum fragments, $\delta^{13}C$ values, and tentative identifications are presented in Appendix A, however only compounds with potential for source apportionment are discussed.

3.2 Results

3.2.1 Quantification

Ten compounds were quantified: benzene, toluene, ethyl benzene, m-xylene, o-xylene, p-xylene, propene, 1-butene, 1-pentene, and 1-hexene. None of these compounds was found in one of the control site samples (Control 2), the new canister sample, or upwind sample. Propene and 1-hexene were not found in any of the samples, and will not be discussed further.

One challenge of the sampling method used in this study is that the concentration of contaminants from the natural gas processing facilities changes with sampling distance from the facility. Because of this, comparison of raw concentrations is not very useful. Instead, the concentration of each contaminant measured has been placed in a ratio relative to the total concentration of all contaminants measured, similar to Scheff *et al.* (1989).

Ideally, the source profile would remain constant over time, enabling it alone to be used as a fingerprint of each plant. Plant 4 was sampled three times: July 2002 during the day from the ground, early December 2002 during the night from the ground, and mid-December 2002 during the day from a helicopter. As all three plant samples were taken at different distances from the flare stack, again the ratio of individual contaminants to total quantified hydrocarbon concentration is most useful and can verify whether ratios of contaminants change over time, assuming that all dominant hydrocarbon species

measured originate from the plant and background contributions are constant. The results from the samples from Plant 4 are shown in Table 3.6. It can be seen that the ratio of each pollutant to the total concentration of pollutants varies by a maximum factor of 13, and the composition of pollutants from the plant over time is not consistent. In Table 3.6, for example, the 1-butene ratio was calculated by:

1-butene = [1-butene] ÷ ([1-butene] + [1-pentene] + [benzene] + [toluene] + [ethyl benzene] + [o-xylene] + [m-xylene] + [p-xylene])

Table 3.6: Ratio of pollutant concentration to total quantified pollutants, from Plant 4 during three different sampling occasions. (b.d. = below detection limit)

Ratio of pollutant concentration to total concentration of contaminants quantified	Plant 4 (Helicopter)	Plant 4 Day (Ground)	Plant 4 Night (Ground)	Maximum Variation Factor
1-Butene	b.d.	0.33	b.d.	n/a
1-Pentene	b.d.	0.044	0.57	13.0
Benzene	0.69	b.d.	0.19	3.6
Toluene	0.21	0.55	0.099	5.6
Ethyl benzene	b.d.	b.d.	0.045	n/a
o-Xylene	b.d.	b.d.	b.d.	n/a
m-Xylene	b.d.	b.d.	0.048	n/a
p-Xylene	0.10	0.074	0.055	1.8

Another ratio was applied to the measured pollutants, which placed the analytes in a ratio relative to all area counts measured by the GC-FID. This ratio would allow for comparison of all organic compounds in the sample relative to the analytes of interest, perhaps giving a more robust measure of source profile (Table 3.7). Although the ratios of pollutants still vary by a maximum factor of 5.7, this provides more consistent chemical profiles than the previous ratio. In Table 3.7, for example, the 1-butene ratio in this case was calculated by:

1-butene = (FID area of 1-butene peak) ÷ (total area counts detected by FID)

Table 3.7: Ratio of pollutant area counts to total area counts of all contaminants detected, from Plant 4 during three different sampling occasions. (b.d. = below detection limit)

Ratio of pollutant concentration to total concentration of all contaminants detected	Plant 4 (Helicopter)	Plant 4 Day (Ground)	Plant 4 Night (Ground)	Maximum Variation Factor
1-Butene	b.d.	0.0036	b.d.	n/a
1-Pentene	b.d.	0.0023	0.0049	2.2
Benzene	0.0072	b.d.	0.0028	2.6
Toluene	0.0036	0.0088	0.0016	5.7
Ethyl benzene	b.d.	b.d.	0.00068	n/a
o-Xylene	b.d.	b.d.	b.d.	n/a
m-Xylene	b.d.	b.d.	0.00070	n/a
p-Xylene	0.0025	0.0017	0.00071	3.5

Scheff *et al.* (1989) normalized source profiles to chosen fitting compounds (similar to Table 3.6), providing a better estimate of the source profile, and not of the source contribution to the total VOC composition of the atmosphere, including biogenic sources that vary seasonally and daily. We would expect that variation from values in Table 3.6 would vary less than those in Table 3.7 but this is not the case, possibly as a result of a small number of samples or negligible contribution from biogenic sources. Therefore, further ratios are expressed relative to total measured hydrocarbon contamination to provide a better estimate of the source profiles from each natural gas plant (suspected to be the dominant sources where the samples were taken).

The concentrations of all contaminants that were quantified are displayed in Table 3.8. All concentrations are below 1.5 ppbv. No toluene was found in Receptor 1 or Control 1, however the Receptor samples that contain toluene are within the ranges found at plant sites. 1-Pentene was found in 5 of 9 plant samples, as well as in one control site sample and one receptor site sample. Benzene was present in 5 of 9 plant samples, and in 3 of 4 receptor site samples. p-Xylene was found in 4 of 9 plant samples, in 3 of 4 receptor site samples, and in very small amounts at the control site.

Table 3.8: Concentrations of VOCs in all samples (b.d. = below detection limit)

Sample	1-Butene (ppbv)	1-Pentene (ppbv)	Benzene (ppbv)	Toluene (ppbv)	Ethyl Benzene (ppbv)	o-Xylene (ppbv)	m-Xylene (ppbv)	p-Xylene (ppbv)
Plant 1	b.d.	1.02	0.73	1.25	b.d.	b.d.	b.d.	0.51
Plant 2	b.d.	b.d.	0.023	0.13	b.d.	b.d.	b.d.	b.d.
Plant 3	b.d.	b.d.	b.d.	0.005	b.d.	b.d.	b.d.	b.d.
Plant 4 Helicopter	b.d.	b.d.	0.28	0.087	b.d.	b.d.	b.d.	0.043
Plant 4 Ground (Day)	0.75	0.10	b.d.	1.24	b.d.	b.d.	b.d.	0.17
Plant 4 Ground (Night)	b.d.	0.82	0.27	0.14	0.065	b.d.	0.070	0.080
Plant 5	b.d.	b.d.	b.d.	0.12	b.d.	b.d.	b.d.	b.d.
Plant 6	b.d.	0.33	b.d.	0.14	b.d.	b.d.	b.d.	b.d.
Plant 7	b.d.	0.57	0.023	0.066	b.d.	b.d.	b.d.	b.d.
Control 1	b.d.	0.13	b.d.	b.d.	b.d.	b.d.	b.d.	0.005
Receptor 1	b.d.	b.d.	b.d.	b.d.	0.13	b.d.	b.d.	b.d.
Receptor 2	0.44	b.d.	0.11	0.30	0.13	0.073	0.076	0.11
Receptor 3	0.35	b.d.	0.41	0.51	0.12	0.10	0.24	0.21
Receptor 4	b.d.	0.10	0.11	0.17	b.d.	0.061	b.d.	0.16

Similar to what was seen at Plant 4, the ratios of pollutants to total contaminants measured at all sites are different (Table 3.9). As the chemical profile of Plant 4 varied over time, it is likely that the same inference can be extrapolated to other plants.

Table 3.9: Ratio of individual pollutants to total measured pollutants in all samples (b.d. = below detection limit)

Sample	1-Butene	1-Pentene	Benzene	Toluene	Ethyl Benzene	o-Xylene	m-Xylene	p-Xylene
Plant 1	b.d.	0.29	0.21	0.36	b.d.	b.d.	b.d.	0.15
Plant 2	b.d.	b.d.	0.15	0.85	b.d.	b.d.	b.d.	b.d.
Plant 3	b.d.	b.d.	b.d.	1.0	b.d.	b.d.	b.d.	b.d.
Plant 4 Helicopter	b.d.	b.d.	0.69	0.21	b.d.	b.d.	b.d.	0.10
Plant 4 Ground (Day)	0.33	0.044	b.d.	0.55	b.d.	b.d.	b.d.	0.074
Plant 4 Ground (Night)	b.d.	0.57	0.19	0.099	0.045	b.d.	0.048	0.055
Plant 5	b.d.	b.d.	b.d.	1.0	b.d.	b.d.	b.d.	b.d.
Plant 6	b.d.	0.71	b.d.	0.29	b.d.	b.d.	b.d.	b.d.
Plant 7	b.d.	0.87	0.034	0.10	b.d.	b.d.	b.d.	b.d.
Control 1	b.d.	0.96	b.d.	b.d.	b.d.	b.d.	b.d.	0.034
Receptor 1	b.d.	b.d.	b.d.	b.d.	1.0	b.d.	b.d.	b.d.
Receptor 2	0.36	b.d.	0.088	0.24	0.10	0.059	0.061	0.090
Receptor 3	0.18	b.d.	0.21	0.26	0.063	0.053	0.12	0.11
Receptor 4	b.d.	0.67	0.076	0.11	b.d.	0.041	b.d.	0.11

3.2.2 Isotopic Analysis

Because the chemical profile of plant emissions changes over time, concentration profiling alone is not ideal for source apportionment, therefore it may be more helpful to look at their isotope composition. For this, it is most useful to examine the isotope composition of compounds found in more than one plant sample to enable comparisons to be made. Unfortunately, toluene, which was present in all plant samples, was present at concentration levels below the limit of linearity of the CF-IRMS for all samples in the current configuration, therefore $\delta^{13}C$ values generated for those peaks are less reproducible, and as such, are not reported. Also, although isotopic data were collected

reproducible, and as such, are not reported. Also, although isotopic data were collected for Receptor 3 on two separate occasions, the mass spectral files failed to be saved by the computer both times, therefore Receptor 3 will be disregarded as identification of compounds would be speculation.

Compound 1 was found in only two plant samples, differing by a $\delta^{13}C$ value of 2.7‰ (Figure 3.4). Identification of this compound with the spectral data available was not possible, but it should boil at a temperature lower than 36°C.

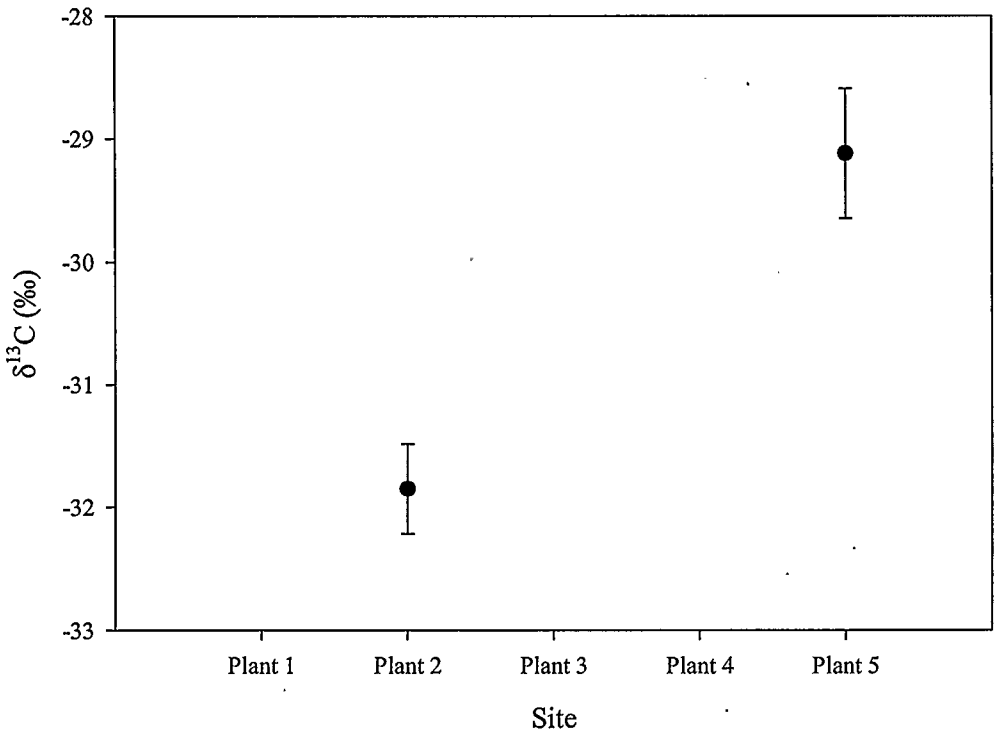

Figure 3.4: $\delta^{13}C$ values (‰) Compound 1, $\pm$ standard deviation

Compound 3 was found in all helicopter samples of gas plants, and had $\delta^{13}C$ values that ranged over 8.0‰ (Figure 3.5). However, it was not found in receptor site, control site, or upwind helicopter samples. Despite relatively large uncertainty provided by analyzing the sample from Plant 6 twice, there still appears to be significant

differences in isotopic composition between plants, particularly between Plants 1 and 7. Compound 3 was tentatively identified to be isopentane (CAS 78-78-4) or 2-methyl-2-propen-1-ol (CAS 513-42-8), but both of these possibilities were discarded due to their boiling points (30°C and 114°C, respectively). The mass spectrum indicates that Compound 3 likely contains 5 carbon atoms (molecular weight 72 g/mol), and boils between approximately 36 and 69°C.

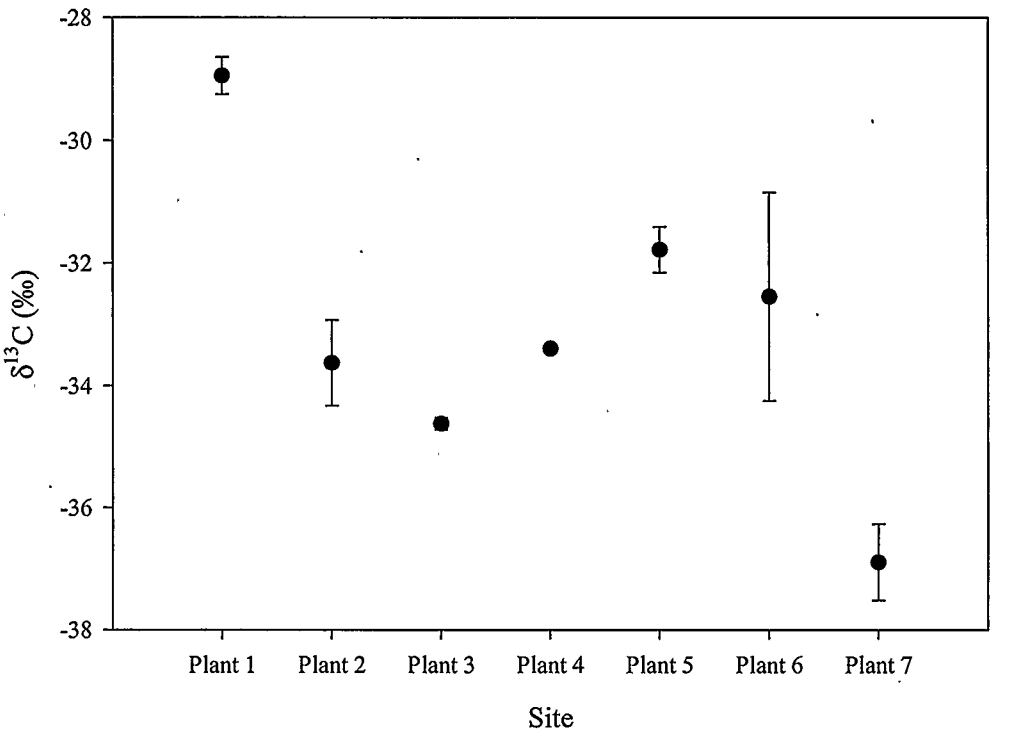

Figure 3.5: $\delta^{13}C$ values (‰) of Compound 3, $\pm$ standard deviation.

Compound 7 may also be useful for distinguishing between multiple natural gas processing facilities, as it is present in samples from four different gas plants. However, the $\delta^{13}C$ range of this compound is only 2.4‰ (Figure 3.6), so it may not be as useful given present limitations of instrument reproducibility. Compound 7 was tentatively identified as 5-methyl-1-hexene (CAS 3524-73-0).

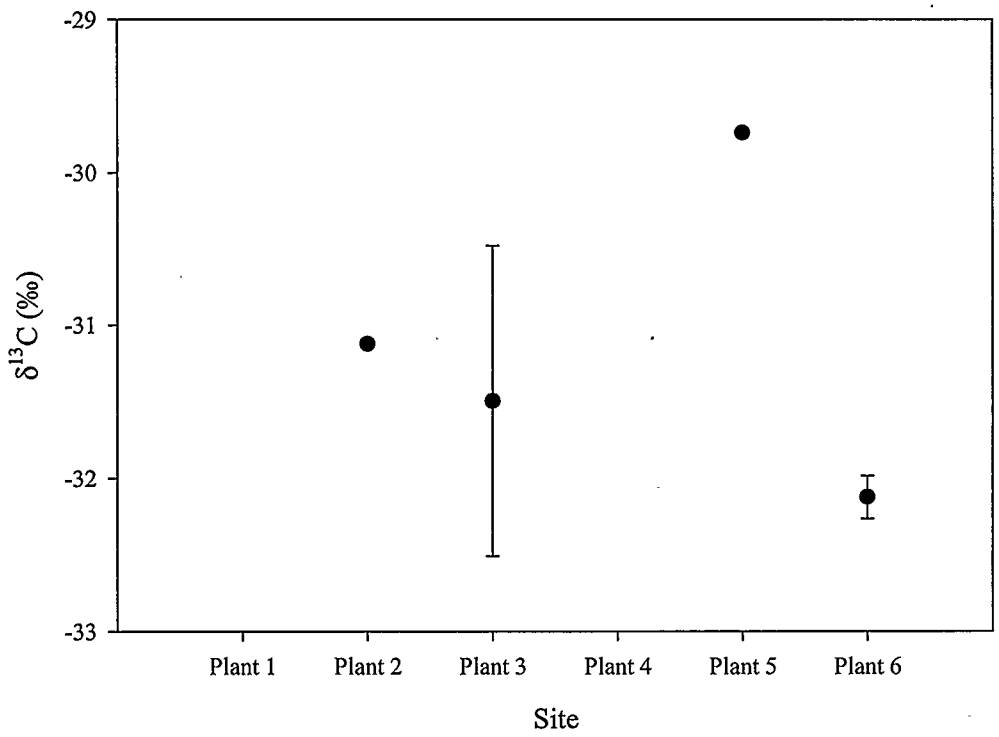

Figure 3.6: $\delta^{13}C$ values (‰) of Compound 7, $\pm$ standard deviation.

Compound 11 may be valuable for source apportionment, as it was present at all seven gas plants, and ranges in $\delta^{13}C$ over 5.0‰ (Figure 3.7). This compound was tentatively identified based on boiling point and fragmentation pattern to be 1-butyl nitrite (CAS 544-16-1) or 2-methyl-1-hexene (CAS 6094-02-6). Compound 11 is also isotopically light, with $\delta^{13}C$ values ranging between –36‰ and -42‰.

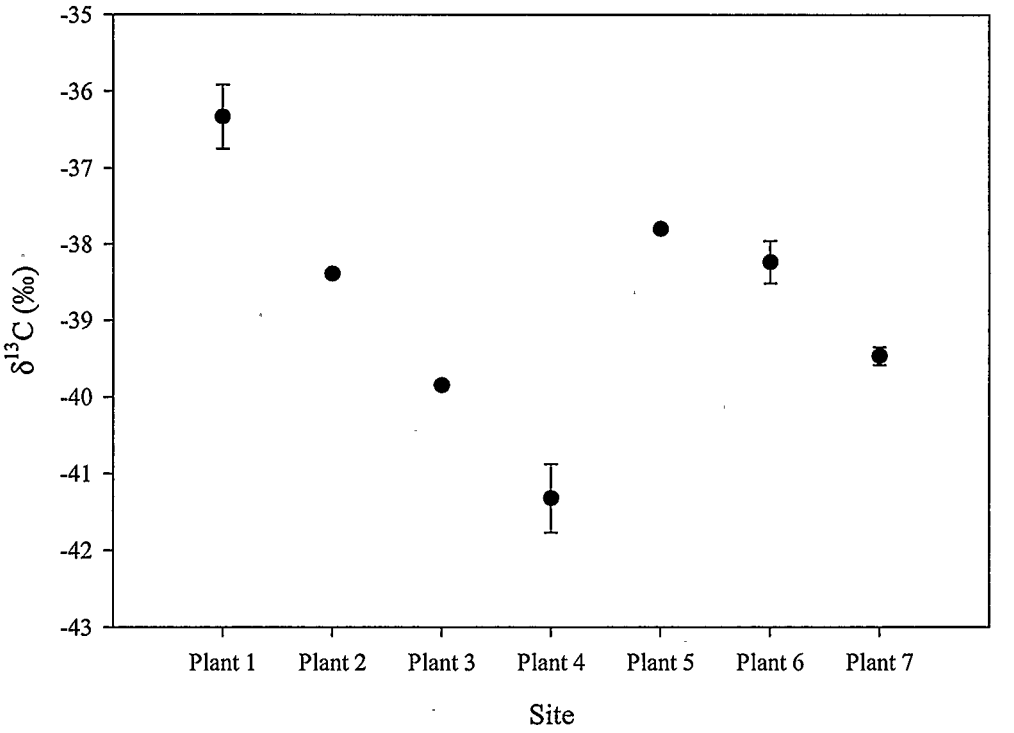

Figure 3.7: $\delta^{13}C$ values (‰) of Compound 11, $\pm$ standard deviation.

Compounds 13a and 13b were found in multiple samples, with nearly identical fragmentation patterns, but Compound 13a eluted nine minutes prior to Compound 13b. Compound 13a was found in five plant samples and one receptor site sample, with a $\delta^{13}C$ range of 1.8‰ (Figure 3.8). Compound 13b was found in one plant sample and one receptor sample, with a $\delta^{13}C$ difference between the two samples of 7.2‰ (Figure 3.9). Without any possible indication as to why there would be a nearly ten minute shift in retention time, one must conclude that they are indeed different compounds, despite their similar fragmentation patterns. These have been tentatively identified as 1-isothiocyanato butane (CAS 592-82-5), diethylacetamide (CAS 685-91-6), or 4-ethyl-morpholine (CAS 100-74-3).

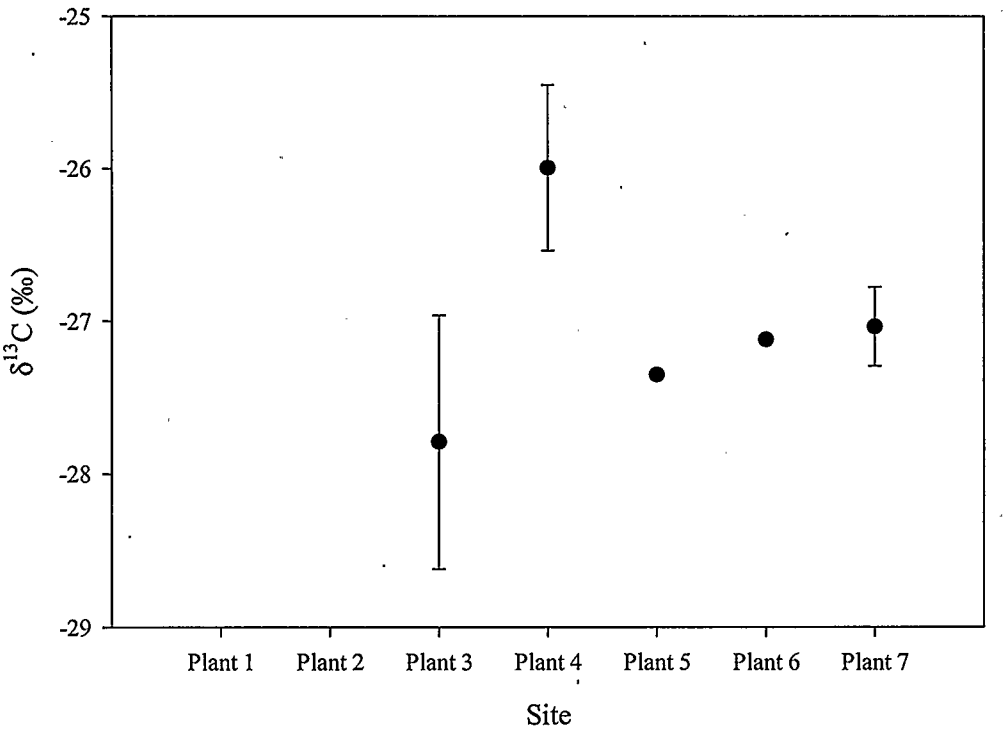

Figure 3.8: $\delta^{13}C$ values (‰) of Compound 13a, $\pm$ standard deviation.

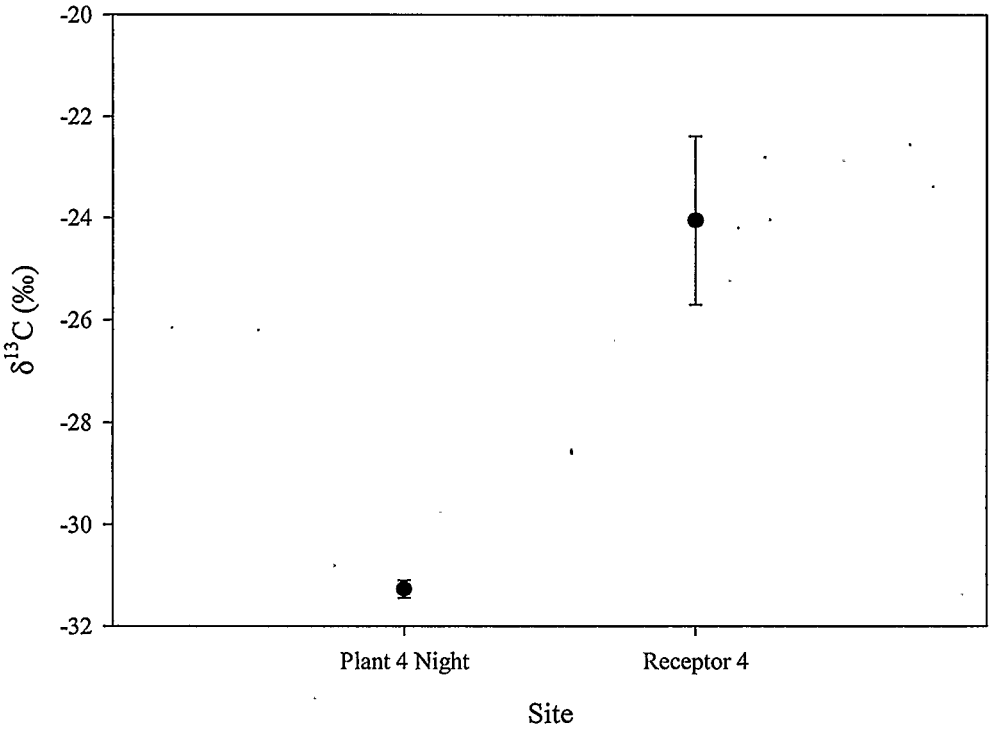

Figure 3.9: $\delta^{13}C$ values (‰) of Compound 13b, $\pm$ standard deviation.

Compound 15 may be a useful compound, as it was found in five of seven plant samples, and had $\delta^{13}C$ values ranging over 5.3‰ (Figure 3.10). It was tentatively identified as 1-butoxy-2-methoxyethane (CAS 13343-98-1).

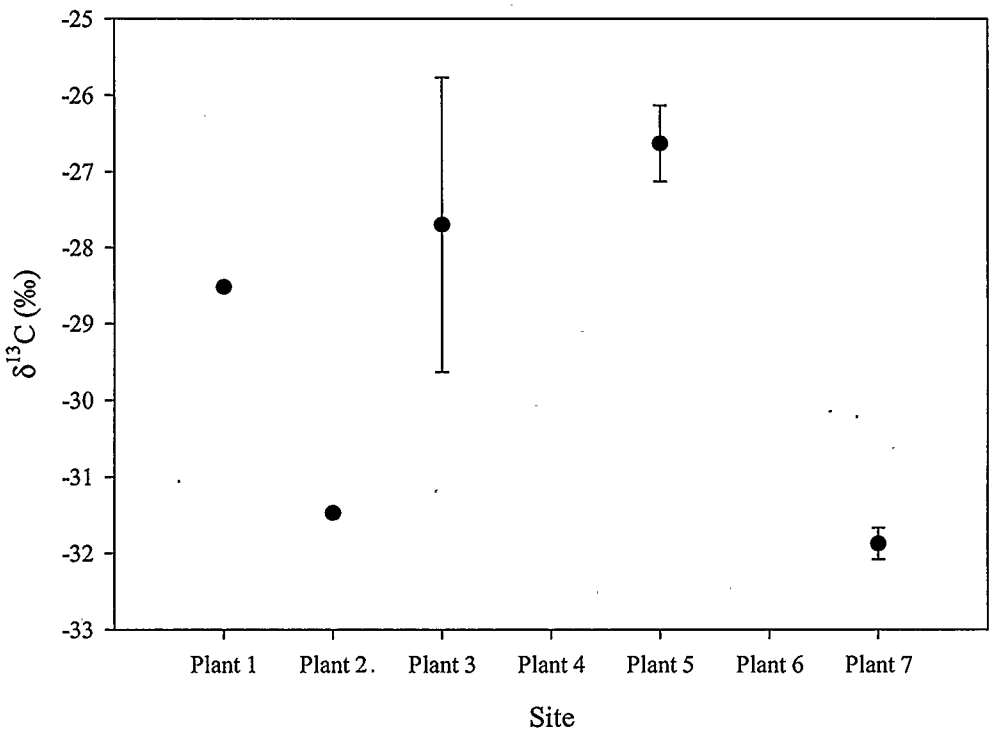

Figure 3.10: $\delta^{13}C$ values (‰) of Compound 15, $\pm$ standard deviation

Compound 17 was also found in three of seven plant samples, and had $\delta^{13}C$ values that ranged over 8.5‰ (Figure 3.11). Compound 17 was tentatively identified as 1-propoxy-butane (CAS 3073-92-5), but this identification is incorrect as 1-propoxy-butane would likely elute earlier based upon its low boiling point. The unknown compound likely contains seven carbon atoms, with a molecular weight of 100 g/mol.

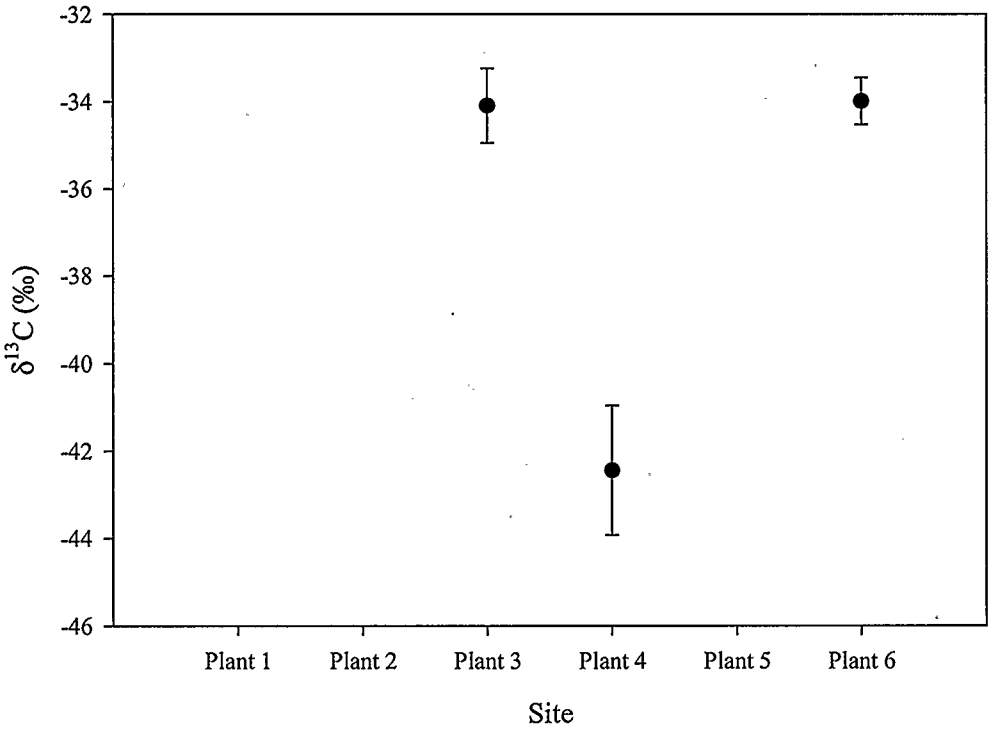

Figure 3.11: $\delta^{13}C$ values (‰) of Compound 17, $\pm$ standard deviation.

Compound 20 may be useful, as it is found in three of seven plant samples, but its $\delta^{13}C$ values only range over 3.5‰ (Figure 3.12). Compound 20 was tentatively identified by the libraries to be 2-ethyl-1-hexanethiol (CAS 7341-17-5), 2-ethyl-1-hexanol (CAS 104-76-7), or 2,4-dimethyl-1-decene (CAS 55170-80-4).

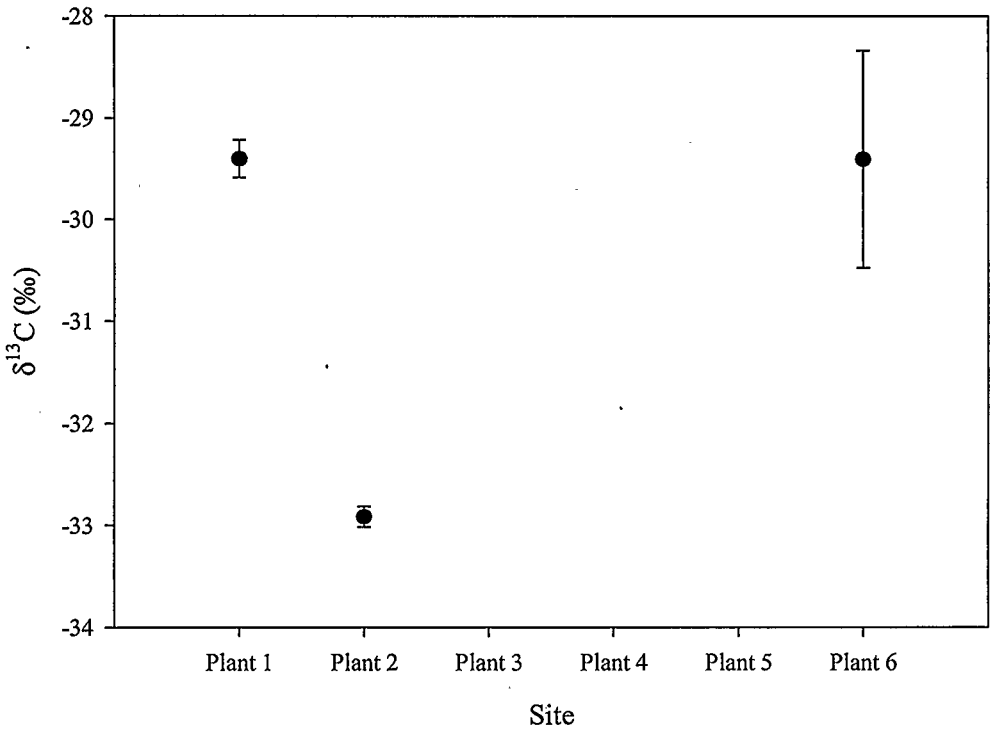

Figure 3.12: $\delta^{13}C$ values (‰) of Compound 20, $\pm$ standard deviation.

An interesting compound is Compound 21, which is found in both ground samples from Plant 4, two receptor site samples, Control 1 sample, and upwind control sample (Figure 3.13). Its presence in both helicopter and control samples indicates that it is a compound not produced by the natural gas processing facilities, and may be of biogenic origin. Its $\delta^{13}C$ values range over 3.5‰ and it was tentatively identified by the library to be 2-butoxy ethanol (CAS 111-76-2).

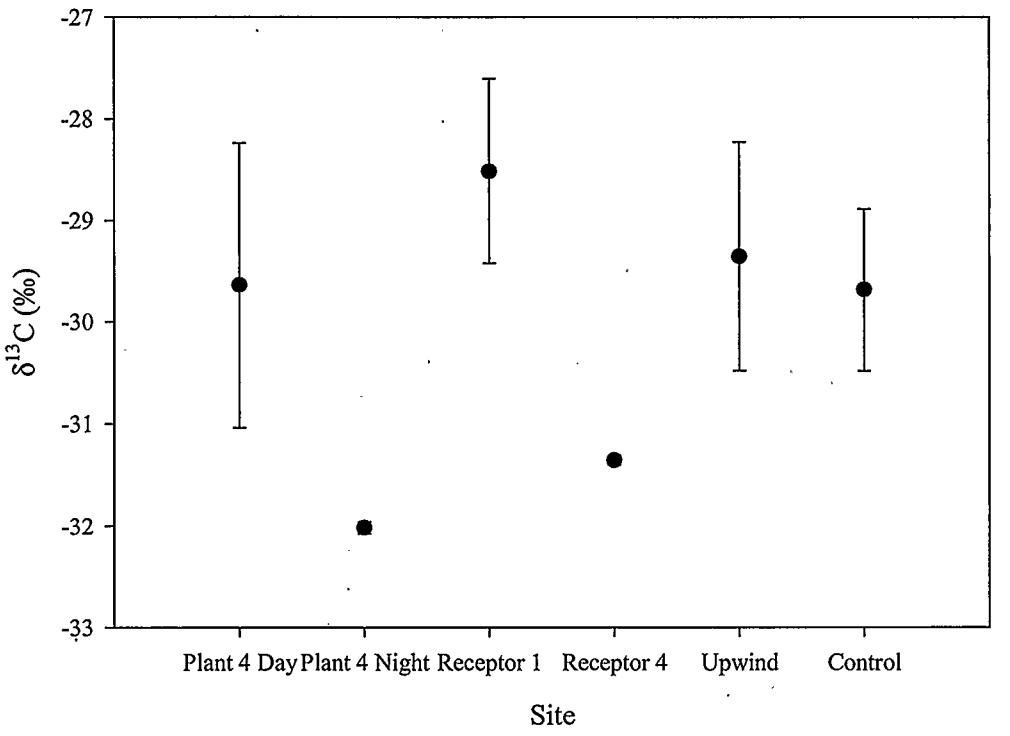

Figure 3.13: $\delta^{13}C$ values (‰) of Compound 21, $\pm$ standard deviation.

If natural gas reservoirs are isotopically unique, trends in $\delta^{13}C$ values would be expected between gas plants. The expectation would not be that all compounds from one plant would be isotopically identical, but that their isotopic compositions should remain consistent relative to the other plants. The relative isotopic values of the pollutants emitted from the natural gas plants show the same general relative trend of $\delta^{13}C$ values for six of eight compounds found at more than one plant (Figure 3.14). Emissions from Plant 7 are typically the lightest isotopically, and the same compounds from Plant 1 are typically the heaviest. Other plants produce emissions with intermediate $\delta^{13}C$ values. This trend is seen with Compounds 1, 3, 7, 11, 15, and 20, and is demonstrated by positive slopes with the same relative order of gas plants in Figure 3.13. Although there

are some small deviations from the expected trends, the order of $\delta^{13}C$ values from the plants generally stays the same.

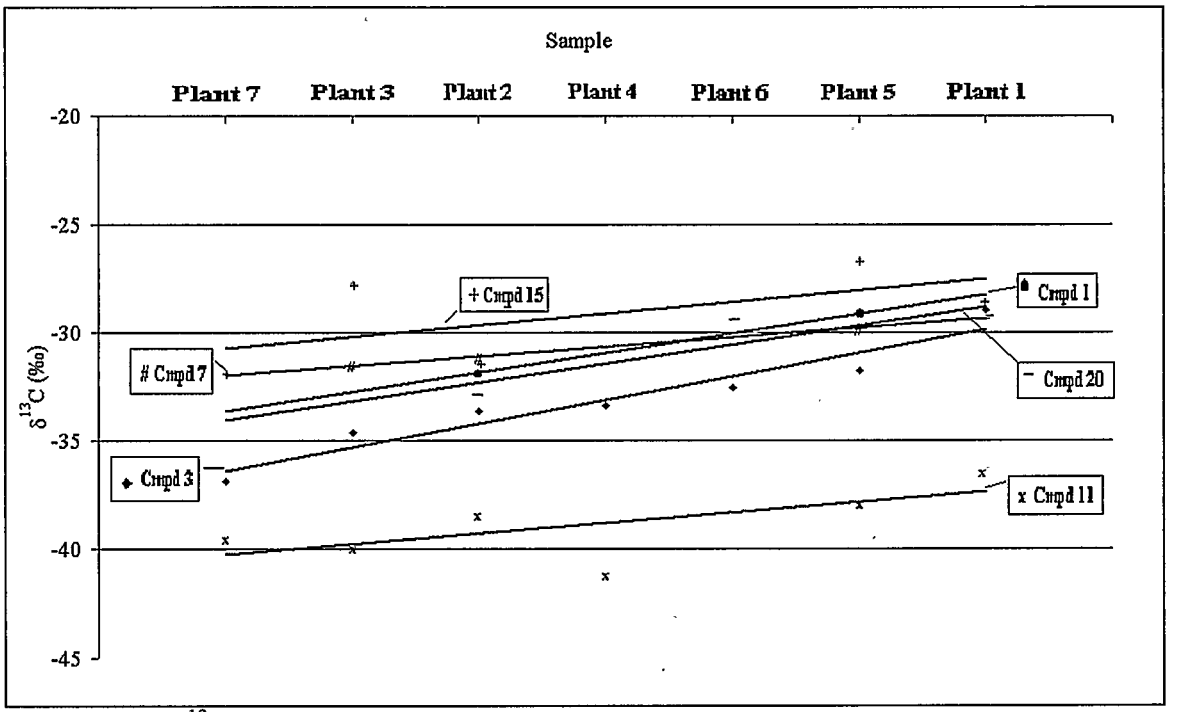

Figure 3.14: $\delta^{13}C$ values (‰) of Compounds 1, 3, 7, 11, 15 and 20, with plants showing similar isotopic trends relative to each other

The two exceptions to the above trend are with Compounds 13a and 17. Compound 13a does not show a significant trend, demonstrated by a slope of nearly zero (Figure 3.15). Compound 17 shows the reverse trend as was seen in Figure 3.14, with a negative slope while maintaining the same relative order of plants.

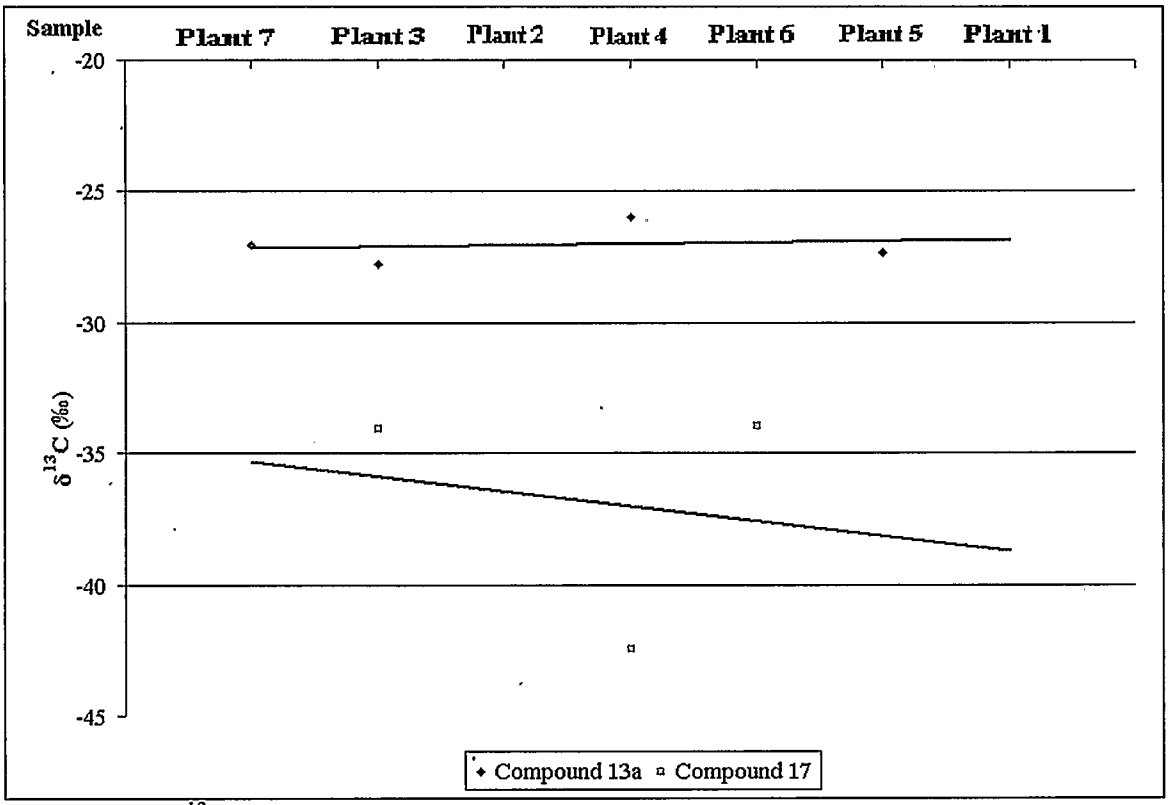

Figure 3.15: $\delta^{13}C$ values (‰) of Compounds 13a and 17 shown with same relative order of plants as those shown in Figure 3.14

3.3 Discussion

3.3.1 Quantification

Source profiling using ratios of compounds can be used with chemical mass balance models and it is common to ratio the concentration of one pollutant to the concentration of all pollutants measured (e.g. Scheff *et al.*, 1989). A combination of ratios of multiple fitting compounds often generates a unique profile, or fingerprint, for a particular source, and multiple species' abundance in the source emissions can provide a unique source profile (Conner *et al.*, 1995). In an ideal case, there is one dominant source at the location where measurements are being made, and this dominant source generates a unique profile from background and other minor sources present. Source profiling has been applied to a variety of VOC sources, including vehicle emissions,

gasoline vapour, refinery emissions, dry cleaning, and auto painting (Scheff *et al.*, 1989). To our knowledge, it has not yet been used to distinguish individual natural gas plants from one another. The concentrations of individual pollutants relative to the total measured hydrocarbon concentration were not consistent over samples taken at different times at Plant 4. This indicates that source profiling using these fitting compounds for identification of individual gas plants is not possible because emissions from the plants and/or contribution from background sources vary greatly, and cannot be assumed to be consistent over time. However, different, more appropriate fitting compounds may be emitted from the natural gas plants that could generate a unique source profile for distinguishing between facilities. There are a number of factors that may cause the chemical composition of plant emissions to change over time, as was the case at Plant 4. Changes in inlet gas composition to the gas plant can occur if there is the addition or removal of a well to the inlet gas stream, flaring from different sections of the plant, or daily variability in routine fugitive emissions.

The atmospheric lifetimes of VOCs are typically on the order of a few hours to weeks (Table 3.10). These atmospheric lifetimes greatly exceed the time required to transport VOCs to the receptor site from the sources in this study. Travel time from the plants to the receptor site was approximately 1 to 3 hours, based upon distances from the receptor site to the plants (between 20 and 70 km) and the average wind speed measured at the receptor site (approximately 27 km/h). There are also a number of factors that can affect VOC behaviour in the troposphere by manipulating VOC removal rates and mechanisms. Local meteorological conditions, including temperature, humidity, sunlight intensity, and atmospheric pressure, can influence the behaviour of VOCs in the

atmosphere. Tropospheric concentrations of compounds known to react with VOCs (hydroxyl radicals, NO_x radicals, and ground-level O_3) can also vary daily and seasonally. Hydroxyl radical reactions are the most important removal mechanism for VOCs (Atkinson, 2000), and tend to dominate VOC removal from the troposphere. Atmospheric lifetimes of VOCs vary, with removal of unsaturated hydrocarbons tending to occur faster than saturated hydrocarbons.

Table 3.10: Atmospheric lifetimes of VOCs given in the literature

Compound	Atmospheric Lifetime	Reference
n-Butane	11 hours	Atkinson and Carter, 1984
Toluene	2.4 days	Prinn *et al.*, 1992
Benzene	12 days	Prinn *et al.*, 1992
Phenol	23 days	Atkinson and Carter, 1984

The presence of toluene in every natural gas plant sample appears promising for source apportionment, however it is present in similar quantities at the receptor site. High concentrations of toluene in two samples from the receptor site suggest that toluene is a poor candidate for source identification using chemical profiling alone because sources in the airshed additional to the natural gas plants are present. This is problematic because there are many sources of toluene in the atmosphere, and toluene is not solely produced by natural gas processing facilities. Other sources of toluene include vehicular traffic (Lau and Chan, 2003) and wood combustion (Hedberg *et al.*, 2002). As a result, toluene is often the most abundant aromatic compound in urban air (Bahrami, 2001; Singh, 1995), which also tends to be dominated by emissions from combustion processes. Toluene present at the control site indicates that the control site was not immune to

petroleum use impacts, with likely sources including a generator that was operating on site, wood combustion, or vehicular traffic along Highway 11.

The presence of 1-pentene in similar concentrations at the receptor, control, and plant sites indicates that it is likely not a product solely of plant processing. The presence of o-xylene in receptor site samples but not in plant emissions indicate that it is not likely a product of plant activities, and some second source must be investigated. The presence of ethyl benzene, 1-butene, and m-xylene at Plant 4 and in receptor samples indicates that they may be valuable source apportionment tools, but not for all plants. However, none of the compounds quantified was present in adequate quantities to characterize isotopically, and in order to do so, a larger sample volume must be analyzed to obtain sufficient IRMS response. If natural gas plants produce isotopically distinct toluene and benzene emissions, this may be particularly useful because they are comparatively stable within the atmosphere and are present in multiple plant samples. Our findings are consistent with those in the literature: Kalabokas *et al.* (2001) found elevated levels of benzene (averaging 0.81 ppbv) and toluene (averaging 1.67 ppbv) in the air surrounding a refinery, toluene was found by Booher and Janke (1997) in direct emissions from petroleum hydrocarbon fires, and Strosher (1996) found that toluene, benzene, o-xylene, m-xylene, and p-xylene were emitted from natural gas flares.

Tentatively identified compounds have been compared to Strosher (1996), and no matches between his findings and the findings in this thesis were found. Strosher (1996) found primarily aromatic species, with some cyclic alkanes and dimethyl alkenes. Strosher (1996) tested flares in the field, but they were oilfield batteries, which are much more likely to contain heavier source hydrocarbons. Sampling methods also differed, as

Strosher (1996) used Teflon bags and adsorbants to collect volatile samples. Natural gas flares were tested, but only in a laboratory setting, and all samples were taken much closer to the flare itself, as opposed to in the plume. The main reaction mechanism of hydrocarbons in the flame is hypothesized to be pyrolytic (thermal decomposition) (Edwards, 1974).

Although the chemical compositions of emissions from natural gas facilities vary over time, it may be possible to identify the sources of emissions based on their isotopic compositions if they can be shown to be isotopically unique and isotopically stable over time. Clearly the source profiles differ between different plants. However, as evidenced by Plant 4, differences in emission composition are not exclusively due to differences in plant design and/or source reservoirs, but likely are due to variability in plant operating conditions discussed above. However, if the isotopic compositions of these emissions remain constant despite variability in operating conditions, profiling of natural gas plant emissions using isotopic compositions of VOCs may be useful.

3.3.2 Isotopic Analysis

Isotopes can be used to distinguish between emissions where multiple sources emit the same, but isotopically distinct, compound. In order for source apportionment using isotopes to be a useful technique, a number of conditions must be satisfied:

1.) compounds must be present in samples in high enough quantities to be integrated reliably by CF-IRMS,

2.) compounds must be present in multiple plant samples,

3.) compounds must show significant isotopic differences between plants and this range in $\delta^{13}C$ must be large enough to be distinguished from instrument variability,

4.) the compounds must not undergo chemical reactions in the atmosphere that significantly affect their carbon isotopic composition, and

5.) if the same compounds are present at high concentrations at the control site, they must have different isotopic composition than those at the natural gas plants.

Relatively high variability in the isotopic compositions between duplicate runs of standards and samples is evident in this study (average standard deviation = 0.5‰ over all sample compounds, n = 50), although standard deviations presented here are similar to those presented by Rudolph *et al.* (2002), which range from < 0.1‰ to 6.5‰. In this study, the differences in isotopic composition of pollutants between sites are often similar in magnitude to instrument variability. This is limiting because only sources with isotopic compositions differing by greater than 3.0‰ (twice the average difference between analytical duplicates) were able to be distinguished from one another with confidence with the limitations of the GC-MS-IRMS set-up used here. In these cases, the use of more than one element to isotopically resolve different sources may be useful (e.g. ^{1}H and ^{2}H). Measuring isotopic fractionations involving carbon are challenging, as they are often mass dependent, and the relative mass difference between ^{12}C and ^{13}C is not as large as that with ^{1}H and ^{2}H, systematically resulting in less isotopic fractionation with carbon than hydrogen (less ‰ difference). Because of this, source apportionment using hydrogen isotopes has recently been attempted (Pond *et al.*, 2002).

Trends exist within the isotopic data when comparing different plants to one another. The $\delta^{13}C$ values for Compounds 3, 11, and 15 are isotopically heavier at Plant 1 than Plant 7, with $\delta^{13}C$ differences ranging between 1.8‰ and 8.0‰. Similarly, the $\delta^{13}C$ values of compounds found in emissions from both Plant 2 and Plant 5 consistently show that Plant 2 is isotopically heavier than Plant 5. This is shown with Compounds 1, 3, 7, 11, and 15, with $\delta^{13}C$ differences ranging between 0.6‰ and 4.8‰.

Compound 11 is isotopically light, with $\delta^{13}C$ values ranging from –36.3‰ to –41.3‰. For comparison, the $\delta^{13}C$ values of methane present in natural gas reservoirs (not produced bacterially) typically range from –35.1‰ to –47.2‰ (Stahl and Carey, 1975). The isotopically light $\delta^{13}C$ values characteristic of methane are similar to those $\delta^{13}C$ values found for Compound 11, which contains significantly more carbon atoms than methane. Compounds that have a lower molecular weight tend to fractionate more significantly than those with higher molecular weights, and as such, with increasing molecular weight, the carbon isotopic composition typically approaches that of the source material (James, 1990). Compound 11 is the only compound that is unusually isotopically light and this characteristic of Compound 11 is seen in all plant samples. Therefore, the isotopic lightness of Compound 11 is not likely due to differences in the sources of organic matter in the reservoirs (because the other compounds found do not show this trend), and Compound 11 instead may be the product of a thermal cracking reaction that takes place in the reservoir or the gas plant, resulting in an isotopically light product.

Many compounds were present at high abundance at the source locations, but not present at the receptor site at detectable levels. Compounds found at plant sites are

diluted and dispersed during transport through the atmosphere to levels below the current detection limits of the instruments used in this study. However, there are other factors that may contribute, in part, to lower concentrations at the receptor site. Without conclusive identifications of compounds, speculation on their removal mechanism from the atmosphere would be premature, although reactions with the hydroxyl radical tend to be the dominant removal mechanism for VOCs (Atkinson, 1995). Compounds may also undergo condensation and coagulation processes, resulting in secondary aerosol formation, and removal of these hydrocarbons from the gaseous phase.

The presence of Compounds 1, 3, 7, 11, 15, 17, and 20 at plant sites but not at the receptor site indicates that some atmospheric removal or dilution mechanism is occurring. Collecting and analyzing larger sample volumes may allow for detection of these compounds at the receptor site in future. In comparison, Compounds 13a and 13b are present at the plant sites as well as at the receptor, and the $\delta^{13}C$ value of Compound 13a at the receptor site is intermediate of the $\delta^{13}C$ values of the plant sites. This is an interesting finding, because it may indicate that mixing of Compound 13a during atmospheric transport has resulted in a $\delta^{13}C$ value intermediate of the natural gas plants which may have produced it.

The understanding of the atmospheric chemistry of VOCs in the troposphere is improving, however the atmospheric lifetimes of many compounds are still unknown. Any chemical reaction of VOCs in the atmosphere creates the potential for isotopic fractionation. As a result, the extent of isotopic fractionation with VOC atmospheric reactions must be examined to identify if differences present in natural gas plant isotopic compositions of compounds found in this study are still present after atmospheric

transport. Varying meteorological conditions must be taken into consideration. It is possible that atmospheric reactions may significantly affect the isotopic compositions of compounds, although the relatively short transfer time to the site in this case may make isotopic fractionations due to atmospheric transport negligible. Rudolph *et al.* (2000) found that kinetic isotope effects of unsaturated hydrocarbons are higher than those of saturated hydrocarbons with the same number of carbon molecules, by an average factor of three, with kinetic isotope effects for saturated hydrocarbons ranging between 1 and 4‰. Rudolph *et al.* (2000) also found that kinetic isotope effects for unsaturated hydrocarbons (e.g. alkenes, benzene) were substantial, in some cases exceeding 10‰. Regardless, given that the isotopic differences between natural gas processing facilities in this study are not even 4‰ in many cases, isotopic fractionation as a result of atmospheric transport may be significant, resulting in enrichment of the heavy isotope in compounds at the receptor site.

CHAPTER 4: AEROSOLS

4.1 Methods

4.1.1 Filter extraction

Organic aerosols were extracted from filters using a method developed by Zheng *et al.* (1997). Filters were torn into pieces and placed into 270 ml Qorpak straight-sided round borosilicate bottles with Teflon-lined caps. A recovery standard, o-terphenyl (Accustandard, 2.0 mg/ml in acetone) was diluted to 500 μg/ml in isooctane and 10 μl added to each sample extraction to monitor the extraction efficiency of each sample in case of sample loss (e.g. spillage), for a final recovery standard concentration of 10 μg/ml in 0.5 ml. The filter extraction procedure consisted of three ultrasonic agitations, each utilizing 200 ml of dichloromethane (Omnisolv), and subsequent concentration of the sample by rotary evaporation using a water bath maintained at approximately 30°C. The samples were then reconstituted in 500 μl isooctane (EMD Chemicals Inc.). Extraction efficiencies of different compounds varied based largely on volatility. Extraction of the more volatile hydrocarbons was not a priority because the sampling method lost these compounds prior to extraction. Breakthrough of the more volatile species through quartz filters is common, particularly during warmer summer months (Mader and Pankow, 2001). Recovery efficiencies ("raw") and recovery efficiencies normalized relative to the recovery standard ("normalized") are displayed in Table 4.1 for n-alkanes and Table 4.2 for PAHs (polycyclic aromatic hydrocarbons).

Table 4.1: Extraction efficiencies of n-alkane standards from quartz aerosol filters (n = 3)

Compound	Retention Time (minutes)	Raw Extraction Efficiency (%)	Normalized Extraction Efficiency (%)	Standard Deviation (%)
Undecane (C11)	21.38	14	15	20
Dodecane (C12)	25.94	20	22	26
Tridecane (C13)	30.41	31	34	29
Tetradecane (C14)	34.71	46	52	19
Pentadecane (C15)	38.82	58	66	6
Hexadecane (C16)	42.78	64	72	1
Heptadecane (C17)	46.52	67	76	3
Pristane	46.96	66	76	3
Phytane	50.64	68	77	4
Nonadecane (C19)	53.50	68	78	3
Eicosane (C20)	56.72	69	79	3
Heneicosane (C21)	59.86	69	79	3
Docosane (C22)	62.81	70	80	3
Tricosane (C23)	65.66	66	75	3
Tetracosane (C24)	68.51	68	78	4
Pentacosane (C25)	71.70	70	80	6
Hexacosane (C26)	75.36	69	79	4
Heptacosane (C27)	79.76	69	79	4
Octacosane (C28)	84.99	70	80	4
Nonacosane (C29)	91.30	70	80	3
Triacontane (C30)	99.00	69	79	3
Hentriacontane (C31)	108.43	87	99	29

Table 4.2: Extraction efficiencies of PAH standards from quartz aerosol filters (n = 5)

Compound	Retention Time (minutes)	Raw Extraction Efficiency (%)	Normalized Extraction Efficiency (%)	Standard Deviation (%)
Naphthalene	25.19	3	3	5
Acenaphthylene	36.92	18	28	14
Acenaphthene	38.37	24	36	18
Fluorene	42.36	46	60	24
Phenanthrene	49.76	59	83	8
Fluoranthene	59.26	65	78	3
Pyrene	60.97	67	94	6
Benzo(a)anthracene	70.95	63	87	6
Chrysene	71.27	63	86	8
Benzo(k)fluoranthene	84.20	68	94	5
Benzo(b)fluoranthene	84.55	68	94	5
Benzo(a)pyrene	89.07	58	79	14
Benzo(g,h,i)perylene	113.48	81	104	21
Dibenz(a,h)anthracene	114.02	64	79	N/A
Indeno(1,2,3-c,d)pyrene	120.16	185	271	5

The recovery efficiencies for analytes did not become semi-quantitative (> 50%) until pentadecane (C15), so this was used as the starting point for quantification and identification. Coelution of anthracene and octadecane made quantification using the GC-FID difficult, therefore confirmation was done using the GC-MS (gas chromatograph coupled with a mass spectrometer) to identify which compound was present. Indeno(1,2,3-cd)pyrene was not quantified due to coextraction of an unidentified contaminant during filter extractions, resulting in recovery efficiencies greater than one hundred percent.

4.1.2 Aerosol quantification

Quantification of PAHs and n-alkanes was performed using a Varian 3800 gas chromatograph equipped with a flame ionization detector and CP-8410 Autosampler. The column used was a Varian CP-Sil5-CB WCOT (wall coated open tubular) column

with a dimethylpolysiloxane non-polar stationary phase. The column was 60 meters in length, with an inside diameter of 0.32 mm and a stationary phase of 1 μm thickness.

The autosampler program consisted of two pre-injection solvent flushes and three post-injection solvent flushes of the syringe with both dichloromethane and isooctane. One μl of isooctane (solvent plug) and 1 μl of internal standard solution were automatically injected along with 1 μl of sample (splitless injection). Hexyl benzene (Supelco) diluted to approximately 6 μg/ml in isooctane acted as an internal standard to compensate for instrument variability. The injection port and detector were held at 300°C, and column flow was maintained at 1.0 ml/minute. The oven temperature started at 90°C and was ramped at 3°C per minute until it reached 290°C, where it was held for 60 minutes, for a total run time of approximately 127 minutes.

Calibration used PAH standards purchased from Supelco (TCL Polynuclear Aromatic Hydrocarbons at 2000 μg/ml) and n-alkane standards purchased from Accustandard (Multistate hydrocarbon window defining standard, 500 μg/ml, containing C8-C40 n-alkanes, pristane, and phytane). The results for PAH and n-alkane calibrations are presented in Tables 4.3 and 4.4 respectively. For PAH calibration, concentration levels of approximately 0.8, 4, 20, 50, and 100 μg/ml were used. For n-alkane calibration, concentration levels of approximately 1, 10, 40, and 100 μg/ml were used. N-alkanes eluting past hentriacontane (C31) were not calibrated, as the retention times were greater than two hours and analyte responses were poor.

Table 4.3: Calibration information for PAH calibration of 16 analytes in isooctane

Compound	Coefficient of Determination of Calibration Curve (r^2)	Response Factor Relative Standard Deviation (%)	Lowest Calibration Concentration Detected (µg/ml)
Naphthalene	0.9887	7.8	0.8
Acenaphthylene	0.9902	7.1	0.8
Acenaphthene	0.9907	7.0	0.8
Fluorene	0.9895	7.5	0.8
Phenanthrene	0.9905	7.4	0.8
Anthracene	0.9892	7.8	0.8
Fluoranthene	0.9906	6.5	0.8
Pyrene	0.9912	6.4	0.8
Benzo(a)anthracene	0.9930	11. 6	0.8
Chrysene	0.9925	13.6	0.8
Benzo(k)fluoranthene	0.9881	11.3	4
Benzo(b)fluoranthene	0.9895	13.0	4
Benzo(a)pyrene	0.9881	12.2	4
Benzo(g,h,i)perylene	0.9912	30.0	4
Dibenzo(a,h)anthracene	0.9987	10.9	20
Indeno(1,2,3-cd)chrysene	0.9863	16.4	4

Table 4.4: Calibration information for n-alkane calibration of analytes in isooctane

Compound	Coefficient of Determination of Calibration Curve (r^2)	Response Factor Relative Standard Deviation (%)	Lowest Calibration Concentration Detected (µg/ml)
Pentadecane (C15)	0.9998	1.8	1
Hexadecane (C16)	0.9998	1.7	1
Heptadecane (C17)	0.9997	2.9	1
Pristane	0.9998	4.2	1
Octadecane (C18)	0.9999	1.6	1
Phytane	0.9998	2.2	1
Nonadecane (C19)	0.9996	4.2	1
Eicosane (C20)	0.9994	4.1	1
Heneicosane (C21)	0.9992	4.7	1
Docosane (C22)	0.9990	7.0	1
Tricosane (C23)	0.9989	4.0	1
Tetracosane (C24)	0.9987	6.8	1
Pentacosane (C25)	0.9989	11.9	1
Hexacosane (C26)	0.9986	8.0	1
Heptacosane (C27)	0.9985	7.8	1
Octacosane (C28)	0.9604	17.1	1
Nonacosane (C29)	0.9987	6.8	10
Triacontane (C30)	0.9978	9.7	10
Hentriacontane (C31)	0.9986	7.0	10

Blank runs were performed and were analyzed as part of quality assurance and quality control after each sample for the first day of runs. No carryover between runs was observed. After the first day of samples, blank runs were performed at the beginning and end of each day to ensure that a consistent baseline was maintained. Also, a 4 µg/ml standard PAH mixture was analyzed twice daily to ensure adequate response (within twenty percent) and to ensure that retention times relative to the calibration curve had not changed. In addition, performance of the internal standard was monitored for every run, and found to have a relative standard deviation of 14.3% (n = 20).

As an additional quality assurance check, a NIST standard reference material (SRM 1597) coal tar PAH mixture was purchased and analyzed using the GC-FID (Table 4.5). Generally, the SRM concentrations showed good agreement between certified

concentrations and GC-FID concentrations, with the exception of benzo(a)anthracene and benzo(g,h,i)perylene, which differed from the NIST certified concentration by 55% and 87% respectively. Concentration of benzo(a)anthracene is higher than the NIST standard due to coelution of an unknown compound, and benzo(g,h,i)perylene response is extremely poor following elution from the 60 meter GC column, resulting in poor quantitative results.

Table 4.5: Certified results from NIST SRM 1597 compared to GC-FID concentration findings; [a] Certified concentrations in mg/kg multiplied by density at 23°C (combined analytical results of GC and LC analyses, expressed as 2 standard deviations of the mean values of the two techniques); [b] Uncertified values provided by NIST (uncertified because they are not based on agreement from two independent methods)

Compound	Retention Time (minutes)	NIST Certified Concentration (µg/ml)[a]	GC-FID Concentration (µg/ml)	Difference (µg/ml)	% Difference
Naphthalene	25.19	1000 ± 50	1137	137	14
Acenaphthylene[b]	36.92	220	237	17	8
Fluorene[b]	42.36	120	132	12	10
Anthracene	50.14	87.4 ± 2.4	104	17	19
Phenanthrene	49.76	400 ± 4	448	48	12
Fluoranthene	59.26	278 ± 4	306	28	10
Pyrene	60.97	204 ± 3	259	55	27
Benzo(a)anthracene	70.95	85.3 ± 3.4	132	47	55
Chrysene	71.27	62.0 ± 1.1	85	23	37
Benzo(a)pyrene	89.07	82.9 ± 5.3	100	17	21
Benzo(ghi)perylene	113.48	46.5 ± 6.7	87	41	87
Indeno(1,2,3-cd)pyrene	120.16	52.1 ± 4.0	53	1	2

A total of four analytical duplicates were extracted, and the final concentration of analytes only differed on average by 0.89 µg/ml (standard deviation 1.12 µg/ml). The average concentration of analyte in samples was 5.1 µg/ml. One travel blank, two field blanks, and four lab blanks were extracted to determine whether sample preparation, handling, travel, exposure, or extraction introduced contaminants. PAH contamination was not found, however n-alkanes were found in significant amounts, constituting an

was not found, however n-alkanes were found in significant amounts, constituting an average of 47% of analytes quantified prior to blank subtractions. Consequently, all samples had the maximum contaminant concentrations subtracted (in units of μg/ml) prior to calculation of airborne concentrations (in units of ng/m^3). N-alkanes that were present as contaminants were: nonadecane, eicosane, heneicosane, docosane, tricosane, tetracosane, pentacosane, hexacosane, heptacosane, and octacosane. Other contaminants were present in extracted samples, and were found to be mainly phthalates (Table 4.6). Response of phthalates far exceeded the response of analytes (by approximately 80 times, in some cases), and as a result, limited sensitivity.

Table 4.6: Contaminants found in extracted aerosol samples (response given with split ratio 5:1 using the GC-MS)

Tentative Contaminant Identification	CAS #	Retention Time (minutes)	Approximate GC-MS Response (Abundance Counts)
Dibutyl phthalate	84-74-2	17.14	820,000
Benzyl butyl phthalate	85-68-7	22.99	33,000
Bis(2-ethylhexyl)adipate	103-23-1	23.65	1,000,000
Dicyclohexyl phthalate	84-61-7	25.52	1,800,000
Diisooctyl phthalate	27554-26-3	25.89	35,000

It was concluded that, due to presence of these contaminants in lab blanks (including those which did not contain a quartz filter), the contamination likely was from the extraction procedure itself, a likely source being the glue inside the lid of the Teflon-lined Qorpack jars, or the dichloromethane solvent.

4.1.3 Confirmation of Peak Identification

Analyte identification was confirmed using GC-MS after quantification was complete. This was done to ensure that the compounds were identified correctly, particularly given the coelution of octadecane and anthracene. The GC-MS system

consisted of an Agilent 6890N gas chromatograph coupled with a 7683 Series automatic injector and a 5973Network mass selective detector. The column was a 30 meter HP-5-MS column with a 0.25 μm (5% phenyl-)methylpolysiloxane stationary phase and 0.25 mm inside diameter.

The temperature program had a starting temperature of 80°C, held for 2 minutes, followed by an increase in temperature to 200°C at a rate of 10°C per minute, where temperature was held for 1 minute, and a final increase from 200°C to 280°C at a rate of 5°C per minute, where temperature was maintained for 7 minutes, for a total run time of 38 minutes. Injection used varying split ratios (5:1, 10:1, and 20:1), determined by maximum contaminant peak size from prior GC-FID analysis. The maximum desired peak height was 1,000,000 abundance counts, to avoid damaging the MS filament and detector. The mass spectrometer was operated in total ion collection (TIC) mode, and compound identifications were confirmed using main fragment ions and retention time comparison with standards previously analyzed on the GC-MS. Tentative identifications of additional peaks not quantified used the NIST mass spectral library (FairCom, 2002) and boiling point confirmation to identify contaminants and potential future analytes of interest.

4.2 Results

The importance of identification verification by mass spectrometry was confirmed with the presence/absence of fluorene, a PAH. It was determined by the GC-FID to be in nearly every plant sample, but was confirmed by mass spectrometry to indeed not be fluorene, but instead appears to be likely a carboxylic acid. Fluorene was not found in any samples: receptor, plant, or control.

All statistical analyses were performed using JMP-IN Version 4.0.2 statistical software. Data were tested for normality and found to be non-parametric in nature, most likely as a result of small sample size. As a result, the Kruskal-Wallis and Wilcoxon tests were used to test for significant differences between the sites. The Kruskal-Wallis test was run to test for significant differences on greater than two levels, and the Wilcoxon test was performed on data showing that significant differences existed within the set to identify where the difference existed. All statistical analyses were performed using a Type I error rate (α) of 0.05.

4.2.1 N-Alkanes

Pentadecane was found in receptor samples (n = 11) and one control sample, but did not appear in plant samples, indicating that the source of pentadecane was not the natural gas processing facilities, and instead was likely from something else not included in the study. Hexadecane was found in receptor samples (n = 10), one control sample, and in samples from Plants 4 and 5 (n = 3). The presence of hexadecane in samples at the control site indicates that it cannot be attributed exclusively to the plants, and may be from some biogenic or anthropogenic source also present at the control site. Heptadecane was also found in the control site samples (n = 2), receptor site samples (n = 20), and in samples from all plants (n = 19). Octadecane was found in most plant samples (n = 17), as well as receptor site samples (n = 20) and control site samples (n = 2). Nonadecane was found in samples from all plants (n = 12), as well as in receptor site (n = 19) and control site (n = 2) samples. Concentrations for pentadecane, hexadecane, heptadecane, octadecane, and nonadecane are presented in Figure 4.1, and statistical comparisons are summarized in Table 4.7.

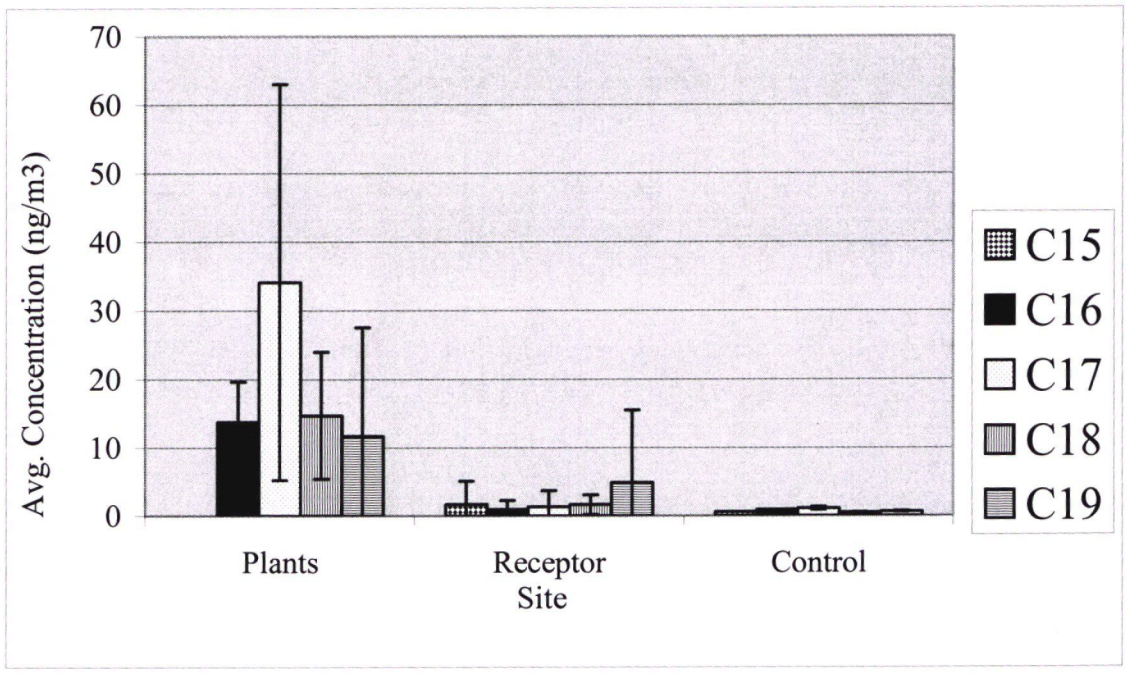

Figure 4.1: Average concentrations of pentadecane, hexadecane, heptadecane, octadecane, and nonadecane at the plant, receptor, and control sites (± standard deviation)

Table 4.7: Summary of statistical comparisons between sites for pentadecane, hexadecane, heptadecane, octadecane, and nonadecane

Compound	Sites where compound was present	Significant differences between sites
Pentadecane	Receptor, Control	None (Wilcoxon, $\chi^2 = 1.03$, d.f. = 1, $p > 0.31$)
Hexadecane	Receptor, Control, Plants	Plants higher than receptor (Wilcoxon, $\chi^2 = 6.43$, d.f. = 1, $p < 0.02$) Plants and control not different (Wilcoxon, $\chi^2 = 1.80$, d.f. = 1, $p > 0.17$) Control and receptor not different (Wilcoxon, $\chi^2 = 0.90$, d.f. = 1, $p > 0.34$)
Heptadecane	Receptor, Control, Plants	Plants higher than receptor (Wilcoxon, $\chi^2 = 26.53$, d.f. = 1, $p < 0.0001$) Plants higher than control (Wilcoxon, $\chi^2 = 5.10$, d.f. = 1, $p < 0.025$) Control and receptor not different (Wilcoxon, $\chi^2 = 1.88$, d.f. = 1, $p > 0.17$)
Octadecane	Receptor, Control, Plants	Plant higher than receptor (Wilcoxon, $\chi^2 = 22.60$, d.f. = 1, $p < 0.0001$) Plants higher than control (Wilcoxon, $\chi^2 = 5.10$, d.f. = 1, $p < 0.025$) Control and receptor not different (Wilcoxon, $\chi^2 = 1.30$, d.f. = 1, $p > 0.25$)
Nonadecane	Receptor, Control, Plants	Plants higher than receptor (Wilcoxon, $\chi^2 = 7.38$, d.f. = 1, $p < 0.01$) Plants and control not different (Wilcoxon, $\chi^2 = 3.33$, d.f. = 1, $p > 0.06$) Control and receptor not different (Wilcoxon, $\chi^2 = 0.13$, d.f. = 1, $p > 0.71$)

Eicosane was found at the receptor site (n = 21), all plants sites (n = 12), and control site (n = 2). Heneicosane was only found in two samples from the receptor site. Docosane was found in samples from Plants 2 and 5 (n = 2), the control site (n = 1), and receptor site (n = 13). Tricosane was only found in receptor samples (n = 4). Tetracosane was found in receptor samples (n = 7), as well as one sample from Plant 5. Concentrations for pentadecane, hexadecane, heptadecane, octadecane, and nonadecane are presented in Figure 4.2, and statistical comparisons are summarized in Table 4.8.

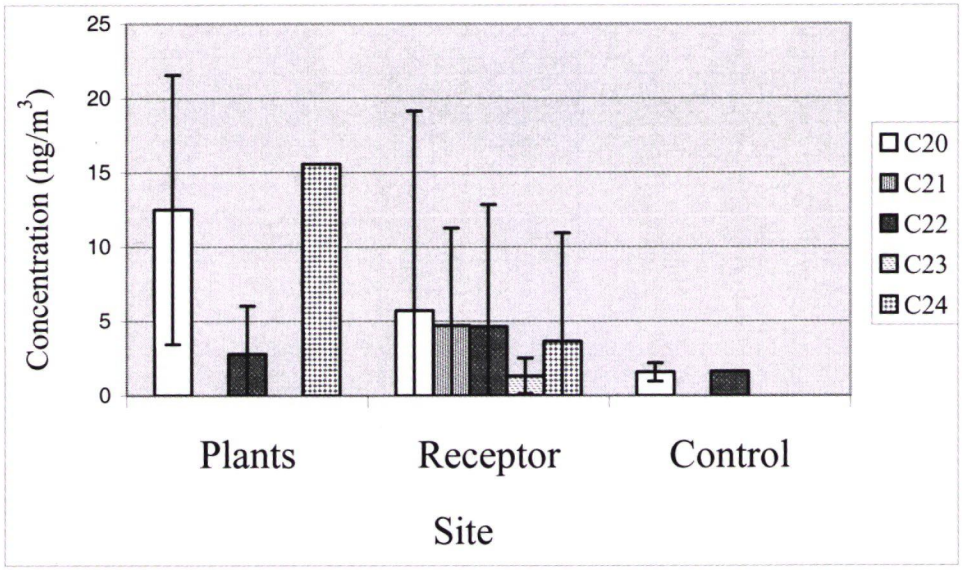

Figure 4.2: Average concentrations of eicosane, heneicosane, docosane, tricosane, and tetracosane at the plant, receptor, and control sites (± standard deviation)

Table 4.8: Summary of statistical comparisons between sites for eicosane, heneicosane, docosane, tricosane, and tetracosane

Compound	Sites where compound was present	Significant differences between sites
Eicosane	Receptor, Control, Plants	Plants higher than receptor (Wilcoxon, $\chi^2 = 9.88$, d.f. = 1, $p < 0.002$) Plants higher than control (Wilcoxon, $\chi^2 = 4.03$, d.f. = 1, $p < 0.05$) Receptor and control not different (Wilcoxon, $\chi^2 = 0.96$, d.f. = 1, $p > 0.32$)
Heneicosane	Receptor	N/A
Docosane	Receptor, Control, Plants	None (Kruskal-Wallis, $\chi^2 = 0.19$, d.f. = 2, $p > 0.91$)
Tricosane	Receptor	N/A
Tetracosane	Receptor, Plants	None (Wilcoxon, $\chi^2 = 1.19$, d.f. = 1, $p > 0.27$)

Pentacosane was only found in receptor site samples (n = 4) and in one plant sample from Plant 5. Hexacosane was found in one plant sample each from Plants 2 and 3, three samples from Plant 5, two samples from Plant 7 (n = 7 total), as well as in receptor site samples (n = 8). Heptacosane was found in samples from all plants (n = 10) except Plant 4, as well as in receptor site samples (n = 18). Concentrations for

pentacosane, hexacosane, and heptacosane are presented in Figure 4.3, and statistical comparisons are summarized in Table 4.9.

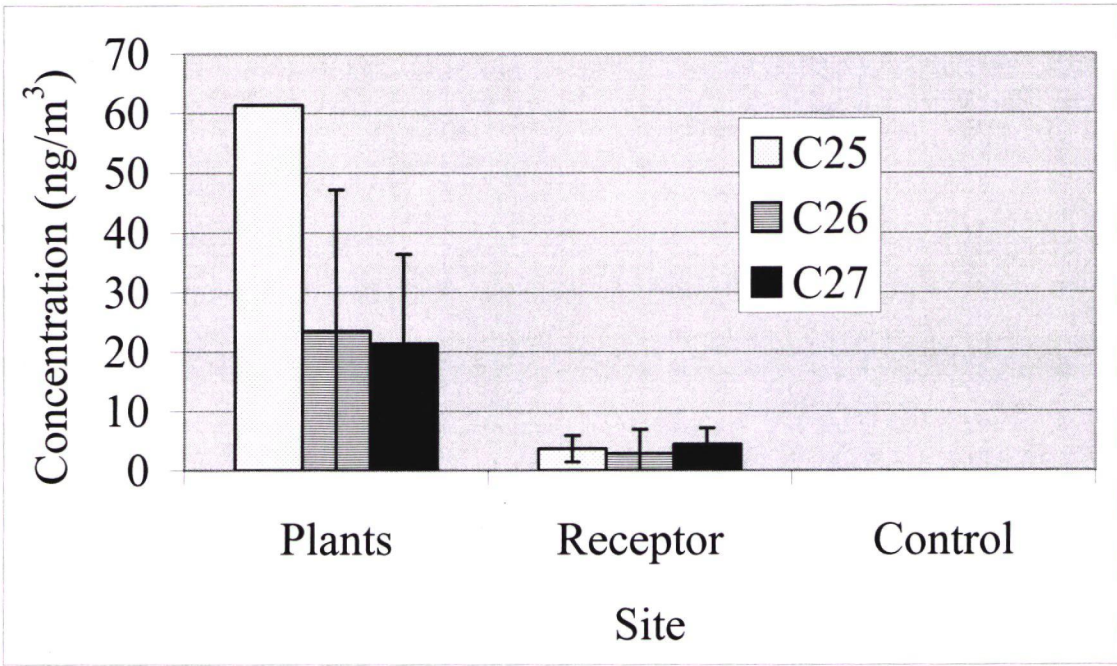

Figure 4.3: Average concentrations of pentacosane, hexacosane, and heptacosane at the plant, receptor, and control sites (± standard deviation)

Table 4.9: Summary of statistical comparisons between sites for pentacosane, hexacosane, and heptacosane

Compound	Sites where compound was present	Significant differences between sites
Pentacosane	Receptor, Plants	None (Wilcoxon, $\chi^2 = 2.00$, d.f. = 1, $p > 0.15$)
Hexacosane	Receptor, Plants	Plants higher than receptor (Wilcoxon, $\chi^2 = 5.91$, d.f. = 1, $p < 0.02$)
Heptacosane	Receptor, Plants	Plants higher than receptor (Wilcoxon, $\chi^2 = 12.59$, d.f. = 1, $p < 0.0001$)

Octacosane was found in samples from all plants (n = 15), as well as in control (n = 2) and receptor site samples (n = 18). Nonacosane was found in samples from all plants (n = 14), the receptor site (n = 20), and in one control site sample. Triacontane was found in samples from all plants except Plant 4 (n = 7), as well as in receptor site samples (n = 14), and in one control site sample. Hentriacontane was found in samples

from Plants 3, 5, and 6 (n = 3 total), as well as receptor site samples (n = 18). Concentrations for octacosane, nonacosane, triacontane, and hentriacontane are presented in Figure 4.4, and statistical comparisons are summarized in Table 4.10.

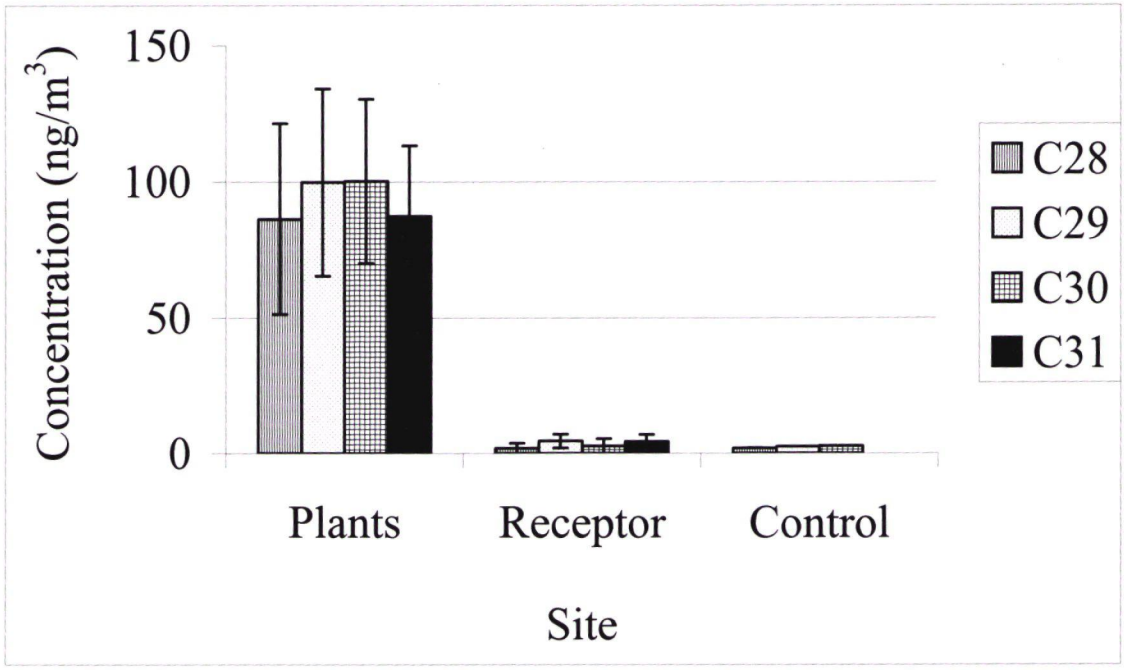

Figure 4.4: Average concentrations of octacosane, nonacosane, triacontane, and hentriacontane at the plant, receptor, and control sites (± standard deviation)

Table 4.10: Summary of statistical comparisons between sites for octacosane, nonacosane, triacontane, and hentriacontane

Compound	Sites where compound was present	Significant differences between sites
Octacosane	Receptor, Control, Plants	Plants higher than receptor (Wilcoxon, $\chi^2 = 23.82$, d.f. = 1, $p < 0.0001$) Plants higher than control (Wilcoxon, $\chi^2 = 5.00$, d.f. = 1, $p < 0.03$) Control and receptor not different (Wilcoxon, $\chi^2 = 1.02$, d.f. = 1, $p > 0.31$)
Nonacosane	Receptor, Control, Plants	Plants higher than receptor (Wilcoxon, $\chi^2 = 24.00$, d.f. = 1, $p < 0.0001$) Plants and control not different (Wilcoxon, $\chi^2 = 2.63$, d.f. = 1, $p > 0.10$) Control and receptor not different (Wilcoxon, $\chi^2 = 0.98$, d.f. = 1, $p > 0.32$)
Triacontane	Receptor, Control, Plants	Plants higher than receptor (Wilcoxon, $\chi^2 = 13.36$, d.f. = 1, $p < 0.001$) Plants and control not different (Wilcoxon, $\chi^2 = 2.33$, d.f. = 1, $p > 0.12$) Control and receptor not different (Wilcoxon, $\chi^2 = 0.21$, d.f. = 1, $p > 0.64$)
Hentriacontane	Receptor, Plants	Plants higher than receptor (Wilcoxon, $\chi^2 = 7.36$, d.f. = 1, $p < 0.01$)

4.2.2 Biomarkers

Pristane ($C_{19}H_{40}$) and phytane ($C_{20}H_{42}$) are biomarkers that confirm the presence of petroleum residues, such as diesel and coal combustion (Simoneit, 1984). Pristane was found in samples from the receptor site (n = 6), and samples from Plants 4 and 5 (n = 3). There was no significant difference between sites with respect to pristane concentration (Wilcoxon, $\chi^2 = 1.67$, d.f. = 1, $p > 0.19$) (Figure 4.5). Phytane was found in samples from Plants 4, 5, and 7 (n = 6), as well as samples from the receptor site (n = 11) and control site (n = 1) (Figure 4.5). There is no significant difference between the control site and the plant sites (Wilcoxon, $\chi^2 = 2.25$, d.f. = 1, $p > 0.13$), or between the control site and receptor site (Wilcoxon, $\chi^2 = 0.07$, d.f. = 1, $p > 0.78$), however the plant sites are

significantly higher than the receptor site with respect to phytane concentration (Wilcoxon, $\chi^2 = 9.55$, d.f. = 1, $p < 0.0025$).

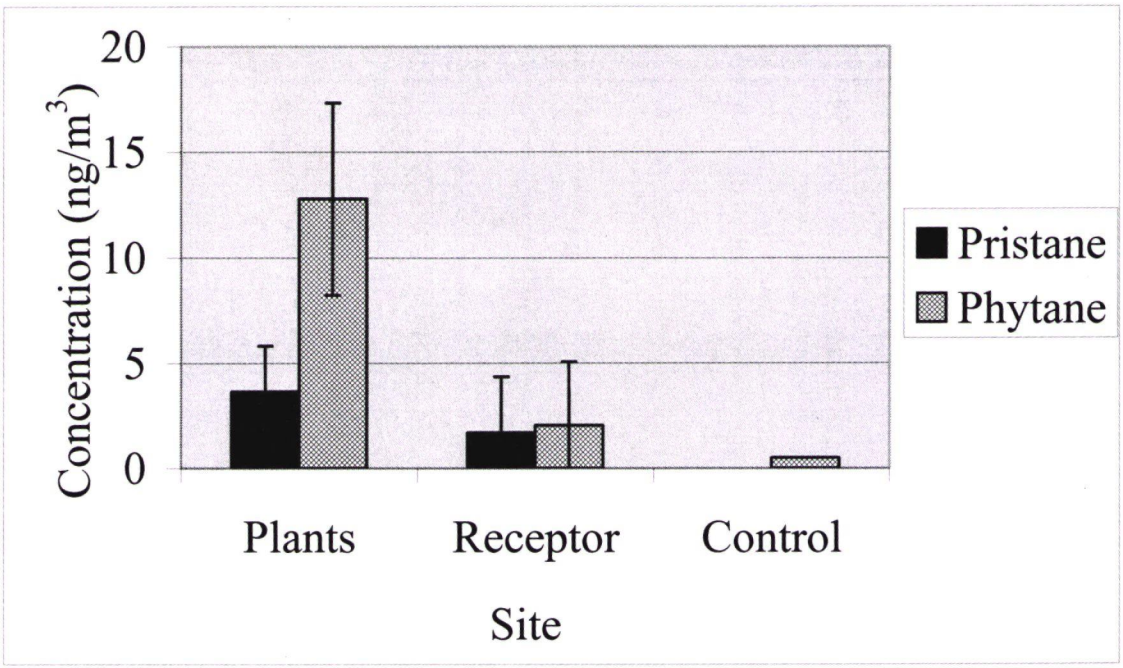

Figure 4.5: Average concentrations of pristane and phytane at the plant, receptor, and control sites (± standard deviation)

4.2.3 Polycyclic Aromatic Hydrocarbons

Anthracene (n = 2), benzo(a)anthracene (n = 4), chrysene (n = 5), benzo(b)fluoranthene (n = 1), and benzo(k)fluoranthene (n = 1) were only found in receptor site samples (Figure 4.6).

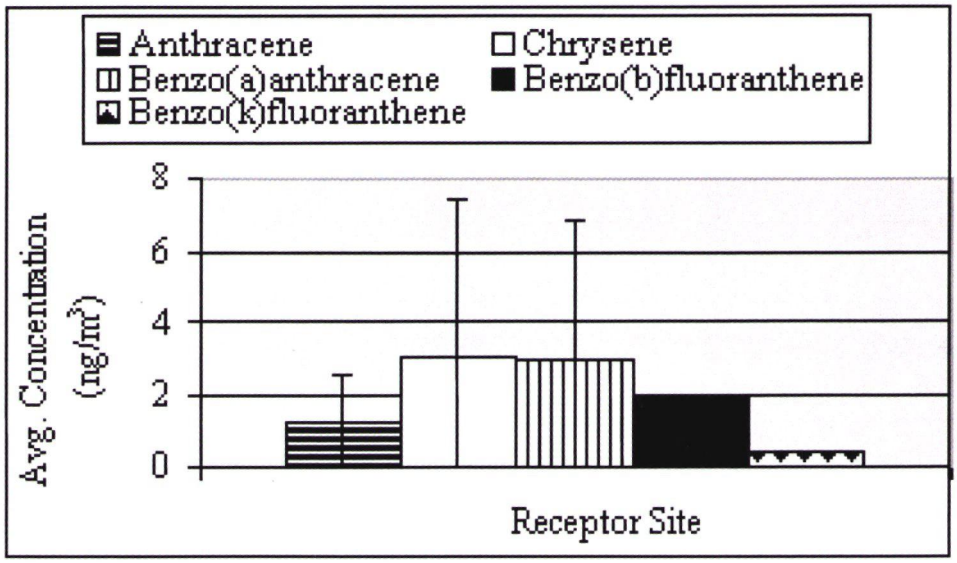

Figure 4.6: Average concentrations of anthracene, chrysene, benzo(a)anthracene, benzo(b)fluoranthene, and benzo(k)fluoranthene at the receptor site (± standard deviation)

Fluoranthene was found in receptor site samples (n = 15), as well as one sample from the control site, but there was no significant difference between the concentrations at these sites (Wilcoxon, $\chi^2 = 0.11$, d.f. = 1, $p > 0.74$) (Figure 4.7). Pyrene was found in receptor site samples (n = 16), in one sample from Plant 4 (weeklong), and at the control site (n = 1) but there was no significant difference between the sites (Kruskal-Wallis, $\chi^2 = 1.18$, d.f. = 1, $p > 0.55$) (Figure 4.7).

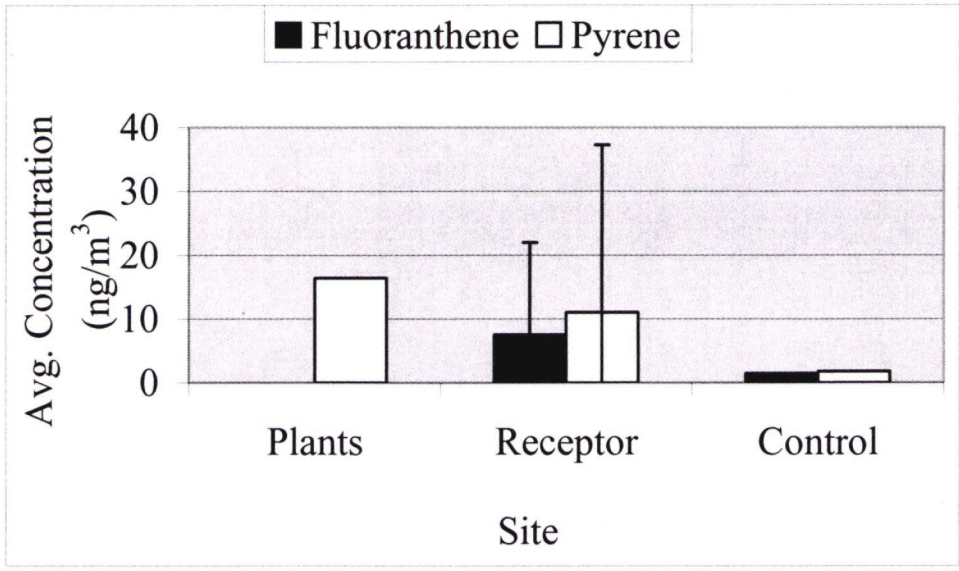

Figure 4.7: Average concentrations of fluoranthene and pyrene at plant, receptor, and control sites (± standard deviation)

Benzo(a)pyrene, benzo(g,h,i)perylene, dibenz(a,h)anthracene, and indeno(1,2,3-c,d)pyrene were not detected in any samples.

4.2.4 Seasonal Variations

To gain a better understanding of seasonal variations of aerosol composition in the atmosphere, the aerosol concentrations at the receptor site were ordered chronologically. Concentrations of total aerosols (total aerosol concentration in ng/m^3, determined by summing all measured aerosol hydrocarbon concentrations) were higher in samples taken between December and February, the winter months when the average temperature at the receptor site was below $0^{\circ}C$ (Figure 4.8). In addition, concentrations of total PAHs, total alkanes, and total biomarkers (pristane + phytane) were also investigated (Figure 4.8).

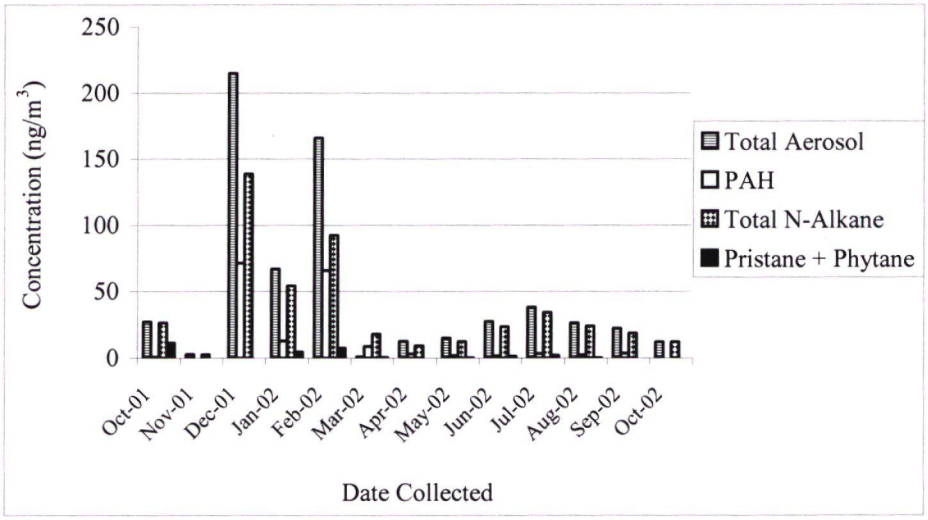

Figure 4.8: Variations of average total aerosol, total PAH, total n-alkane, and total biomarker concentration over time at the receptor site

It is also useful to compare the n-alkanes with an odd number of carbon atoms to those with an even number of carbon atoms, to help determine whether the origin of n-alkane aerosols is anthropogenic or biogenic. Petroleum-derived aerosols are expected to contain approximately equal distributions of odd and even n-alkanes, whereas biogenic sources tend to be dominated by n-alkanes with an odd number of carbon atoms. A good measure of this is the Carbon Preference Index (CPI), which is the ratio of odd-carbon numbered n-alkanes to even-carbon numbered n-alkanes. During the summer months at the receptor site, the n-alkane aerosol fraction contains higher concentrations of odd n-alkanes, and from December to April, concentrations are more equally distributed between odd-carbon n-alkanes and even-carbon n-alkanes (Figure 4.9). This results in a Carbon Preference Index (CPI) of approximately 1 for the winter months of December until April, with a CPI of greater than one for the summer months of May until November (Figure 4.10).

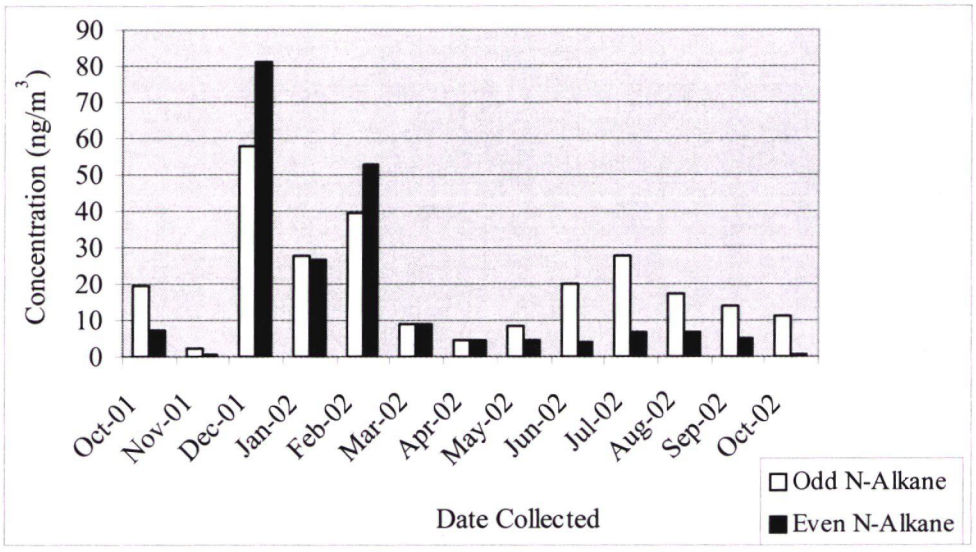

Figure 4.9: Variations of average total odd n-alkane and even n-alkane concentrations over time at the receptor site

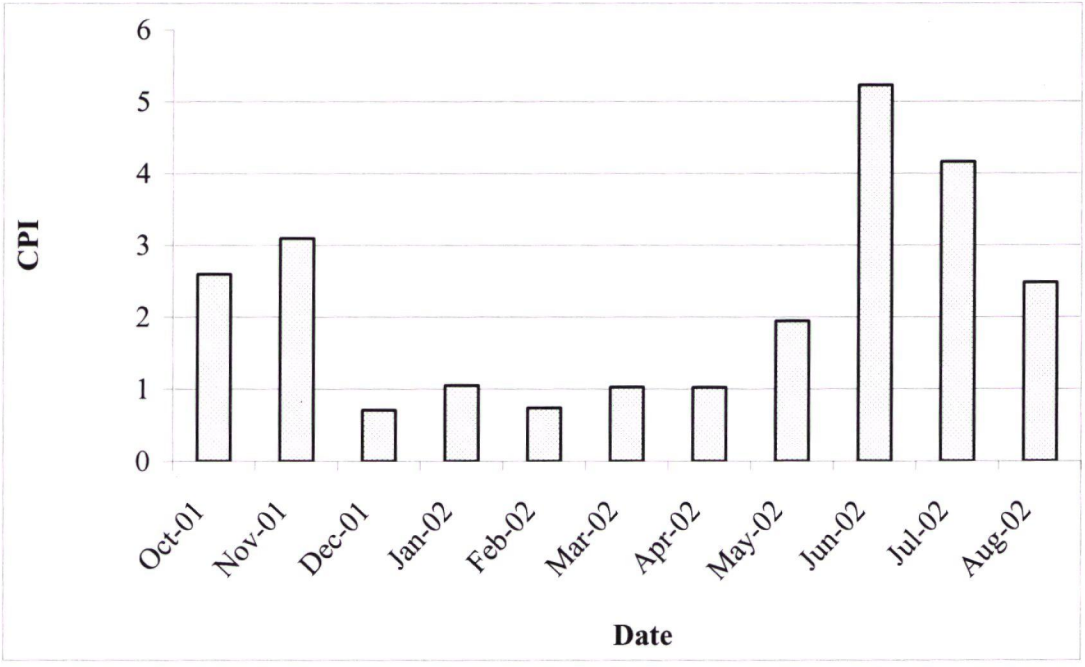

Figure 4.10: Variations in Carbon Preference Index (CPI) with time of year

The above finding suggests that seasonal variation in aerosol abundance may be linked to temperature. In Figure 4.11, the concentration of total aerosols is plotted against temperature. The average total measured aerosol concentration was 8 times higher when the average monthly temperature was below zero degrees Celsius.

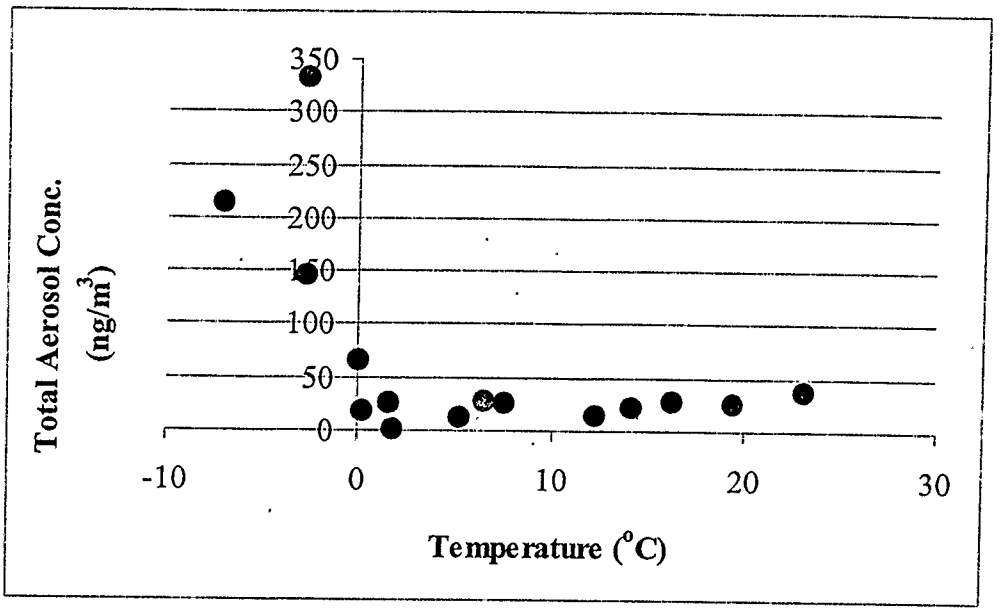

Figure 4.11: Temperature versus total aerosol concentration at the receptor site

The same trend is seen with total PAH concentration at the receptor site (Figure 4.12). Average total PAH concentration increased 19 times when the temperature averaged below zero degrees Celsius.

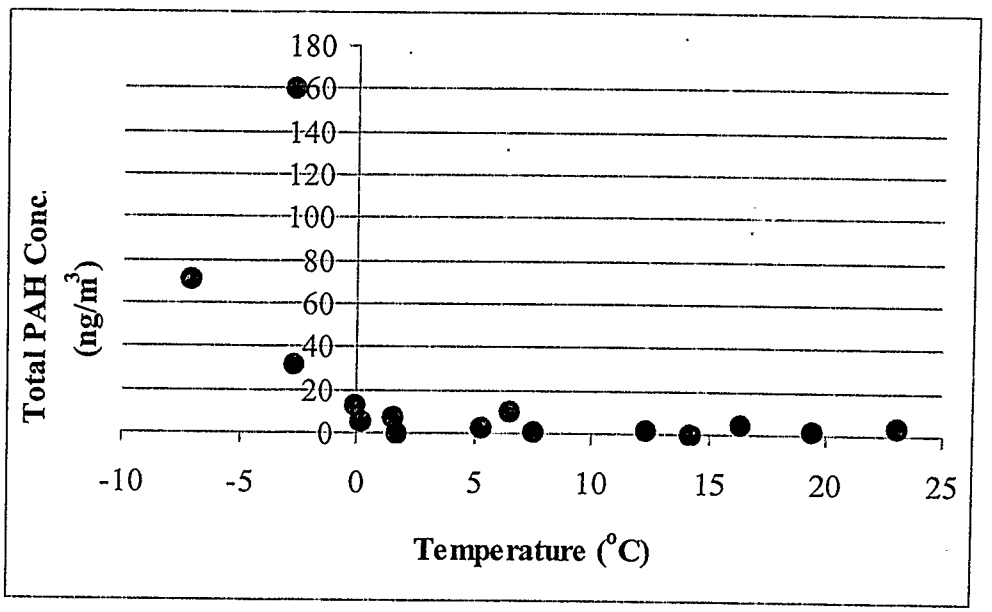

Figure 4.12: Temperature versus total PAH concentration at the receptor site

Temperature also appears to be related to the concentration of total n-alkanes at the receptor site (Figure 4.13). Average total n-alkane concentration increased 6 times when the average temperature was below zero degrees Celsius.

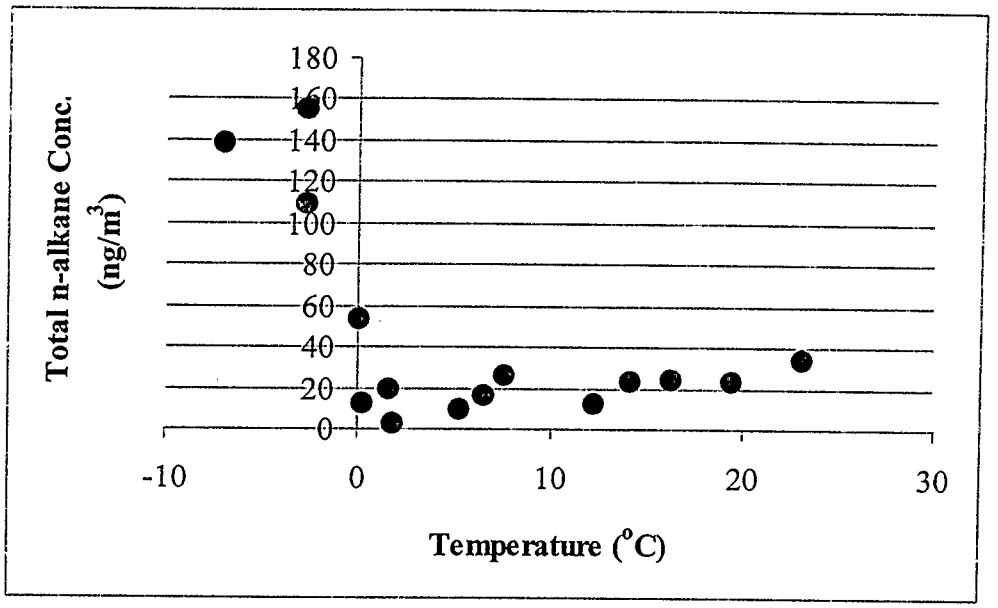

Figure 4.13: Temperature versus total n-alkane concentration at the receptor site

Perhaps the most interesting results pertaining to seasonal variation are displayed in Figure 4.14. The biomarkers used in this study (pristane and phytane) do not demonstrate the same seasonal trend seen with the other aerosol components. In fact, no visible correlation is seen between temperature and total biomarker concentration.

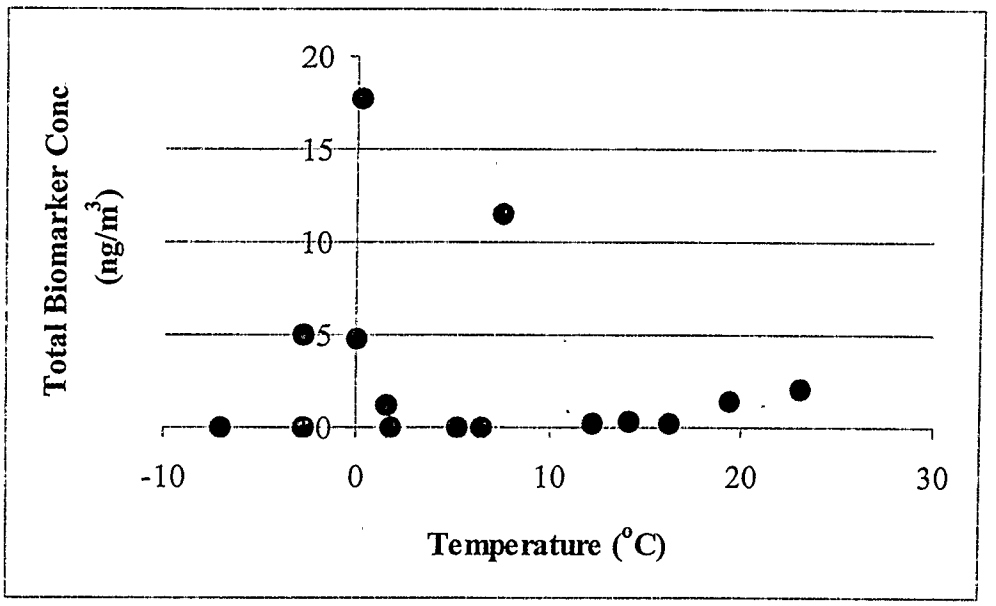

Figure 4.14: Temperature versus total concentration of biomarker compounds, phytane and pristane

4.2.5 Other compounds found but not quantified

A variety of other compounds were found in plant, receptor, and control site samples, and the most abundant of these were investigated further. These compounds were not quantified, but were tentatively identified using the NIST mass spectral library (FairCom, 2002), and tentative identifications deemed to be reasonable based upon agreement between boiling point and elution order are presented here. In order to confirm these identifications, standards must be analyzed to compare retention times and mass spectra. The majority of the tentatively identified compounds are oxygenated, existing as ketones, carboxylic acids, and esters (Table 4.7).

When quantifying using the GC-FID, initially fluorene was identified based on retention time as being present in every plant sample. Upon confirmation using the GC-MS, it was discovered that fluorene was not present, and instead this compound was tentatively identified to be 2,2,4-trimethyl-3-carboxyisopropyl isobutyl ester pentanoic acid (NIST 140775). Other compounds tentatively identified are presented in Table 4.7.

Table 4.11: Additional hydrocarbons tentatively identified from aerosol samples for possible future research

Compound Name	CAS #	Sample Containing Compound
2-(2-butoxyethoxy)ethanol	112-34-5	Control
2,3-pinanediol	22422-34-0	Control, Receptor – January, February, March, April, July, August, September, October, November, December
nopinone	24903-95-5	Control, Receptor – February, June
dipentene dioxide	96-08-2	Control
di(2-ethylhexyl)azelate	103-24-2	Control, Receptor – February, March, April, May, June, July, August, October
2,5-bornanedione	4230-32-4	Control
erucamide	112-84-5	Plant 1
benzyl benzoate	120-51-4	Plant 2, Plant 4, Plant 6, Plant 7
cetyl isooctanoate	59130-69-7	Plant 2, Plant 5
2-pentadecanone	502-69-2	Plant 2, Plant 6, Plant 7
4-(1-methylethyl)-2-cyclohexen-1-one	500-02-7	Plant 2, Plant 5, Receptor – February, December
2,5-di-tert-butyl-1,4-benzoquinone	2460-77-7	Plant 2
2,6-ditert-butyl-4-ethylphenol	4130-42-1	Plant 4, Receptor – March
elemental sulphur (S_8)	10544-50-5	Plant 4, Plant 5
ditert-butyl benzoquinone	719-22-2	Plant 4, Receptor – March
sulphur hexamer	13798-23-7	Plant 4
methyl tetradecanoate	124-10-7	Plant 4
methyl hexadecanoate	112-39-0	Plant 4
2-octylbenzoate	6938-51-8	Plant 4
hexadecenenitrile	88592-11-4	Plant 4
2,4,7,9-tetramethyl-5-decyn-4,7-diol	126-86-3	Plant 5, Plant 7, Receptor – March
3,5-ditert-butyl-4-hydroxybenzaldehyde	1620-98-0	Plant 6
tetracosanoic acid, methyl ester	2442-49-1	Receptor – January, April, May, November, December
ethyl 4-ethoxybenzoate	23676-09-7	Receptor – January, February, December
dihydroactinidiolide	17092-92-7	Receptor – January, September, November
9-fluorenone	486-25-9	Receptor – February, March
2 pentadecyl acetate	30889-32-8	Receptor – February
benzophenone	119-61-9	Receptor – February

octadecylester octadecanoic acid	2778-96-3	Receptor – March, August
methyl atratate	4707-47-5	Receptor – April, August
octadecyl hexadecanoate	2598-99-4	Receptor – April
1-(10-methylanthracen-9-yl)ethanone	36778-18-4	Receptor – April
25-hydroxy-14,16-hentriacontanedione	52262-75-6	Receptor – April
β-eudesmol	473-15-4	Receptor – May, June, July, October
α-bisabolol	72691-24-8	Receptor – May
15-nonacosanone	2764-73-0	Receptor – July
7-oxadehdroabietic acid, methyl ester	110936-78-2	Receptor – October
3-phenoxyphenol	713-68-8	Receptor – December
methyl ester hexacosanoic acid	5802-82-4	Receptor – December

4.3 Discussion

Many of the compounds quantified were present at every site type: control, receptor, and plant. These compounds include: hexadecane, heptadecane, octadecane, nonadecane, eicosane, docosane, octacosane, nonacosane, triacontane, phytane, and pyrene. Based on their prevalence at all locations, and the size range of aerosols collected, it is likely that these compounds are not exclusively a product of natural gas processing facilities. However, with respect to all of the above compounds with the exception of docosane and pyrene, natural gas plant sites have significantly higher concentrations of these compounds than receptor sites. Therefore, all but docosane and pyrene are likely produced in part by natural gas processing activities. Other possible sources of these compounds at the control and receptor sites may include biogenic sources, operation of residential furnaces, vehicle traffic, wood combustion, and generators. Consequently, isotopic information for these compounds may be useful as a

possible means of distinguishing sources from one another. Without isotopic information, one cannot say whether the sources of these compounds differ.

The presence of phytane at the control site indicates that although attempts were made to find a region un-impacted by petroleum processing and/or use, there were still some anthropogenic impacts at the control site. Phytane and pristane are indicative of petroleum fuel use, particularly coal products and heavier distillate petroleum fractions (Simoneit, 1984). As a result, we can deduce that compounds found at the control site are not necessarily of biogenic origin, and may indeed be partially and/or wholly of anthropogenic origin.

Compounds found only at the receptor site include heneicosane, tricosane, anthracene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, and benzo(k)fluoranthene. These compounds are likely formed by some anthropogenic or biogenic process other than natural gas processing. N-alkanes can be produced by both biogenic and anthropogenic processes. Epicuticular waxes of vascular plants tend to produce n-alkanes in the range from C23 to C35 (Simoneit, 1986), and n-alkanes can also be detected in the air from direct suspension of pollen, microorganisms, and insects (Simoneit *et al.*, 1977). Anthropogenic sources of n-alkanes include combustion of fossil fuels, wood, agricultural debris, and leaves (Bi *et al.*, 2002). PAHs are the result of incomplete combustion, and tend to be emitted in diesel and gasoline engine exhausts, coal-fired power plants, tobacco smoke, residential wood combustion, residential coal combustion, forest and agricultural burning, and waste incineration (Bjorseth and Ramdahl, 1985). At the receptor site, the likely sources of PAHs can be reduced to diesel

and gasoline engine exhausts, residential wood combustion, forest and agricultural burning, and waste incineration.

Compounds found at both gas plant and receptor sites are promising for source apportionment techniques. This includes tetracosane, pentacosane, hexacosane, heptacosane, and hentriacontane. Chemical removal or alteration of these compounds prior to atmospheric deposition is unlikely due to long atmospheric lifetimes, often several days to weeks (Pandis *et al.*, 1995), which would make source apportionment using stable isotopes more viable.

Seasonal variations in concentrations of the components of aerosols studied here are evident at the receptor site and can be the result of many factors. Some relationship exists between average temperature at the receptor site and aerosol concentration, with the sum of all aerosol components measured, total PAH, and total n-alkanes elevated when the average monthly temperature dips below zero degrees Celsius. Possible explanations for seasonal variations at the receptor site include:

1.) colder temperatures increase condensation and coagulation of Aitken nuclei, resulting in more aerosol formation,

2.) colder temperatures increase the ability of quartz filters to trap aerosols due to less filter breakthrough of semi-volatile organic compounds (typically assumed to include compounds less volatile than nonacosane), or,

3.) more aerosols, or gaseous emissions that condense to form aerosols, are produced during the wintertime.

Biomarker concentrations did not increase during winter months, which differs from the results found for the other compounds associated with aerosols. Therefore, it is

not a convincing argument that the increase in aerosols during the winter months can be strictly attributed to an increase in petroleum use and/or processing activities, at least not those that produce these biomarkers. Pristane and phytane are indicative of the use of heavier petroleum fractions, including diesel and coal. Therefore, increased aerosol concentrations because of natural gas heating, gasoline combustion, and wood combustion may be possible sources, as these do not produce pristane and phytane (Simoneit, 1986). Guo *et al.* (2003) also found the highest concentrations of PAHs and n-alkanes in a study of urban aerosols during the winter months in China.

This observed increase in aerosols during winter months is likely partially temperature dependent. Secondary organic aerosols are formed in higher yields at lower temperatures under laboratory conditions (Takekawa *et al.*, 2003), with Strader *et al.* (1999) demonstrating that at zero degrees Celsius, the greatest fraction of secondary organic aerosols exist in the aerosol phase relative to higher temperatures. It has also been found that winter conditions are particularly favourable towards secondary aerosol formation due to favourable meteorological conditions including clear skies, low winds, and low mixing heights (Strader *et al.*, 1999). These conditions maximize secondary aerosol formation by increasing the residence time of an air mass within a region, allowing for accumulation of reactants that produce secondary aerosols (Strader *et al.*, 1999).

The atmospheric oxidation of volatile species can lead to aerosol formation, but exact reaction mechanisms are still largely unknown. However, the atmospheric oxidation of toluene (by reaction with hydroxyl radicals in a laboratory environment) has been shown to produce benzaldehyde, o-, m-, and p-cresol, 2-methyl-p-benzoquinone,

benzyl alcohol, benzyl nitrate, o-, m-, and p-nitrotoluene, maleic anhydride, α-angelica lactone, 4-oxo-2-pentanal, methylglyoxal, and glyoxal (Hurley *et al.*, 2001; Smith *et al.*, 1998). All of these species contain oxygen, similar to the tentatively identified species associated with aerosols found in high abundances at the plant sites and receptor sites. This could explain why a large amount of these species found in aerosol samples were oxygenated, indicating that during atmospheric reactions in an environment containing hydroxyl radicals, these aerosols were formed. Carboxylic acids, ketones, and esters were present in the aerosol fraction.

Oxygenated species found in this study often included carboxylic acids. Carboxylic acids were also found by Harrad *et al.* (2003) in the UK near vehicular traffic, and Fraser *et al.* (2002) found that carboxylic acid concentrations in Houston, Texas (a region also impacted by petroleum processing) are dominated by hexadecanoic acid and octadecanoic acid. In this study, cetyl isooctanoate (a derivative of hexadecanoic acid) was found at Plant 2 and Plant 5. Booher and Janke (1997) also found that aldehydes and ketones were emitted directly from petroleum hydrocarbon fires, comprising 0.12% of the total emissions, with PAHs constituting 0.03%, and VOCs constituting 0.27% of total emissions.

Biogenic sources tend to produce isoprene and monoterpenes, including α-pinene (Hakola *et al.*, 2003; Penuelas and Llusia, 2003). An α-pinene compound was found at control, receptor, and plant sites in this study. Biogenic VOCs tend to maximize in the summer and minimize in the winter. Hakola *et al.* (2003) found that biogenic sources from coniferous forests continued during the winter months due to existing coniferous sources and increased atmospheric lifetimes of biogenic VOCs in the winter. Seasonal

variations of VOCs were not tested in this thesis. The gas plants were typically surrounded by boreal forest, while the receptor site was located in a farming area near the edge of the boreal forest. Esters can be associated with biogenic vegetation sources, and were found at Plant 2, Plant 4, Plant 5, and the receptor site.

Amine compounds were found at two of the sour plant sites (Plant 1 and Plant 4), possibly as a result of the natural gas processing techniques, which use monoethanolamine, diethanolamine, and triethanolamine to remove carbon dioxide and hydrogen sulphide from natural gas. Elemental sulphur, likely as a result of dust blowing off the sulphur storage block, was found in two forms at sour gas plants: octasulphur (S_8) and hexasulphur (S_6). S_8 was found at Plant 4 and Plant 5, while S_6 was found at Plant 4. Aldehydes and ketones can be typical of low temperature pyrogenic processes (Simoneit, 1986), and were found at Plant 4, Plant 5, Plant 6, Plant 7, and at the receptor site. Alkylbenzoic acids and benzenedioic acids were found at the receptor site, and can be typical of vehicular emissions (Simoneit, 1986). Benzoic acid compounds were also found at Plant 2, Plant 4, Plant 6, Plant 7, and at the receptor site.

The Carbon Preference Index (CPI) is an index that can be used to estimate anthropogenic contributions of n-alkanes relative to biogenic contributions (Simoneit, 1986), and, as mentioned previously, is the ratio of odd-carbon n-alkanes to even-carbon n-alkanes. A CPI of around 1 indicates a dominant contribution from petroleum sources, and a CPI greater than 1 indicates a greater biogenic contribution (Simoneit, 1986). At the receptor site, between December and April the CPI ranged between 0.7 and 1.0. This shows that the contribution to the aerosol n-alkane component is largely petroleum based. Conversely, during the remaining months, the odd numbered n-alkanes dominate,

resulting in higher CPIs ranging between 1.5 and 5.2, with maximum CPIs occurring in June, July, and August. This suggests that biogenic sources contribute more to the aerosol n-alkane concentrations than do petroleum sources during the growing season. This confirms the earlier suggestion that increased anthropogenic sources during the winter months are likely contributing to increased aerosol concentrations during colder weather. Higher biogenic contributions to the aerosol fraction during the summer months can be attributed to plant waxes, which would be expected during the growing months in central Alberta near the boreal forest. Guo *et al.* (2003) also found that the CPI indicated an increase in petroleum use during the colder months in China, but in an urban environment.

Seasonal variations at the receptor site are consistent with those found in the literature. An increase in aerosol concentration is likely a combination of the temperature dependence of aerosol formation and trapping on quartz aerosol filters, and increased combustion sources. However, these combustion sources that increased at the receptor site during the winter months likely do not produce pristane and phytane.

Isotopic information would be valuable to distinguish whether different natural gas processing plants produce n-alkanes with isotopically unique signatures. The absence of PAHs at the natural gas processing facilities indicates that the natural gas processing facilities are diligent with respect to emissions of these chemicals. The natural gas plants appear to be combusting waste gas streams at conditions that do not result in PAH formation. The presence of elevated concentrations of n-alkanes at the natural gas plants indicates that they are likely released in part by the gas plants, but this cannot be confirmed without isotopic analysis. Future research should include isotopic analysis of

aerosol samples, and confirming the identification of oxygenated species associated with these aerosols. Oxygenated species were often present in higher concentrations than those that were not oxygenated, and isotopic analysis of these compounds may be easier due to the current detection limits of CF-IRMS.

The discovery of n-alkanes (C19-C28) and phthalates in blank extractions is a concern, but not unique to this study. Simoneit (1986) found n-alkanes ranging from nonadecane (C19) to triacontane (C30), and Bi *et al.* (2002) encountered n-alkanes ranging from octadecane (C18) to hexacosane (C26). Also, both Simoneit (1986) and Bi *et al.* (2002) co-extracted phthalates as well, with Simoneit (1986) identifying them as diethyl, dibutyl, and diethylhexyl phthalate esters.

CHAPTER 5: FINAL FINDINGS AND RECOMMENDATIONS

Source apportionment of atmospheric pollutants from natural gas plants using isotopic techniques has future potential. However, one factor that must be taken into consideration is that many pollutant sources exist within each natural gas processing facility. The dominant sources of emissions are expected to be the flare and incineration stacks. Fugitive emissions may have been significant sources of pollution at these gas plants, and have not been accounted for in this study during helicopter sampling of the flare stack plume. Also, in future it is important to determine whether the emissions from these sources within one operating facility are isotopically consistent over time. The isotopic composition of petroleum products entering the natural gas plants over time is expected to be consistent, as the addition and removal of individual wells will likely not significantly impact the overall composition of the natural gas being processed. However, the fuel source for the flare itself may change over time, as natural gas plants routinely flare from different sections of the plant. This is dependant on daily operating conditions, and these changes in the fuel source of the flare may alter the isotopic composition of emissions.

Repeat sampling of gas plants is required to identify compounds conclusively that were tentatively identified in this thesis, and the author suggests that fewer plants be chosen and sampled repeatedly over time to confirm that the isotopic compositions remain constant. This was the original study design, but problems were encountered with aerosol sampling at the receptor site, which required the number of plants to be increased to accommodate this thesis. Once conclusive identifications are made, atmospheric lifetimes of volatile pollutants should be investigated to determine whether they, and

other oxidation products, are likely to be found at the receptor site. Larger sample volumes, particularly at the receptor site, may enable detection of the compounds found at the sources, even after dilution during atmospheric transport.

CF-IRMS applicability to isotopic analysis of volatile samples was successful. Although VOC replicates were not as close as desired, this may be improved with greater emphasis on water removal after sample combustion. It has been shown that isobaric interference from water content affects $\delta^{13}C$ values by an average of 0.3‰ when Nafion is used to remove water from a saturated gas stream at room temperature (Leckrone and Hayes, 1998). This thesis verified that cryogenic water removal techniques prior to combustion of the sample are not desirable, nor particularly effective under the conditions used here, and any cryogenic trapping of VOCs creates the possibility of isotopic fractionation, and is therefore not ideal for isotopic analysis.

Concerns regarding flooding of the CF-IRMS detector with carbon dioxide in samples can be alleviated. The CF-IRMS system allows for configuration manipulations such that portions of the sample may be flushed out with helium after elution from the GC column but prior to arriving at the detector, as well as "hiding" the detector in a stream of helium to avoid contact with the sample. Any attempt to chemically remove carbon dioxide from the sample comes with the risk of also reacting with VOCs in the sample, potentially causing isotopic fractionations, and must be tested prior to isotopic analysis. In order for confident mass spectral identifications to be possible, the TIC scanning range must be lowered, perhaps to *m/z* 30 (this should be possible given adequate rinsing of the system with carrier gas prior to GC temperature increase). This would enable better comparison with the available libraries, particularly for volatile

hydrocarbons, many of which have similar fragmentation patterns, and base peaks below *m/z* 45. Final identification confirmation should be done by analyzing standards of the identified compounds, to confirm that the compounds identified are indeed present by comparison of retention time and fragmentation pattern.

Quantification of aerosol samples demonstrated obvious seasonal variability at the receptor site, and confirmed what has been found in the literature. Although isotopic analysis of aerosols was not completed as a part of this thesis, future analyses of these samples may provide conclusive answers as to whether aerosols found at plant sites can be distinguished from those at the receptor and control sites. It may also provide interesting results at the receptor site, giving researchers a better idea of whether increased aerosol concentrations in the winter are the result of increased sources, increased formation, or both. Isotopic analysis of may also enable researchers to distinguish between contaminant and sample n-alkanes.

In the course of this thesis, an effective canister cleaning protocol was developed, and selected volatile and particulate-phase hydrocarbons were quantified. VOCs produced by natural gas facilities that may be promising for source apportionment techniques have been tentatively identified, and most importantly, it has been confirmed that $\delta^{13}C$ values of specific VOCs from different natural gas processing facilities are unique. This thesis developed appropriate sampling methods and analytical techniques applicable to isotopic analysis of organic volatile and particulate-phase emissions from natural gas plants, and these will be useful for further development of source apportionment techniques using stable carbon isotopes.

Compound	GC Ion Trap MS Retention Time (min)	Sample	$\delta^{13}C$ (S.D.) (‰)	IRMS Area (Vs)*	Major Mass Spectral Fragments	Tentative Identifications
Cmpd 1	55.85	Plant 2	-31.85 (0.37)	9.03	57, 58, 59	
		Plant 5	-29.12 (0.53)	12.34		
Cmpd 2	58.19	Plant 1	-22.37	2.86	57, 56, 55	
n-Pentane	58.25				57, 71, 56	Reference in Standard Mix
Cmpd 3	65.14	Plant 1	-28.95 (0.30)	2.02	57, 72, 62	C5 Compound
		Plant 2	-33.63 (0.70)	4.08		
		Plant 3	-34.63 (0.10)	1.55		
		Plant 4	-33.40	0.76		
		Plant 5	-31.78 (0.37)	6.89		
		Plant 6	-32.55 (1.70)	1.40		
		Plant 7	-36.90 (062)	4.85		
Cmpd 4	66.20	Receptor 4	-27.77 (0.82)	3.62	57, 58, 59	
Cmpd 5	66.34	Plant 4 Night	-27.02 (0.08)	1.60	57, 101, 56, 103	
n-Hexane	67.50				57, 56, 55	Reference in Standard Mix
Cmpd 6	69.64	Plant 3	-41.74 (0.34)	0.65	84, 56, 57	1-nitro-2-methyl propene
Benzene	71.53				78, 77, 76	Reference in Standard Mix
Cmpd 7	72.08	Plant 2	-31.12	7.80	56, 55, 57	5-methyl-1-hexene
		Plant 3	-31.50 (1.01)	1.43		
		Plant 5	-29.74 (0.02)	7.41		
		Plant 6	-32.12 (0.14)	1.97		
Cmpd 8	73.58	Plant 1	-29.15	1.50	58, 57, 70, 55	
iso-Octane	74.63				58, 56, 57	Reference in Standard Mix
Cmpd 9	75.15	Plant 4 Night	-32.54 (0.31)	3.08	57, 72, 73	
		Receptor 4	-30.87 (0.29)	2.75		
Cmpd 10	75.24	Receptor 4	-32.06 (0.37)	4.58	73, 57, 72	

n-Heptane	75.45				71, 70, 57	Reference in Standard Mix
Cmpd 11	76.14	Plant 1	-36.33 (0.42)	3.08	56, 57, 55	1-butyl nitrite
		Plant 2	-36.39	30.00		2-methyl-1-hexene
		Plant 3	-39.85	0.84		
		Plant 4	-41.32 (0.45)	1.89		
		Plant 5	-37.80 (0.01)	45.27		
		Plant 6	-38.97 (0.17)	1.64		
		Plant 7	-39.45 (0.12)	11.82		
Toluene	79.52				91, 92, 65	Reference in Standard Mix
Cmpd 12	81.48	Plant 4 Night	-31.08 (0.07)	5.99	56, 55, 57	
		Receptor 4	-29.63 (0.64)	8.42		
		Control 1	-27.24 (0.25)	0.48		
Cmpd 13a	84.37	Plant 3	-27.79 (0.83)	0.67	57, 115, 100	1-isothiocyanato butane
		Plant 4	-26.00 (0.55)	0.74		diethylacetamide
		Plant 5	-27.35	0.84		4-ethyl-morpholine
		Plant 6	-27.12	0.93		
		Plant 7	-27.04 (0.26)	0.57		
		Receptor 1	-26.67 (0.34)	1.91		
Cmpd 13b	94.31	Plant 4 Night	-31.28 (0.17)	0.68	57, 115, 100	1-isothiocyanato butane
		Receptor 4	-24.05 (1.66)	2.42		diethylacetamide
		Control 1	-25.60 (0.13)	1.38		4-ethyl-morpholine
Cmpd 14	85.50	Plant 4 Night	-38.86 (0.09)	13.05	56, 57, 55	2,2-dimethyl-1,3-butanediol
		Receptor 4	-36.99 (0.34)	6.61		
		Control 1	-36.30 (0.09)	0.89		

Cmpd 15	88.55	Plant 1	-28.52	17.35	57, 45, 87	1-butoxy-2-methoxyethane
		Plant 2	-31.47	17.30		
		Plant 3	-27.70 (1.93)	0.67		
		Plant 5	-26.63 (0.50)	4.36		
		Plant 7	-31.88 (0.21)	2.19		
Cmpd 16	89.52	Plant 4 Day	-24.42 (0.17)	0.66	91, 92, 65	C7H8 Compound 1,3-heptadiene-3-yne spiro(2,4)hepta-4,6-diene 1, 3, 5-cycloheptatriene
Cmpd 17	93.98	Plant 3	-34.10 (0.85)	1.35	57, 73, 45	C7 Compound
		Plant 4	-42.45 (1.48)	3.21		
		Plant 6	-33.99 (0.54)	1.16		
Cmpd 18	93.92	Plant 5	-34.97	26.68	73, 57, 45	
n-Decane	94.84				57, 71, 56	Reference in Standard Mix
Cmpd 20	95.58	Plant 1	-29.40 (0.19)	3.06	57, 55, 70	2-ethyl-1-hexanethiol
		Plant 2	-32.91 (0.10)	2.73		2-ethyl-1-hexanol
		Plant 6	-29.41 (1.07)	0.67		2,4-dimethyl-1-decene
Cmpd 21	98.00	Plant 4 Day	-29.64 (1.40)	0.96	57, 45, 87	2-butoxy ethanol
		Plant 4 Night	-32.02 (0.06)	20.24		
		Receptor 1	-28.51 (0.91)	1.91		
		Receptor 4	-31.35 (0.05)	5.63		
		Control 1	-29.68 (0.80)	1.33		
		Upwind	-29.35 (1.13)	3.30		
Cmpd 22	98.03	Plant 5	-27.51 (0.05)	0.52	71, 73, 45	
Cmpd 23	103.85	Receptor 1	-24.73 (0.22)	0.47	54, 79, 107	
		Receptor 4	-20.93 (0.22)	1.34		
Cmpd 24	103.95	Plant 4 Night	-28.94 (1.14)	1.05	57, 73, 45	

Cmpd 25	105.53	Receptor 1 Receptor 4 Control 1	-29.33 (1.22) -27.61 (0.13) -26.99 (0.02)	0.48 0.98 0.52	57, 55, 97	
Cmpd 26	129.74	Plant 4 Day	-28.36 (0.22)	0.93	193, 95, 123	
Cmpd 27	134.49	Plant 4 Day	-32.47 (0.05)	2.68	193, 137, 123	

*** IRMS areas normalized so that areas are all equivalent to having 1 L of sample volume injected**

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